

# ATOMIC AND MOLECULAR STRUCTURE

## SYLLABUS

- Atomic orbitals (s,p,d,f) orbital shapes, Electronic Configuration
- Molecular orbital theory (MOT), bonding and anti-bonding orbitals
- Molecular orbital diagrams of Homonuclear and Heteronuclear diatomic molecules- Be<sub>2</sub>, O<sub>2</sub>, CO, NO their bond order and magnetic properties

### 1.1 CONCEPT OF ATOMIC ORBITAL

According to the wave-mechanical theory, electrons patrol in three-dimensional space around the nucleus; sometimes near the nucleus, and sometimes farther away. Thus, electrons effectively occupy a relatively vast space around the nucleus. It has been found that the probability of finding an electron around the nucleus is maximum in a space, called atomic orbital. Thus, atomic orbital is the region in the space around the nucleus within which there is high probability of finding the electron.

An atom can have many possible number of orbitals. These orbitals can be categorized on the basis of their size, shape or orientation. A smaller sized orbital means there is a greater chance of getting an electron near the nucleus. The orbital wave function or  $\psi$  is a mathematical function used for representing the coordinates of an electron. The square of the orbital wave function represents the probability of finding an electron. This wave function also helps us in drawing boundary surface diagrams. Boundary surface diagrams of the constant probability density for different orbitals help us understand the shape of orbitals. Let us represent the shapes of orbitals with the help of boundary surface diagrams.

#### Determination of shapes of orbitals:

**s-orbital:** Boundary surface diagram for s orbital looks like a sphere having the nucleus as its center which in two dimensions can be seen as a circle.

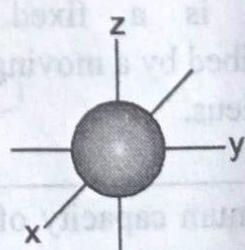


Fig. 1.1 : s-orbital

Hence, we can say that s-orbitals are spherically symmetric having the probability of finding the electron at a given distance, equal in all the directions. The size of the s orbital is also found to increase with the increase in the value of principal quantum number (n), thus,  $4s > 3s > 2s > 1s$ .

**❖ p-orbitals:** Each p orbital consists of two sections known as lobes which lie on either side of the plane passing through the nucleus.

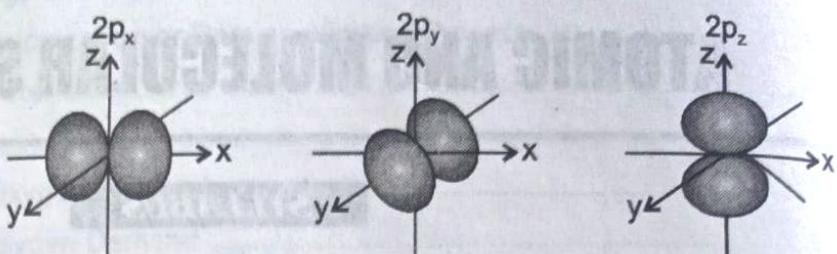


Fig. 1.2 : p-orbital

The three p orbitals differ in the way the lobes are oriented; whereas they are identical in terms of size, shape and energy.

As the lobes lie along one of the x, y or z-axis, these three orbitals are given the designations  $2p_x$ ,  $2p_y$ , and  $2p_z$ . Thus, we can say that there are three p orbitals whose axes are mutually perpendicular. Similar to s orbitals, size, and energy of p orbitals increases with an increase in the principal quantum number ( $4p > 3p > 2p$ ).

**❖ d-orbital:** Magnetic orbital quantum number for d orbitals is given as (-2, -1, 0, 1, 2). Hence, we can say that there are five d-orbitals. These orbitals are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{x^2-y^2}$  and  $d_z^2$ . Out of these five d orbitals, shapes of the first four d-orbitals are similar to each other, which is different from the  $d_z^2$  orbital. However, the energy of all the five d orbitals is the same.

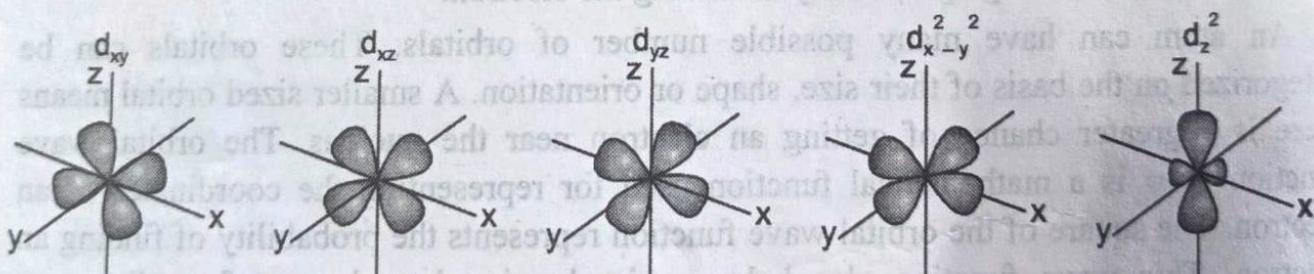


Fig. 1.3 : d-orbital



### Comparison: Orbit and Orbital:

Orbit	Orbital
1. Orbit is a fixed circular path, described by a moving electron around a nucleus.	1. Orbital is a three-dimensional region in space around the nucleus, where there is maximum probability of finding an electron.
2. Maximum capacity of any orbit is $2n^2$ electrons, where n is the number of orbit.	2. Maximum capacity of any orbital is two electrons.

3. It has two dimensional representation.	3. It has three-dimensional representation.
4. The position and velocity of a moving electron, in an orbit can be calculated with great accuracy.	4. The position and velocity of moving electron, in an orbital can be determined within limits of Heisenberg's uncertainty principle.
5. The distance of the orbit from the nucleus for a given electron is fixed.	5. It is impossible to know the exact trajectory of an electron in an orbital of an atom.

## 1.2 ELECTRONIC CONFIGURATION

The distribution of electrons in various orbitals is known as electronic configuration of the atom. The atom is built up by filling electrons in various orbitals one at a time, by placing it in the lowest energy orbital. The atom is said to be in the ground state when it is in its lowest energy state. This is the most stable state for the atom. The filling of orbitals by electrons in the ground state is determined by following rules.

**1. Aufbau principle:** The Aufbau principle states that in the ground state of an atom, the orbital with lower energy is filled first, before the filling of the orbital with higher energy. In other words, the electrons enter the orbitals in order of their increasing energies. The order in which the energies of the orbitals increase, and hence the order in which the orbitals are filled is as follows.

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s,.....

The order may be remembered by using the graphical representation shown in the Fig. 1.4.

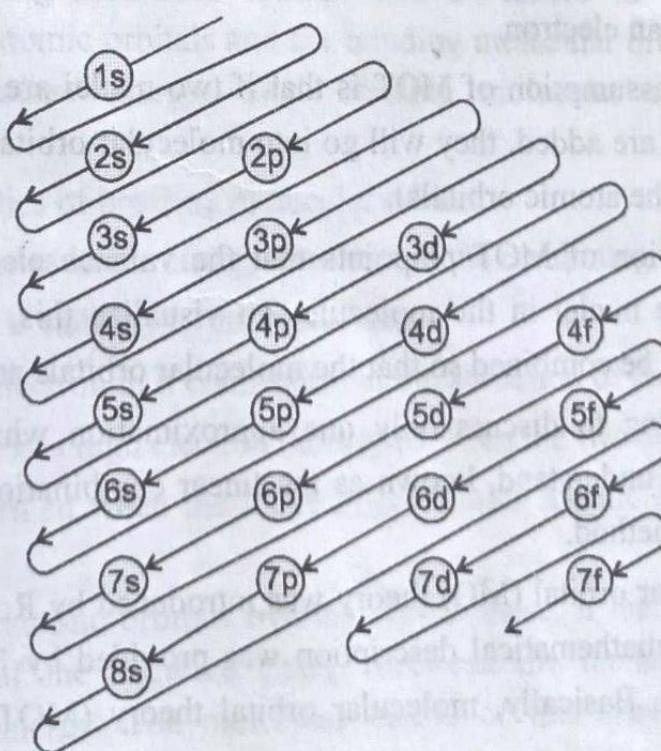


Fig. 1.4 : Order of filling the Orbitals

Starting from the top, the direction of the arrows gives the order of filling of orbitals.

**2. Pauli's exclusion principle:** According to this principle, no two electrons in an atom can have the same set of four quantum numbers. It can also be stated as "Only two electrons may exist in the same orbital and they must have opposite spin". This means that the two electrons can have the same value of three quantum numbers n, l and m, but must have the opposite spin quantum number.

**3. Hund's Rule of maximum multiplicity:** This rule deals with the filling of electrons into the orbitals belonging to the same subshell i.e. orbitals of equal energy. It states "pairing of electrons in the orbitals belonging to the same subshell (p, d, f) does not take place until each orbital belonging to that subshell has got one electron each i.e. it is singly occupied".

E.g. There are three p orbitals ( $p_x, p_y, p_z$ ). According to Hund's rule, each of the three p orbitals must get one electron each of parallel spin before any one of them gets the second electron of opposite spin.

### 1.3 MOLECULAR ORBITAL THEORY (MOT)

We know that the electrons have a dual character and they are considered either as particles or as waves. An electron in an atom may therefore be described as occupying an atomic orbital, or described by a wave function  $\Psi$  (an abstract mathematical concept). By itself,  $\Psi$  has no physical significance except that it represents the amplitude of the wave, and it is obtained as a solution of the Schrodinger wave equation, where  $\Psi^2$  stands for the probability of finding an electron.

The fundamental assumption of MOT is that if two nuclei are placed at equilibrium distance and electrons are added, they will go into molecular orbitals (which are in many respects analogues to the atomic orbitals).

The basic assumption of MOT pinpoints that the valence electrons are essentially associated with all the nuclei in the molecule. To visualize this, atomic orbitals from different atoms have to be combined so that the molecular orbitals are produced.

Hence, we are going to discuss only one approximation which is rather simple, qualitative and easy to understand, known as the linear combination of atomic orbitals, abbreviated as LCAO method.

Qualitative molecular orbital (MO) theory was introduced by Robert S Mulliken and Friedrich Hund, and a mathematical description was provided by Douglas Hartree and Vladimir Fock in 1930. Basically, molecular orbital theory (MOT) was developed to explain,

1. The formation of chemical bond

2. Relative bond strength

3. Paramagnetic or diamagnetic nature of molecules.

The salient features of MOT are as follows :

1. When two atoms approach each other, their atomic orbitals lose their identity and mutually overlap to form new orbitals called molecular orbitals.
2. The number of MO formed is equal to the number of overlapping atomic orbitals.
3. Maximum capacity of a MO is two electrons with opposite spins. MO is a polycentric region in space defined by its size and shape, associated with two or more atoms in a molecule and each has a capacity of two electrons with opposite spins.
4. Only atomic orbitals having comparable energies as well as proper orientations interact significantly. For example, 1s atomic orbital can overlap with 1s atomic orbital but not with 2s atomic orbital or 2s atomic orbital can overlap with 2p<sub>x</sub> atomic orbital.
5. When two atomic orbital overlap, they interact to form two molecular orbitals, in the following two ways.
  - When the atomic orbitals overlap in-phase it leads to an increase in the intensity of the negative charge in the region of overlap. The molecular orbital thus formed has lower potential energy than the separate atomic orbitals and is called bonding molecular orbital. The difference in energy between the combining atomic orbitals and the bonding molecular orbital formed is called the stabilization energy. Thus bonding molecular orbital stabilizes the molecule.

Characteristics of bonding molecular orbital:

- (a) It possesses lower energy than that of the combining atomic orbitals.
- (b) It imparts stability to the molecules.
- (c) Every electron in it contributes to the attraction of two combining atoms.
- (d) It possesses high electron density between the two nuclei.
- (e) It is formed when the lobes of combining atomic orbitals have the same signs.
- When the atomic orbitals overlap out-of-phase, it leads to a decrease in the intensity of the negative charge between the nuclei and leads to higher potential energy. The molecular orbital of this type is called antibonding molecular orbital. The difference in energy between the antibonding

molecular orbital and combining atomic orbitals is called destabilization energy. Thus antibonding molecular orbital destabilizes the molecule.

Characteristics of antibonding molecular orbital:

- It possesses higher energy than that of the combining atomic orbitals.
  - It imparts instability to the molecules.
  - Every electron in it contributes to the repulsion of two combining atoms.
  - It possesses low electron density between the two nuclei.
  - It is formed when the lobes of combining atomic orbitals have the opposite signs.
6. The shape of MO formed depends on the type of combining atomic orbitals.
7. The bonding MO are represented by  $\sigma$ ,  $\pi$ ,  $\delta$  etc., whereas antibonding MO are represented by  $\sigma^*$ ,  $\pi^*$ ,  $\delta^*$  etc.
8. Inner orbital MO which do not take part in bond formation are called non bonding MO.

## 1.4 LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO) METHOD

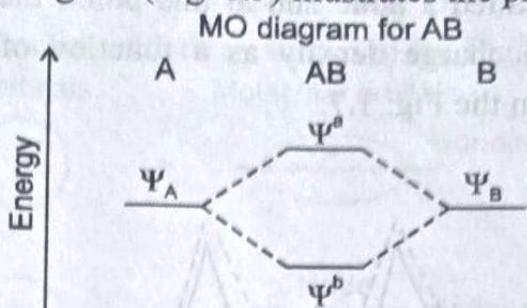
Molecular orbitals of a molecule, i.e. solutions to the molecular Schrodinger equation can be obtained by a method known as linear combination of atomic orbitals (LCAO). As per this method, linear combination is brought about by taking the summation or difference of atomic orbital wave functions. Consider two atoms A and B which have atomic orbitals described by the wave functions  $\Psi_A$  and  $\Psi_B$ , then the wave function for the molecule AB can be obtained by a linear combination of the atomic orbitals  $\psi_A$  and  $\psi_B$ .

$$\Psi = N(C_1 \Psi_A \pm C_2 \Psi_B)$$

Where  $\Psi$  is the wave function of MO,  $\Psi_A$  and  $\Psi_B$  are wave functions of AOs belonging to atom A and B respectively,  $C_1$  and  $C_2$  are constants chosen to give minimum energy for  $\Psi$ ,  $N$  is a normalizing constant chosen to ensure that the probability of finding an electron in the whole of the space is unity.

The equation clearly shows that linear combination gives rise to formation of two MOs. One is obtained by taking the sum of two AO wave functions i.e.  $\Psi^b = N(C_1 \Psi_A + C_2 \Psi_B)$ . This results in an increased electron density between the two nuclei. This is the **bonding MO** having a lower energy than the combining AOs. The other MO is obtained by taking the difference of two AO wave functions i.e.  $\Psi^a = N(C_1 \Psi_A - C_2 \Psi_B)$ . It has a node with zero electron density between the nuclei due to cancellation of two wave

functions. This is the **antibonding MO** having a higher energy than the combining AOs. The following energy level diagram (Fig. 1.5) illustrates the process.



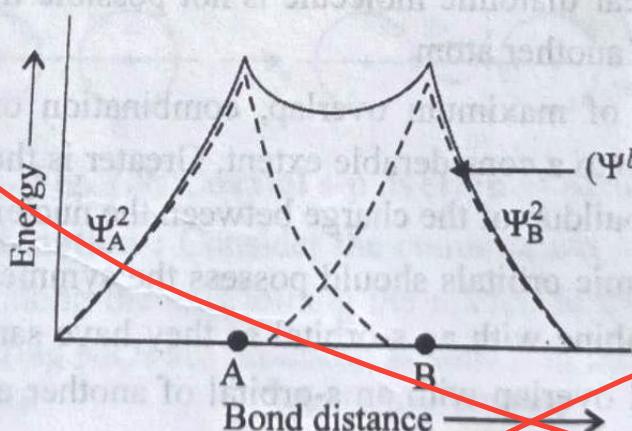
**Fig. 1.5 : Formation of bonding and antibonding MOs**

#### Significance of bonding and antibonding MOs :

Taking squares of the bonding MO wave function ( $\Psi^b$ ), we get

$$(\Psi^b)^2 = \Psi_A^2 + \Psi_B^2 + 2\Psi_A\Psi_B \quad (\text{for identical atoms } C_1 = C_2 = 1).$$

The terms  $\Psi_A^2$  and  $\Psi_B^2$  indicate electronic charge densities of wave functions  $\Psi_A$  and  $\Psi_B$  belonging to isolated atoms A and B respectively.  $(\Psi^b)^2$  is the electronic charge density of the wave function  $\Psi^b$ , i.e., the bonding MO. Thus, the more is the value of  $(\Psi^b)^2$ , the more is the charge density between the two combining nuclei. It is evident from the equation that  $(\Psi^b)^2 > \Psi_A^2 + \Psi_B^2$  by a term  $2\Psi_A\Psi_B$ . This term  $2\Psi_A\Psi_B$  results from the overlap of AOs and is called overlap integral. Larger is the overlap integral more is the charge density between the nuclei and stable is the bond formed. The plot of electron charge density as a function of inter-nuclear distance for bonding MO is shown in the Fig. 1.6.



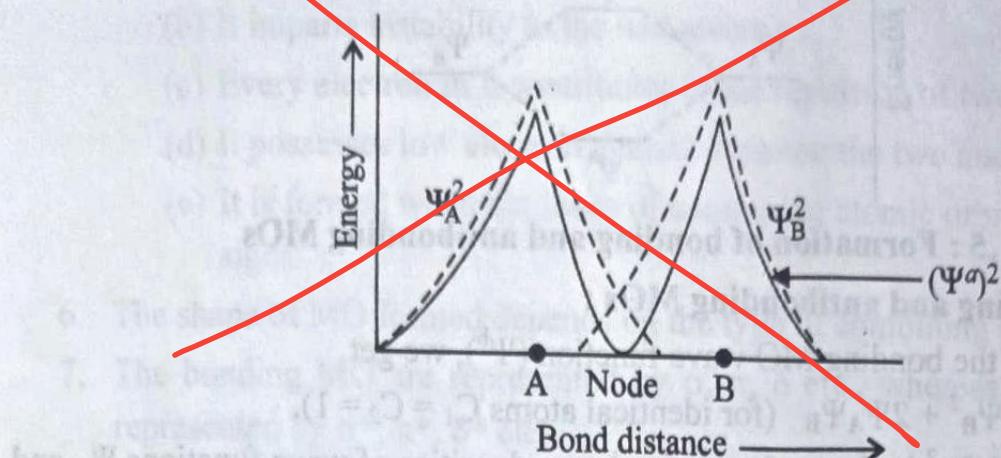
**Fig. 1.6 : Plot of Electron Charge Density for bonding MO**

Taking square of the antibonding MO wave function ( $\Psi^a$ ), we get

$$(\Psi^a)^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

It is evident from the above equation that  $(\Psi^a)^2 < \Psi_A^2 + \Psi_B^2$  by a term  $2\Psi_A\Psi_B$ . That's how, in the antibonding MO, there is less charge density between the nuclei. Therefore, the energy of the antibonding MO is more than the sum of the energies of the two

interacting atoms A and B. The charge density touches the axis at mid-point between the nuclei. This mid-point is called a node and at this point, the electron charge density is zero. The plot of electron charge density as a function of inter-nuclear distance for antibonding MO is shown in the Fig. 1.7.



**Fig. 1.7 : Plot of Electron Charge Density for antibonding MO**

## 1.5 SHAPES OF MOLECULAR ORBITALS



### Conditions for the formation of molecular orbitals:

There are certain limitations to the combination of atomic orbitals which are as follows :

1. The energies of combining atomic orbitals should be of similar magnitude. Formation of a homonuclear diatomic molecule is not possible if 1s-orbital of one atom overlaps with 2s-orbital of another atom.
2. According to rule of maximum overlap, combination of atomic orbitals takes place only if overlapping is to a considerable extent. Greater is the overlapping of atomic orbitals, the greater is the buildup of the charge between the nuclei.
3. The combining atomic orbitals should possess the symmetry about the molecular axis. A  $p_x$ -orbital will combine with an s-orbital as they have same symmetry. But a  $p_z$ -orbital of an atom will not overlap with an s-orbital of another atom as they don't have same symmetries.

When two atomic orbitals overlap along the internuclear axis, then the resulting molecular orbital is called sigma ( $\sigma$ ) molecular orbital. When two atomic orbitals overlap sideways, then the resulting molecular orbital is called pi ( $\pi$ ) molecular orbital. Some simple cases of combinations of atomic orbitals to form molecular orbitals are given.

- (a) **s-s combination of orbitals (1s with 1s or 2s with 2s)** : The two molecular orbitals formed may be designated as bonding  $\sigma$  (1s) or  $\sigma$  (2s) and antibonding

$\sigma^*$  (1s) or  $\sigma^*$  (2s). This indicates that the overlap is along internuclear axis.  $\sigma$  (1s) is formed by constructive overlapping and  $\sigma^*$  (1s) is formed by destructive overlapping of the two s-orbitals as shown in the Fig. 1.8.

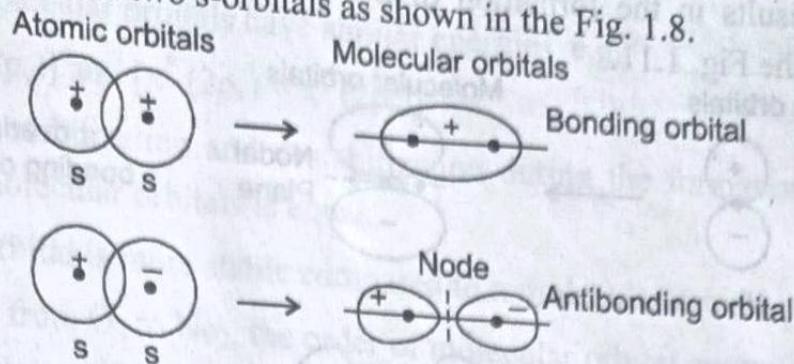


Fig. 1.8 : s-s overlap of orbitals

(b) coaxial s-p combination of orbitals (s-orbital with  $p_x$  orbital) : An s-orbital may combine with a p-orbital provided that the lobes of the p-orbital are pointing along the axis joining the nuclei. When the lobes which overlap have the same sign, results in a bonding MO with an increased electron density between the nuclei. When the overlapping lobes have opposite signs, it gives an antibonding MO with reduced electron density in between the nuclei as shown in the Fig. 1.9.

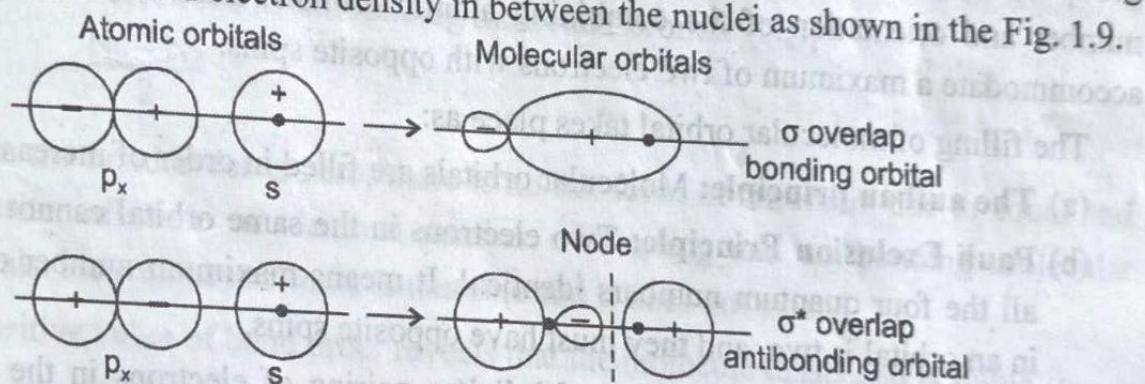


Fig. 1.9: Coaxial s-p overlap of orbitals

(c) axial p-p combination : Consider the combination of two p-orbitals which have lobes pointing along the axis joining the nuclei. In this case, both a bonding MO and an antibonding MOs are produced as shown in the Fig. 1.10.

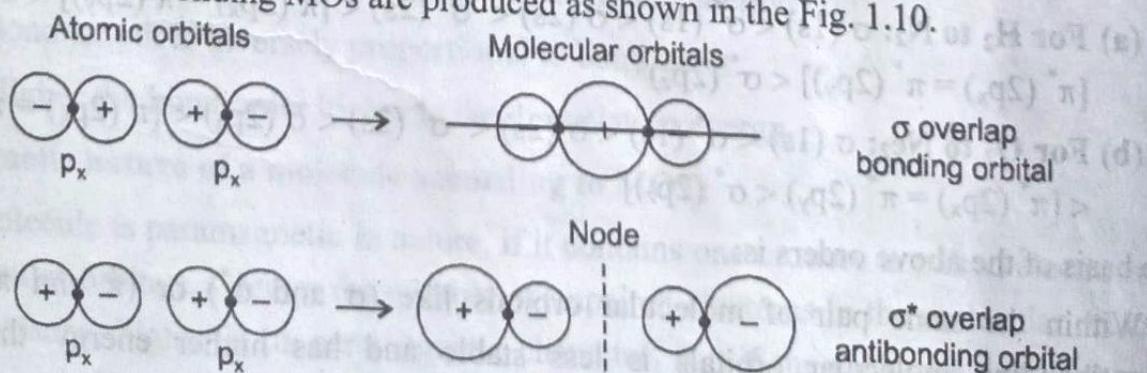


Fig. 1.10 : Axial p-p overlap of orbitals

(d) **Side-to-side p-p combination:** Consider the combination of two orbitals which both have lobes perpendicular to the axis joining the nucleus. Lateral overlap of orbitals results in the formation of  $\pi$  bonding MO and  $\pi^*$  antibonding MO as shown in the Fig. 1.11.

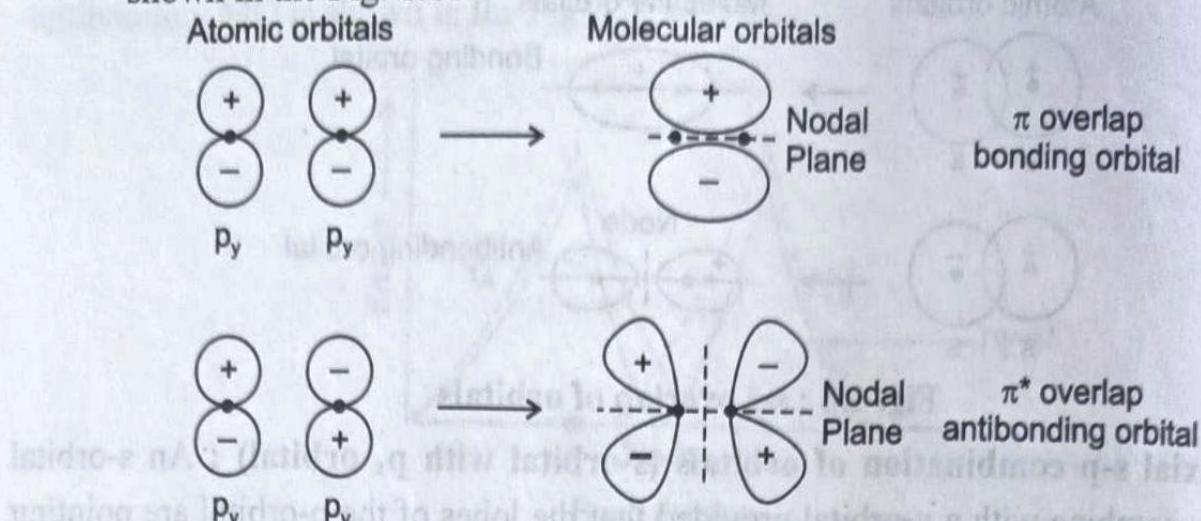


Fig. 1.11 : Side-to-side p-p overlap of orbitals

**Molecular orbitals** give the probability of distribution of electron clouds around a group of nuclei. Shape and size of a molecular orbital depends upon the shape, size, number and orientation of the combining atomic orbitals. Each molecular orbital can accommodate a maximum of two electrons with opposite spins.

The filling of molecular orbital takes place as:

- (a) **The aufbau principle:** Molecular orbitals are filled in order of increasing energy.
- (b) **Pauli Exclusion Principle:** Two electrons in the same orbital cannot have set of all the four quantum numbers identical. It means maximum number of electrons in an orbital is two, and they must have opposite spins.
- (c) **Hund's rule of maximum multiplicity:** pairing of electrons in the degenerate molecular orbitals does not occur until each of them has one electron each.

The relative energies of molecular orbitals in increasing order have been found to be as follows:

- (a) **For H<sub>2</sub> to N<sub>2</sub>:**  $\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < [\pi(2p_x) = \pi(2p_y)] < \sigma(2p_z) < [\pi^*(2p_x) = \pi^*(2p_y)] < \sigma^*(2p_z)$
- (b) **For O<sub>2</sub> to Ne<sub>2</sub>:**  $\sigma(1s) < \sigma^*(1s) < \sigma(2s) < \sigma^*(2s) < \sigma(2p_z) < [\pi(2p_x) = \pi(2p_y)] < [\pi^*(2p_x) = \pi^*(2p_y)] < \sigma^*(2p_z)$

The basis of the above orders is:

- Within the same pair of molecular orbitals like ( $\sigma$  and  $\sigma^*$ ) or ( $\pi$  and  $\pi^*$ ), the antibonding molecular orbitals is less stable and has higher energy than the corresponding bonding molecular orbitals.

- Pair of molecular orbitals ( $\sigma 1s$  and  $\sigma^* 1s$ ) possesses lower energies than pair of molecular orbitals ( $\sigma 2s$  and  $\sigma^* 2s$ ).
- Degenerate molecular orbitals have similar energies. e.g.,  $[\pi(2p_x) = \pi(2p_y)]$  and  $[\pi^*(2p_x) = \pi^*(2p_y)]$
- The extent of stabilization and destabilization during the formation of bonding and antibonding molecular orbitals is equal.
- $\sigma$  molecular orbital is more stable compared to  $\pi$  molecular orbital.  
This explains, from O<sub>2</sub> to Ne<sub>2</sub>, the order of molecular orbital energy level is:  
 $\sigma 2p_z < [\pi(2p_x) = \pi(2p_y)] < [\pi^*(2p_x) = \pi^*(2p_y)] < \sigma^*(2p_z)$

### Bond order of a molecule according to MOT:

Bond order of a molecule is a measure of strength of a bond between two atoms.

It is defined mathematically as:

$$\begin{aligned} \text{Bond order} &= \frac{1}{2} [\text{Number of electrons in bonding molecular orbitals (N}_b\text{)} - \text{Number of} \\ &\quad \text{electrons in antibonding molecular orbitals (N}_a\text{)}] \\ &= \frac{N_b - N_a}{2} \end{aligned}$$

- When the bond order is zero, there is no net force of attraction due to equal and opposite influence of identical number of bonding and antibonding molecular orbitals. Hence, the molecule is unstable and it does not exist.
- A positive value of bond order reveals that the molecule exists and is stable.
- A bond order of +1, +2, +3 indicates that the molecule is formed by joining of two atoms by a single, double or triple bond respectively.
- Greater the value of bond order, greater is the stability of the molecule. Thus higher the bond order, higher is the dissociation energy.
- Bond length is inversely proportional to bond order.
- Higher the bond order higher is the dissociation energy.

### Magnetic nature of a molecule according to MOT:

A molecule is paramagnetic in nature, if it contains one or more unpaired electrons in its molecular orbitals. Greater the number of unpaired electrons in the molecular orbitals of a substance, higher is its paramagnetic character. But if the molecule does not have any unpaired electron, then it is diamagnetic in nature.

**Comparisons:****Bonding Molecular Orbitals and Anti-Bonding Molecular Orbitals:**

Bonding Molecular Orbitals	Anti-Bonding Molecular Orbitals
1. Formed by addition overlap of atomic orbitals.	1. Formed by subtraction overlap of atomic orbitals.
2. Possesses lower energy than that of the atomic orbitals.	2. Possesses higher energy than that of the atomic orbitals.
3. $\Psi_b = \Psi_A + \Psi_B$	3. $\Psi_a = \Psi_A - \Psi_B$
4. Imparts stability to the molecule.	4. Imparts instability to the molecule.
5. Possesses high electron-density in the region between the two nuclei.	5. Possesses low electron-density in the region between the two nuclei.
6. It is formed when lobes of the combining atomic orbitals possess same sign.	6. It is formed when lobes of the combining atomic orbitals possess opposite sign.

 **$\sigma$  and  $\pi$  Molecular orbitals:**

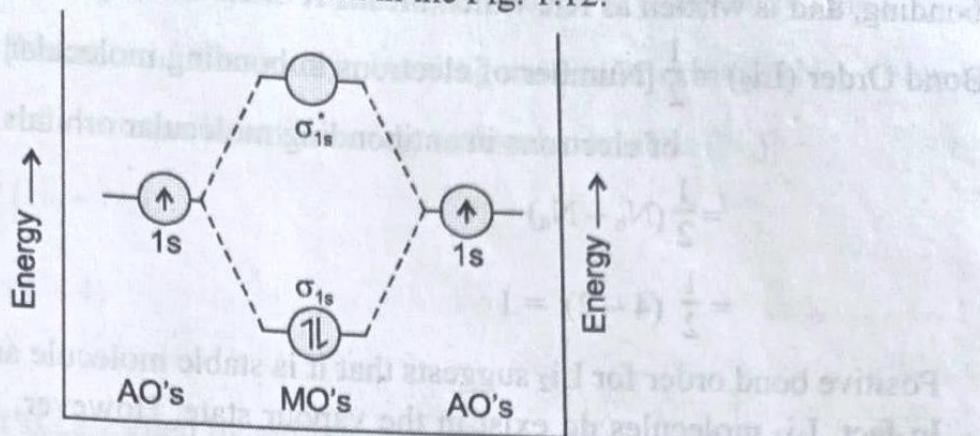
Sigma Molecular Orbital	Pi Molecular Orbital
1. The sigma molecular orbital is obtained when the atomic orbitals overlap collinearly to a large extent.	1. The pi molecular orbital is obtained when atomic orbitals overlap along the side to a lesser extent.
2. For sigma overlap, the lobes of atomic orbitals point along the internuclear axis.	2. For pi overlap, the lobes of the atomic orbitals are perpendicular to the axis.
3. Sigma molecular orbital is denoted by $\sigma$ .	3. Pi molecular orbital is denoted by $\pi$ .
4. For sigma molecular orbital, $\psi$ is along the internuclear axis and the electron density $\psi^2$ is distributed uniformly along the axis.	4. For pi molecular orbital, $\psi$ is zero along the internuclear axis and the electron density $\psi^2$ on the axis is zero.

## 1.6 MOLECULAR ORBITAL TREATMENT FOR HOMONUCLEAR DIATOMIC MOLECULES

**(1) Hydrogen Molecule,  $H_2$  :**

Hydrogen molecule ( $H_2$ ) is formed by the overlap of 1s atomic orbitals of two hydrogen atoms having one electron each. Two molecular orbitals viz. bonding and antibonding are generated from the overlap of these atomic orbitals. In a hydrogen

molecule, there are two electrons with opposite spins which are accommodated in lower energy bonding ( $\sigma_{1s}$ ) molecular orbital as shown in the Fig. 1.12.



**Fig. 1.12 : MO energy level diagram for  $H_2$**

Hence, molecular orbital electronic configuration of  $H_2$  molecule =  $\sigma_{1s}^2$ .

$$\begin{aligned}\text{Bond order } (H_2) &= \frac{1}{2} [\text{Number of electrons in bonding molecular orbitals } (N_b) - \text{Number} \\ &\quad \text{of electrons in antibonding molecular orbitals } (N_a)] \\ &= \frac{N_b - N_a}{2} = \frac{2 - 0}{2} = 1\end{aligned}$$

As the bond order is greater than zero therefore  $H_2$  molecule is stable and it exists.

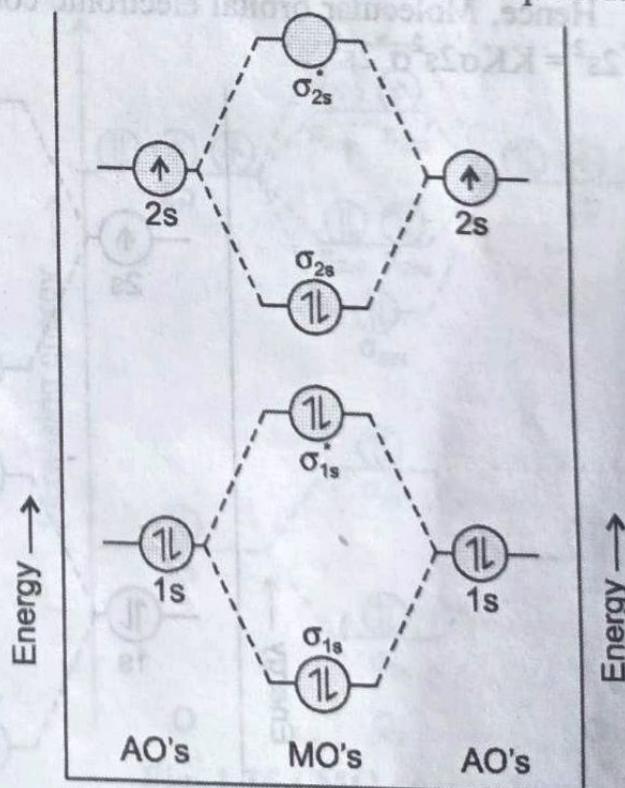
**Magnetic Behaviour of  $H_2$ :**  $H_2$  molecule is diamagnetic as both the electrons are paired.

## (2) Lithium molecule, $Li_2$ :

Lithium molecule is formed by the overlap of two lithium atoms each having the electronic configuration of  $1s^2 2s^1$ . So, there are total six electrons which have to be accommodated in 4 molecular orbitals viz.  $\sigma_{1s}$ ,  $\sigma^*_{1s}$ ,  $\sigma_{2s}$  and  $\sigma^*_{2s}$ .

The six electrons are filled in these 4 molecular orbitals according to aufbau principle and Pauli's exclusion principle as shown in the Fig. 1.13.

Hence, Molecular orbital electronic configuration of  $Li_2$  molecule =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 = KK\sigma 2s^2$ .



**Fig. 1.13 : MO energy level diagram for  $Li_2$**

Since, the inner shell of filled  $\sigma 1s$  and  $\sigma^* 1s$  molecular orbitals do not contribute to the bonding, and is written as KK which means K-shell is completely filled.

$$\begin{aligned}\text{Bond Order} (\text{Li}_2) &= \frac{1}{2} [\text{Number of electrons in bonding molecular orbitals (N}_b\text{)} - \text{Number of electrons in antibonding molecular orbitals (N}_a\text{)}] \\ &= \frac{1}{2} (N_b - N_a) \\ &= \frac{1}{2} (4 - 2) = 1\end{aligned}$$

Positive bond order for  $\text{Li}_2$  suggests that it is stable molecule and it exists.

In fact,  $\text{Li}_2$  molecules do exist in the vapour state. However, it is energetically more favourable for lithium to form a metallic structure in the solid.

**Magnetic behaviour of  $\text{Li}_2$ :**  $\text{Li}_2$  molecule is diamagnetic since both the electrons are paired.

### (3) Beryllium molecule, $\text{Be}_2$ :

Beryllium molecule may be formed by the overlap of two beryllium atoms each having the electronic configuration of  $1s^2 2s^2$ . So, there are total of eight electrons which have to be accommodated in 4 molecular orbitals viz.  $\sigma 1s$ ,  $\sigma^* 1s$ ,  $\sigma 2s$  and  $\sigma^* 2s$ .

The eight electrons are filled in these 4 molecular orbitals according to aufbau principle and Pauli's exclusion principle as shown in the Fig. 1.14.

Hence, Molecular orbital electronic configuration of  $\text{Be}_2$  molecule =  $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 = \text{KK} \sigma 2s^2 \sigma^* 2s^2$ .

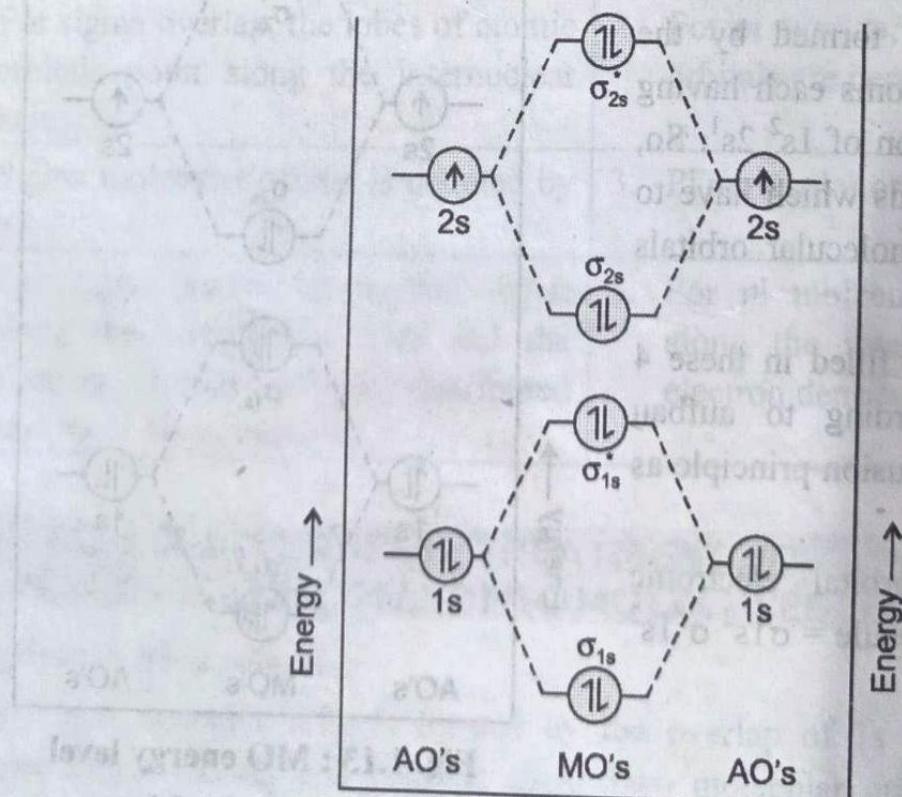


Fig. 1.14 : MO energy level diagram for  $\text{Be}_2$

Since, the inner shell of filled  $\sigma 1s$  and  $\sigma^* 1s$  molecular orbitals do not contribute to the bonding and is sometimes written as KK which means K-shell is completely filled.

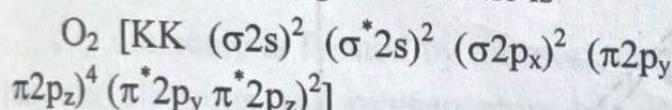
$$\begin{aligned}\text{Bond Order} (\text{Be}_2) &= \frac{1}{2} [\text{Number of electrons in bonding molecular orbitals (N}_b\text{)} - \text{Number of electrons in antibonding molecular orbitals (N}_a\text{)}] \\ &= \frac{1}{2} (N_b - N_a) \\ &= \frac{1}{2} (4 - 4) \\ &= 0\end{aligned}$$

The bonding effect is cancelled by antibonding effect where equal number of bonding and antibonding electrons is present in  $\text{Be}_2$ . Since the bond order is zero, beryllium is an imaginary nonexistent molecule.

#### (4) Oxygen molecule, $\text{O}_2$ :

Oxygen molecule is formed by the overlap of two oxygen atoms each having electronic configuration as  $1s^2 2s^2 2p_x^2, 2p_y^1, 2p_z^1$ . The total of 16 electrons in oxygen molecules can be filled according to aufbau principle, pauli's exclusion principle and Hund's rule of maximum multiplicity. The filled molecular orbitals of oxygen molecule are shown in the Fig. 1.15.

Hence, the molecular orbital electronic configuration of oxygen molecule is



In oxygen, the inner shell does not participate in bonding. The bonding and antibonding 2s orbitals cancel each other. A  $\sigma$  bond results from the filling of  $\sigma 2p_x^2$ . Since  $\pi^* 2p_y^1$  is half filled and therefore cancels half the effect of the completely filled  $\pi 2p_y^2$  orbital, half of a  $\pi$  bond results. Similarly, another half of a  $\pi$  bond arises from  $\pi 2p_z^2$  and  $\pi^* 2p_z^1$  giving a total of  $1 + \frac{1}{2} + \frac{1}{2} = 2$  bonds. Thus, there are two covalent bonds in oxygen one sigma and one pi.

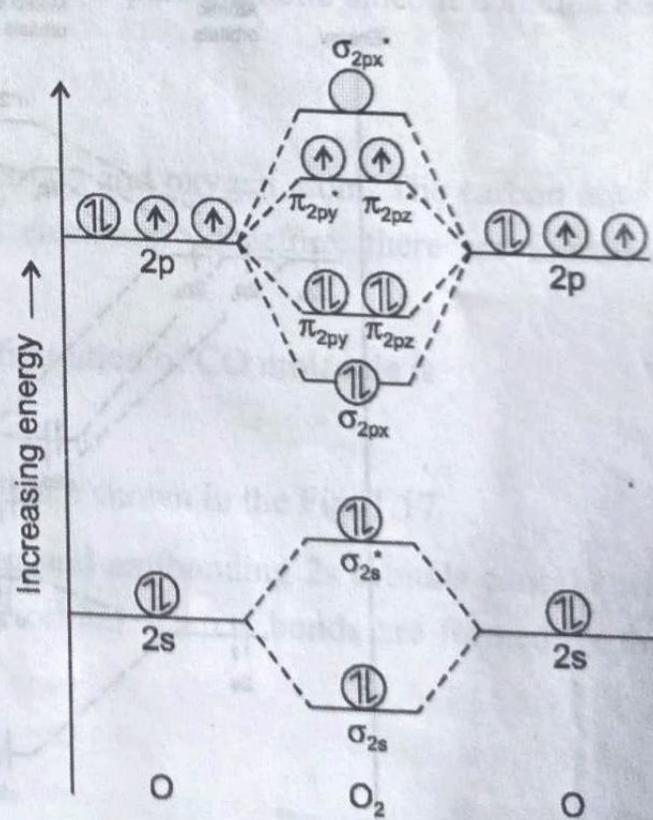


Fig. 1.15 : MO energy level diagram for  $\text{O}_2$

Bond Order ( $O_2$ ) =  $\frac{1}{2}$  [Number of electrons in bonding molecular orbitals ( $N_b$ ) – Number of electrons in antibonding molecular orbitals ( $N_a$ )]

$$= \frac{1}{2} (N_b - N_a)$$

$$= \frac{1}{2} (8 - 4)$$

$$= 2$$

Positive bond order for  $O_2$  suggests that it is stable molecule and it should exist.

**Magnetic behaviour of  $O_2$ :** The antibonding  $\pi^* 2p_y$  and  $\pi^* 2p_z$  orbitals are singly occupied in accordance with Hund's rule. Since there are two unpaired electrons with parallel spins, oxygen molecule shows paramagnetism. This was the success of MOT as valance bond theory failed to explain the paramagnetism of oxygen.

## 1.7 MOLECULAR ORBITAL TREATMENT FOR HETERONUCLEAR DIATOMIC MOLECULES

### 1. NO Molecule:

NO molecule is formed by the overlap of nitrogen and oxygen atom. The nitrogen atom has seven electrons and the oxygen atom has eight electrons. Therefore, there are fifteen electrons in the NO molecule.

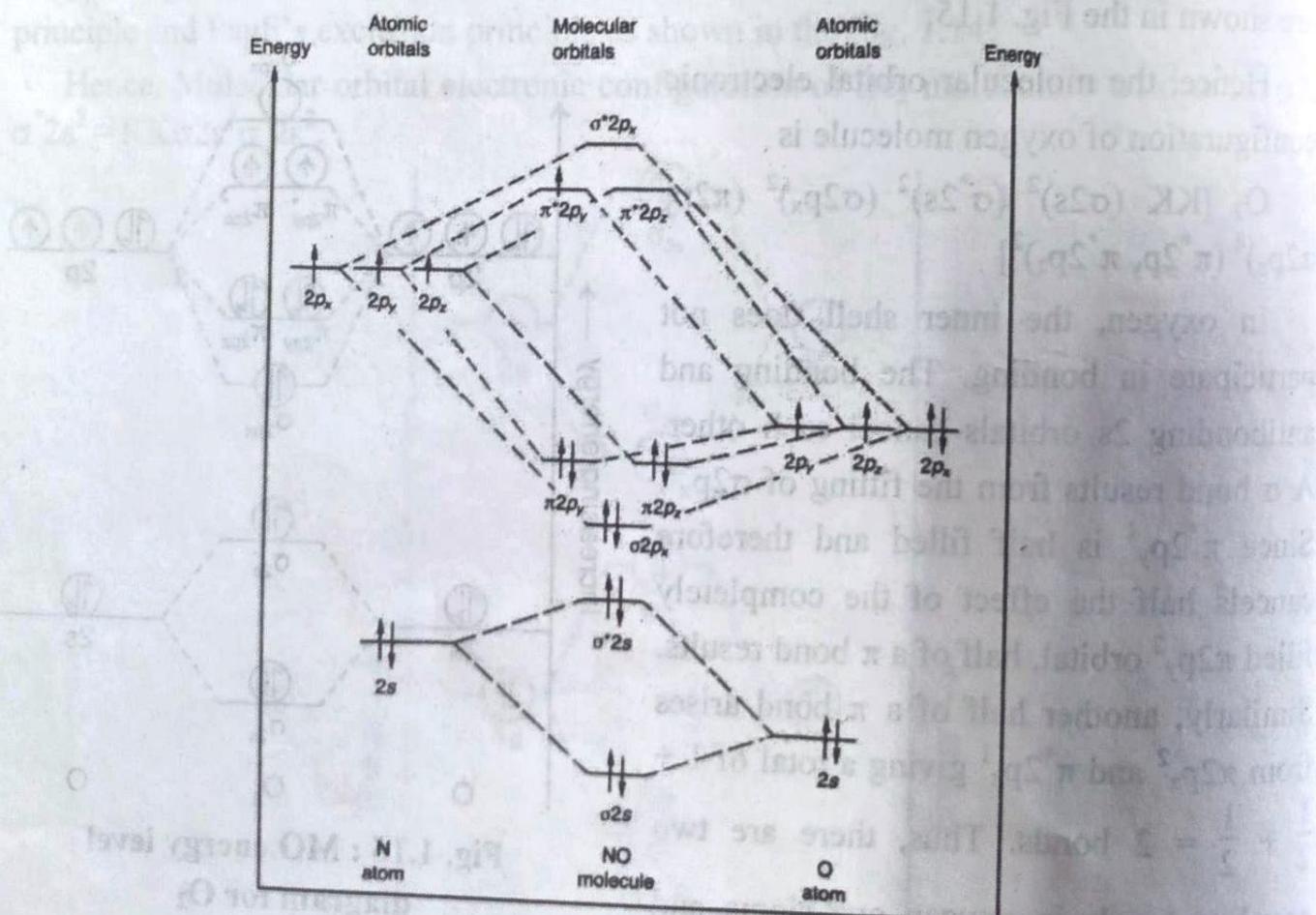
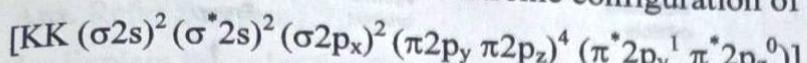


Fig. 1.16 : MO energy level diagram for NO

Hence, the molecular orbital electronic configuration of NO molecule is



The filled molecular orbitals of NO molecule are shown in the Fig. 1.16.

The inner shell is nonbonding. The bonding and antibonding 2s orbitals cancel each other. A  $\sigma$  bond is formed by the filled  $\sigma 2p_x^2$  orbital. A  $\pi$  bond is formed by the filled  $\pi 2p_z^2$  orbital. The half-filled  $\pi^* 2p_y^1$  half cancels the filled  $\pi 2p_y^2$  orbital, giving half a bond.

$$\begin{aligned} \text{Bond Order (NO)} &= \frac{1}{2} [\text{Number of electrons in bonding molecular orbitals (N}_b\text{)} - \text{Number of electrons in antibonding molecular orbitals (N}_a\text{)}] \\ &= \frac{1}{2} (N_b - N_a) \\ &= \frac{1}{2} (8 - 3) \\ &= 2.5 \end{aligned}$$

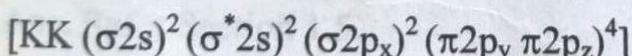
The bond order for NO molecule is 2.5 i.e. in between a double and triple bond.

**Magnetic behaviour of NO:** The NO molecule is paramagnetic since it contains an unpaired electron.

## 2. CO Molecule:

CO molecule is formed by the overlap of carbon and oxygen atom. The carbon atom has six electrons and oxygen atom has eight electrons. Therefore, there are fourteen electrons in the CO molecule.

Hence, the molecular orbital electronic configuration of CO molecule is



The filled molecular orbitals of CO molecule are shown in the Fig. 1.17.

The inner shell is nonbonding. The bonding and antibonding 2s orbitals cancel each other. A  $\sigma$  bond is formed by the filled  $\sigma 2p_x^2$  orbital. Two  $\pi$  bonds are formed by the filled  $\pi 2p_y^2$  and  $\pi 2p_z^2$  orbitals.

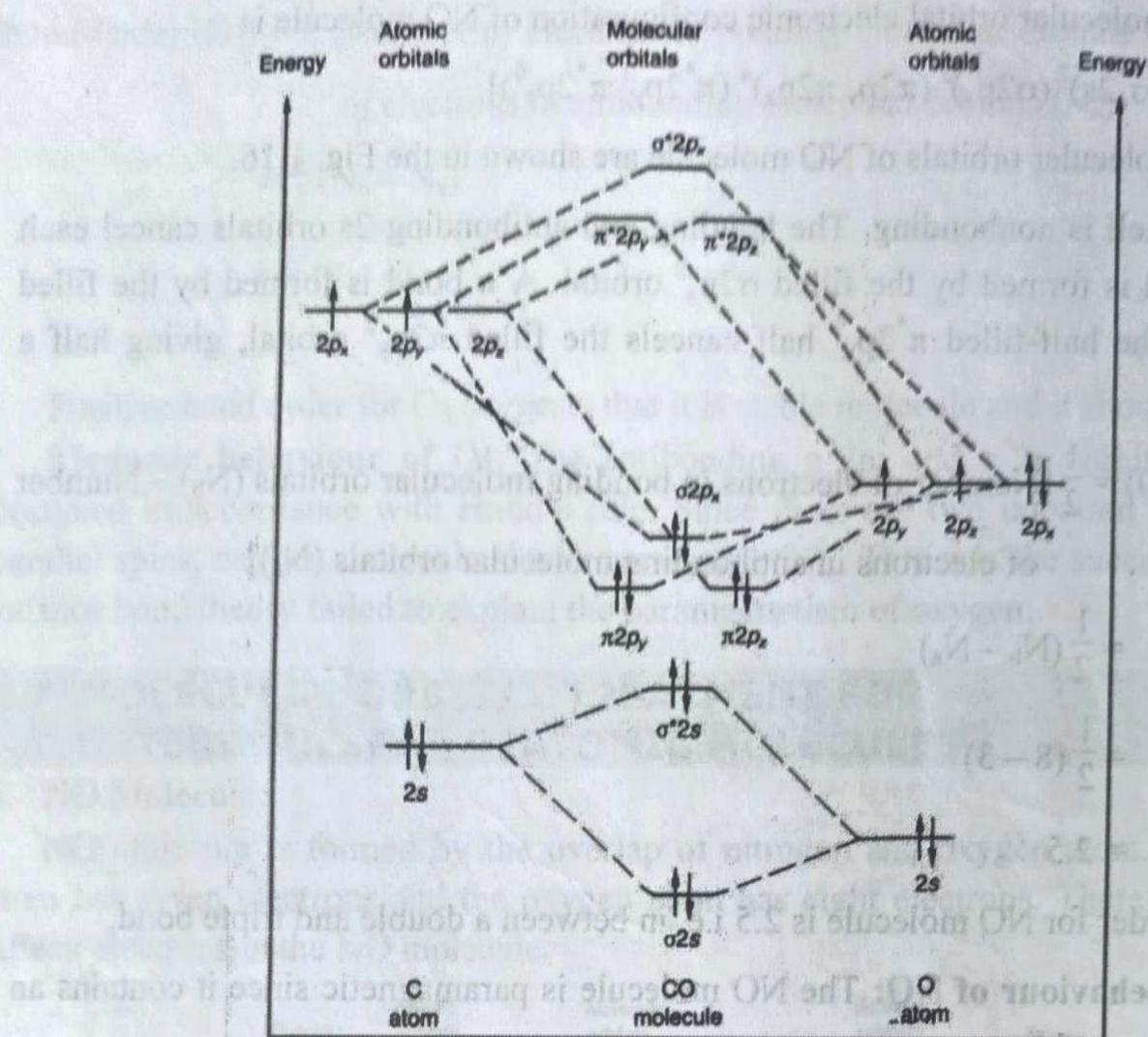


Fig. 1.17 : MO energy level diagram for CO

Bond Order (CO) =  $\frac{1}{2}$  [Number of electrons in bonding molecular orbitals (N<sub>b</sub>) – Number

of electrons in antibonding molecular orbitals (N<sub>a</sub>)]

$$= \frac{1}{2} (N_b - N_a)$$

$$= \frac{1}{2} (8 - 2)$$

$$= 3$$

The bond order for CO molecule is 3. Thus in CO molecule, there is a triple bond out of which one is a sigma bond and the other two are pi bonds and therefore CO is a very stable molecule.

**Magnetic behaviour of CO:** As in the CO molecule all the electrons are paired, it is diamagnetic molecule.

# AROMATIC SYSTEMS AND THEIR MOLECULAR STRUCTURE

## SYLLABUS

- Define Aromaticity, Huckel's rule
- Structure and bonding of benzene and pyrrole

### 2.1 INTRODUCTION

In earlier times, during the study of organic chemistry some sweet smelling compounds were obtained from natural sources. These compounds showed different properties compared to aliphatic compounds. They were called **aromatic** (Greek, aroma = pleasant smell) compounds. Further studies revealed that these compounds contain benzene rings involving six carbon atoms in a ring. Later on, a large number of aromatic compounds were discovered which lacked the sweet smell. Thus this word aroma lost its significance.

### 2.2 AROMATICITY

Aromatic compounds form the most important group of organic compounds and benzene is the simplest member of this group. The determination of the structural formula of benzene was not as simple as its molecular formula  $C_6H_6$ . The molecular formula shows that benzene contains eight hydrogen atoms less than a saturated hydrocarbon containing six carbon atoms i.e. Hexane ( $C_6H_{14}$ ). This leads to expectation that it should be a highly unsaturated compound containing double or triple bonds between its carbon atoms. In such a case, benzene was supposed to give addition reactions which are typical of alkenes or alkynes. Further, it should be readily oxidisable. Surprisingly, benzene was found to behave in an almost exactly opposite manner which is clear from the following Table 2.1.

**Table 2.1 : Comparison of properties of benzene with alkenes**

	<b>Reagent</b>	<b>Reaction with alkenes</b>	<b>Reaction with benzene</b>
1.	KMnO <sub>4</sub> (cold, dilute, aqueous)	Rapid oxidation	No reaction
2.	Br <sub>2</sub> in CCl <sub>4</sub> (in the dark)	Rapid addition	No reaction
3.	HBr	Rapid addition	No reaction
4.	H <sub>2</sub> in presence of Ni	Rapid hydrogenation at 25°C and under a pressure of about 1 atm	Slow hydrogenation at 100-200°C and under a pressure of about 100 atm

[Organic compounds which resemble benzene in their chemical behaviour are called aromatic compounds.] They exhibit certain characteristic properties which are different from those of aliphatic and alicyclic compounds. These characteristic properties are collectively referred to as **aromaticity or aromatic character**. Aromaticity may therefore be defined as the ability of many cyclic compounds containing conjugation in their rings to undergo substitution reactions rather than the addition reactions, to resist oxidation and to exhibit a marked stability of their rings.

#### 4 Characteristics of aromatic compounds:

- They are highly unsaturated as shown by the lesser number of hydrogen atoms in their molecular formulae.
- They are cyclic compounds with five, six or seven membered rings.
- Their molecules are flat or nearly flat as shown by physical methods such as x-ray and electron diffraction methods.
- They undergo readily certain electrophilic substitution reactions such as nitration, halogenation, sulphonation, Friedel-Crafts alkylation and acylation etc.
- Although their molecular formulae suggest a high degree of unsaturation, yet they do not respond to tests characteristics of unsaturated compounds. They fail to decolorize an aqueous solution of potassium permanganate (Baeyer's test).
- They are associated with high thermodynamic stability as is indicated by their low heats of combustion and hydrogenation.]

#### 2.3 HUCKEL'S RULE

[This rule is based upon molecular orbital treatment and is employed for predicting aromaticity in organic compounds. The main theoretical requirements for a substance to possess aromaticity are :

1. The molecule or ion must be flat or nearly flat.
2. It must have cyclic clouds of delocalized  $\pi$ -electrons above and below the plane of the molecule. The  $\pi$ -electron clouds should encompass all the carbon atoms of the cyclic system.
3. The  $\pi$ -clouds in the molecule or ion must contain a total of  $(4n + 2) \pi$  electrons where  $n = 0, 1, 2, 3, \dots$  etc.

The above requirements are collectively known as Huckel rule or  $(4n + 2)$  rule.

Huckel rule for aromaticity states that a cyclic system containing  $(4n + 2) \pi$  electrons, where  $n$  is an integer, such as 0, 1, 2, 3 etc, would have special stability. This special stability is called aromaticity.

This rule can be applied successfully to cyclic polyenes, polycyclic compounds and non-benzenoid compounds to predict aromaticity in them.

The rule is based on quantum mechanics and is strongly supported by facts. The values of  $n$  are called Huckel numbers.

Thus,

$$n = 0$$

$$4n + 2 = 2$$

$$n = 1$$

$$4n + 2 = 6$$

$$n = 2$$

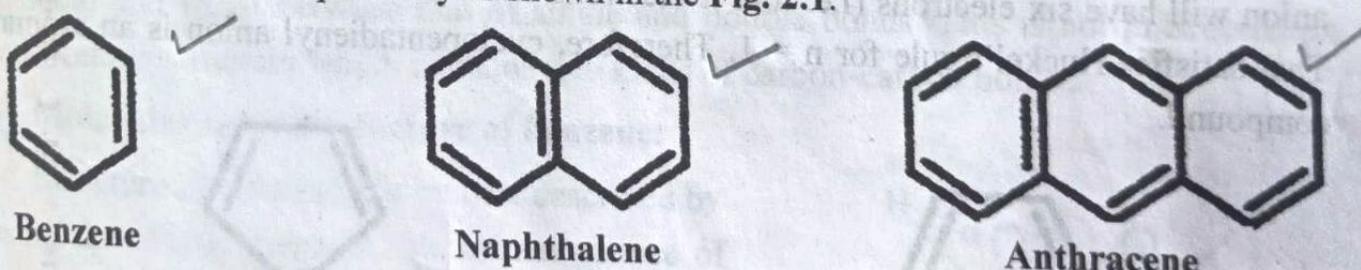
$$4n + 2 = 10$$

$$n = 3$$

$$4n + 2 = 14 \text{ etc.}$$

Therefore, for a molecule to be aromatic, the number of  $\pi$ -electrons on the ring should be either 2 or 6 or 10 or 14, etc.

Thus, benzene, naphthalene and anthracene exhibit aromaticity as they contain 6, 10 and 14,  $\pi$ -electrons respectively as shown in the Fig. 2.1.



**Fig. 2.1 : Aromatic compounds containing  $6\pi$ ,  $10\pi$  and  $14\pi$  electrons**

**Theoretical justification of Huckel rule:** On quantum mechanical ground, an aromatic system possesses a close shell of  $\pi$ -electrons corresponding to inert gas configuration. Huckel pointed out that energies of molecular orbitals of aromatic systems have a pattern where there is always one orbital of lowest energy followed by degenerate (having same energy) pair of orbitals in order of increasing energy. Filling of orbitals takes place as per Hund's rule. For a conjugated planer, monocyclic system having 2, 6, 10, 14, etc.  $\pi$ -electrons, the lowest energy MO and all other degenerate pairs of MOs

would be occupied by two electrons each. Such systems are stable due to their closed shell filling of orbitals. For a monocyclic planer conjugated system with 4, 8, 12, etc. electrons, there will be always two singly occupied degenerate orbitals. Such systems are highly unstable and are anti-aromatic, e.g. cyclobutadiene (4  $\pi$ -electrons) and cyclooctatetraene (8  $\pi$ -electrons).

### Study of some compounds for their aromaticity:

In spite of conjugation in the ring and the planarity of the ring, if the number of  $\pi$ -electrons on the ring is not in accordance with Hückel's rule, the compound would not exhibit aromaticity, e.g., cyclopropenyl anion. It satisfies both the conditions of conjugation and planarity of the ring. However, the number of  $\pi$ -electrons on the ring being four, which is not a Hückel number, it does not show aromaticity. It is an anti-aromatic compound.

The cycloheptatriene has three conjugated double bonds. Thus there are six  $\pi$ -electrons. Even though six is a Hückel number, cycloheptatriene is not an aromatic compound since for a cyclic compound to be aromatic, all the double bonds must be continuously conjugated. Only in that case, there will be a circular cloud of  $\pi$ -electrons.

Cyclopentadiene contains only four  $\pi$ -electrons which is not a Hückel number. As it does not satisfy Hückel's rule, it is anti-aromatic. The corresponding Cyclopentadienyl anion will have six electrons (i.e. four  $\pi$ -electrons and a pair of electrons) for resonance. That satisfies Hückel's rule for  $n = 1$ . Therefore, cyclopentadienyl anion is an aromatic compound.

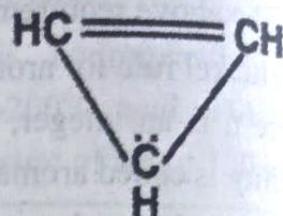


Fig. 2.2 :  
Cyclopropenyl anion

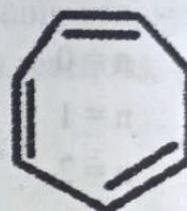
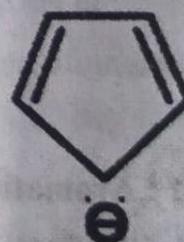


Fig. 2.3 : Cycloheptatriene



Cyclopentadiene

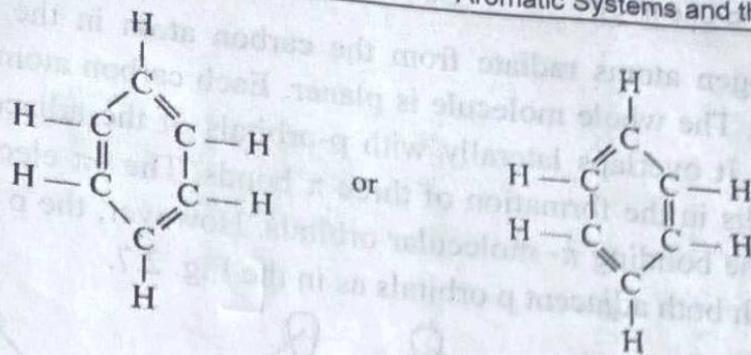


Cyclopentadienyl anion

Fig. 2.4

## 2.4 STRUCTURE AND BONDING OF BENZENE

According to Kekulé, six carbon atoms of benzene are linked to each other by alternate single and double covalent bonds to form a hexagonal ring as shown in the Fig. 2.5.

**Fig. 2.5 : Kekulé structure of benzene**

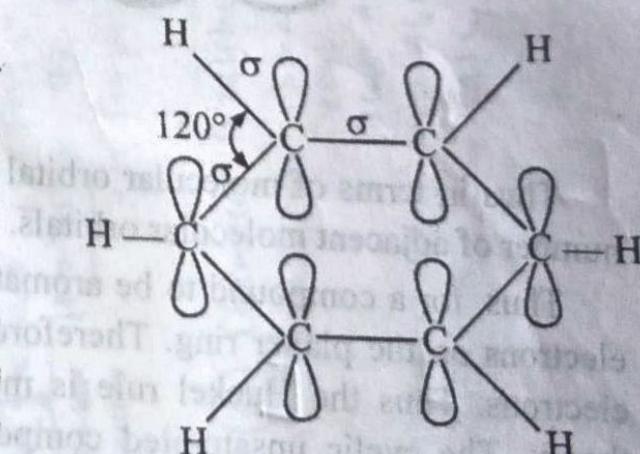
Each carbon atom is linked to one hydrogen atom thus conforming to its molecular formula.

#### ❖ Kekulé structure does not explain the following:

1. Benzene does not give addition reactions and fails to decolorize Baeyer's reagent. Instead, it readily undergoes electrophilic substitution reactions in which the benzene ring is retained.
2. On the basis of Kekulé structure, the heat of combustion of benzene is expected to be 3449.0 kJ/mol, however the experimental value is 3298.5 kJ/mol. Benzene is therefore more stable than expected from Kekulé structure.
3. On the basis of Kekulé structure, the heat of hydrogenation of benzene is expected to be 358.0 kJ/mol, however the experimental value is 208.5 kJ/mol. This shows that benzene is more stable than expected from Kekulé structure.
4. X-ray diffraction studies show that all the carbon-carbon bond lengths are identical and lie in between that of single and double bonds. This is not in accordance with Kekulé structure which contains two kinds of carbon-carbon bonds.

#### ❖ Molecular orbital structure of benzene:

Structure of benzene can be best described by using the orbital concept. The orbital picture of benzene shows that each carbon atom in benzene is  $sp^2$  hybridised. The C-H bonds in benzene are  $sp^2$ -s,  $\sigma$  bond. The C-C bonds are  $sp^2$ - $sp^2$ ,  $\sigma$  bonds. The  $sp^2$  hybridisation of the carbon atoms indicates that all the carbon atoms of the ring are in the same plane with their bonds separated by angles of  $120^\circ$  as shown in the Fig. 2.6.

**Fig. 2.6**

The six hydrogen atoms radiate from the carbon atom in the same plane like the spokes of a wheel. The whole molecule is planer. Each carbon atom has a pure p orbital with one electron. It overlaps laterally with p-orbitals of the adjacent carbon atoms on either side. It results in the formation of three  $\pi$  bonds. The  $6\pi$  electrons of benzene are enough to fill all the bonding  $\pi$ -molecular orbitals. However, the p orbitals may overlap simultaneously with both adjacent p orbitals as in the Fig. 2.7.

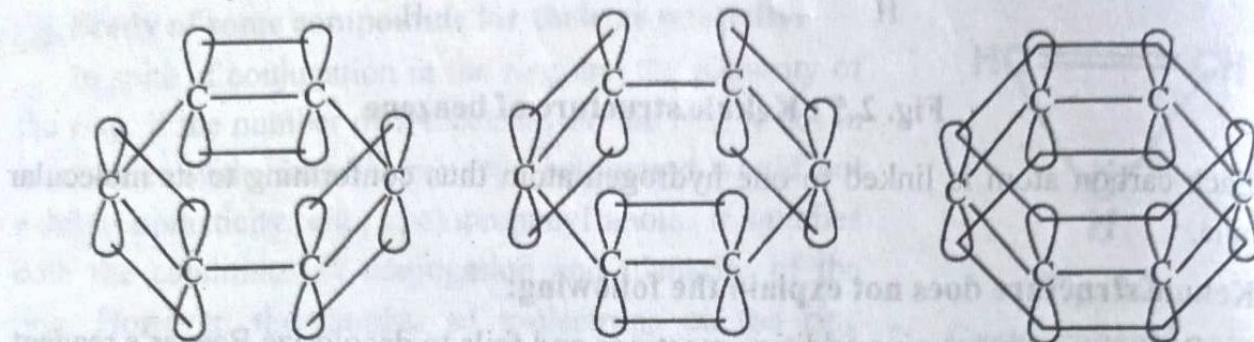


Fig. 2.7

This results in two continuous doughnut-shaped  $\pi$ -electron clouds, one lying above and the other lying below the plane of the ring as shown in the Fig. 2.8. This participation of the p orbital electrons is called delocalization and is responsible for the enhanced stability of the benzene ring.

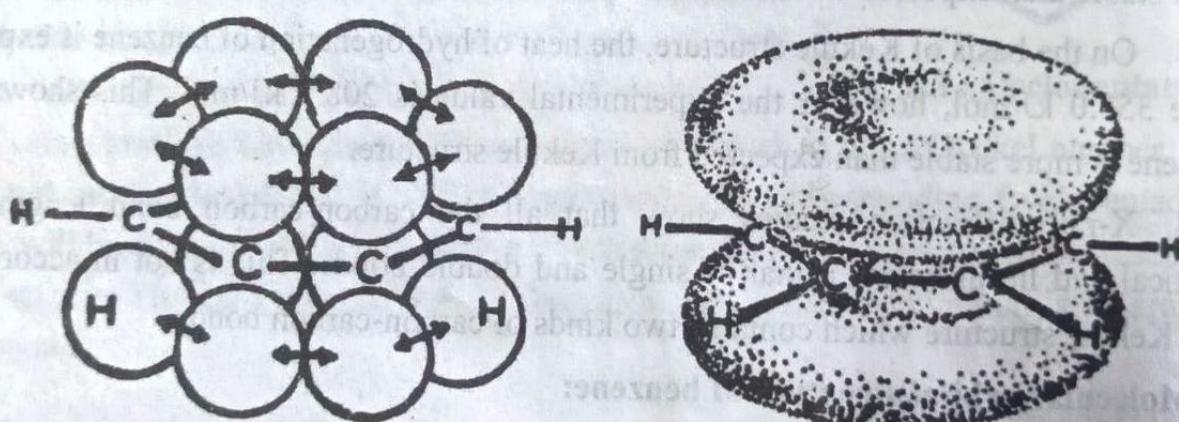


Fig. 2.8

Thus in terms of molecular orbital theory, resonance is delocalization of electrons in number of adjacent molecular orbitals.

Thus, for a compound to be aromatic it is not just enough to have Huckel number of electrons on the planer ring. Therefore, there must be a circular delocalized cloud of  $\pi$  electrons. Thus the Huckel rule is modified as follows in terms of molecular orbital theory. The cyclic unsaturated compounds will be aromatic if they contain  $(4n + 2)$  delocalized  $\pi$  electrons in the form of a circular cloud above and below the plane of the ring.

### **Evidence in support of orbital structure of benzene:**

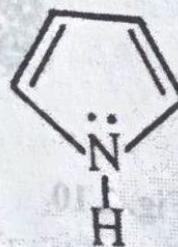
**1. Unusual stability:** Benzene molecule exhibits unusual stability and resists the formation of addition products. This can easily be understood in terms of delocalization of  $\pi$ -electrons which is responsible for aromaticity.

**2. Isomer number:** According to orbital concept, all the six carbons in benzene are completely equivalent. Similarly, all the six hydrogen atoms also occupy identical positions. Thus, benzene should form only one monosubstituted and three disubstituted products. This has been found to be in actual practice.

**3. Electrophilic substitution reactions:** There are two continuous ring like  $\pi$ -electron clouds one above and the other below the plane of carbon atoms. The  $\pi$ -electrons are easily attacked by electrophiles. Hence, benzene undergoes electrophilic substitution reactions.

## **2.5 STRUCTURE AND BONDING OF PYRROLE**

Heterocyclic compounds are cyclic compounds containing hetero atoms such as nitrogen, sulphur, oxygen as a part of the ring system. The heterocyclic compounds may be classified on the basis of the ring size, number of hetero atoms in the ring, number of rings, and nature of the hetero atom. Pyrrole is five membered ring made up of four carbon atoms and the hetero atom nitrogen.



**Fig. 2.9 : Pyrrole**

Since pyrrole has two conjugated double bonds, it is expected to exhibit the properties of conjugated dienes. Being unsaturated compound, it should undergo addition reaction. Also, pyrrole is expected to behave as a secondary amine. However, pyrrole does not show any of these expected properties. It does not give addition reactions, with few exceptions. It readily gives substitution reactions like nitration, sulphonation, Friedel-Crafts reactions, Riemer-Tiemann reaction etc. Instead of showing the properties of a secondary amine, pyrrole is found to be an extremely weak base. Pyrrole has lower heats of hydrogenation and combustion than expected. This indicates that it is more stable than expected. Pyrrole has planar ring structure i.e. all the atoms of the ring including the nitrogen atom are in the same plane. There are two double bonds i.e. 4  $\pi$ -electrons. These

double bonds are conjugated with the lone pair of electrons. Thus there are total  $5 \times 2 = 10$  electrons. Therefore, pyrrole satisfies Huckel's rule for  $n = 1$  and hence it is aromatic in nature.

#### ❖ Molecular orbital structure of pyrrole:

All the atoms of pyrrole heterocyclic rings are in the same plane, and angles between the bonds in the ring are  $120^\circ$ . Further, all the atoms including the nitrogen atom are  $sp^2$  hybridised. Two  $sp^2$  orbitals of each atom are utilized to form  $\sigma$  bond between the carbon atoms and also the nitrogen atom. The third  $sp^2$  orbital forms  $\sigma$  bond between carbon and hydrogen atoms. Then each of the carbon atoms contains a p orbital with one electron and the nitrogen atom contains a p orbital with a pair of electrons. These p orbitals overlap with adjacent p orbitals on either side to produce circular clouds of  $\pi$ -electron. There will be delocalized circular cloud of six  $\pi$ -electrons above and below the plane of the ring. Thus, Huckel's rule is fully satisfied and hence pyrrole ring (Fig. 2.10) shows aromaticity.

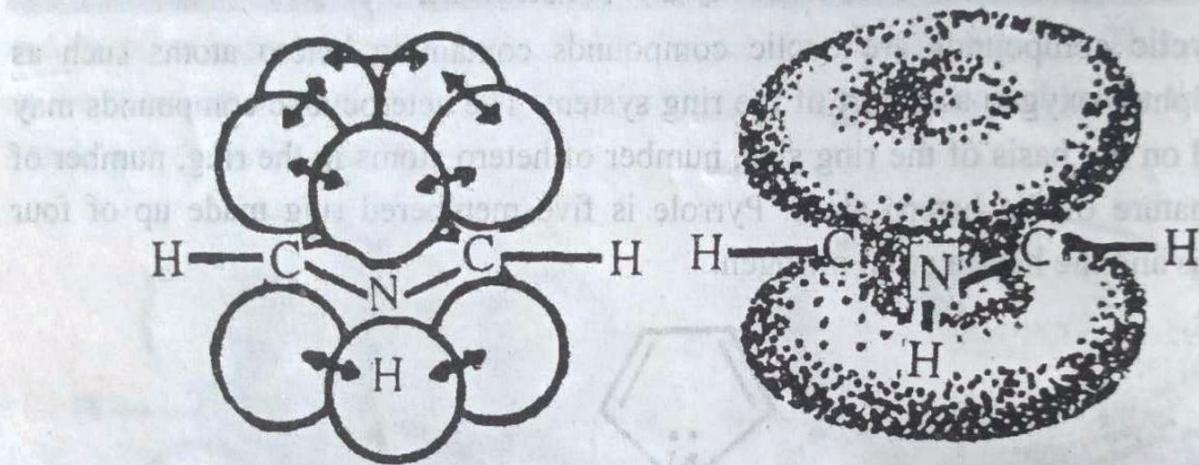


Fig. 2.10

Due to the presence of the  $\pi$ -electron cloud, the molecule is reactive towards electrophilic reagents. If this  $\pi$ -electron cloud is disturbed, the aromaticity is lost. Therefore, pyrrole generally gives substitution reactions. In the case of pyrrole, the lone pair of electrons on the nitrogen atom is also involved in the  $\pi$ -electron cloud. Therefore, it is not available to be shared with a proton. Hence, pyrrole is an extremely weak base.

# **INTERMOLECULAR FORCES AND CRITICAL PHENOMENA**

## **SYLLABUS**

- Ionic, dipolar and Van der Waal's interactions
- Equations of state of real gases and critical phenomena

### **3.1 INTRODUCTION**

Intermolecular forces are the forces which mediate interaction between the molecules, including forces of attraction or repulsion which act between the molecules and other types of neighboring particles, e.g. atoms or ions. Intermolecular forces are weak relative to intramolecular forces (the forces which hold a molecule together) e.g. the covalent bond, involving sharing electron pairs between atoms, is much stronger than the forces present between neighboring molecules.

The strength of the intermolecular forces between the molecules or atoms that compose a substance determines the states (solid, liquid or gas) of the substance at the room temperature. Strong intermolecular forces tend to result in liquids and solids with high melting and boiling points. Weak intermolecular forces tend to result in gases with low melting and boiling points. Here, we will focus on the fundamental types of intermolecular forces.

### **3.2 IONIC INTERACTIONS**

Ionic bonds are formed due to transfer of one or more electrons from one atom to the other between a metal and non-metal atom. The metallic atom loses its electron present in its valence shell and converts into a cation. The non-metallic atom gains electrons and converts into an anion. The electrostatic force of attraction holds the oppositely charged ions together.

The number of electrons that an atom gains or loses while forming an ionic bond is called its electrovalency. The atom which loses electrons is called electropositive and the one which gains electrons is called electronegative atom.

Since ionic bond is the strongest bond, it takes a lot of energy to break it. The greater the charge difference, the stronger the attraction.

### 3.3 VAN DER WAAL'S INTERACTIONS

This is the weak attractive intermolecular force present in all molecules and atoms. It is known as Van der Waals forces or dispersion forces or London forces. They occur between the molecules.

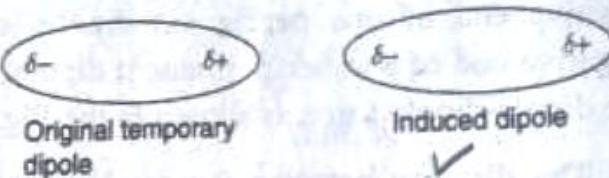


Fig. 3.1

Due to constant movement of electrons, even in nonpolar molecule, at any instant more electrons may be present in one region than in another. It causes an unequal charge distribution which causes temporary dipole. This temporary dipole can induce a similar temporary dipole on a nearby molecule as shown in the Fig. 3.1.

This temporary dipole can extend over large number of molecules in a synchronized way. It holds them together in a lattice. Collectively many such temporary dipoles and induced dipoles result in the weak electrostatic force of attraction, that is, van der Waals forces.

They exist in all types of molecules along with dipole or any other intermolecular forces. These forces are weaker than the covalent bonds present within the molecules. The exact value of these forces cannot be predicted as they vary with size, shape and polarisability of the molecule. Molecules containing large, diffuse electron cloud like polyatomic ions or molecules with multiple bonds, they are as strong as covalent bonding forces.

- Van der Waals forces explain the condensation of gases and freezing of liquids on cooling.
- High molecular weight indicates more electrons and more powerful attractive forces than Van der Waals forces. This is the explanation for why high molecular weight compounds tend to be solids or liquids and low molecular weight compounds tend to be gases.
- At the boiling point of a liquid, the amount of molecular agitation is enough to overcome Van der Waals force of attraction. Hence, boiling point is the measure of these forces. This explains the periodic trend in boiling points for the noble gases e.g. Ne boils at much lower temperature than Xe. Since Ne is having lesser electrons than Xe, its Van der Waals forces are more easily overcome by thermal motion.

### 3.4 DIPOLAR INTERACTIONS

The dipole-dipole force exists in all polar molecules. Polar molecules have permanent dipoles that interact with the permanent dipoles of neighboring molecules. The positive end of one permanent dipole is attracted to the negative end of another permanent dipole. This attraction is the dipole-dipole force as shown in the Fig. 3.2.

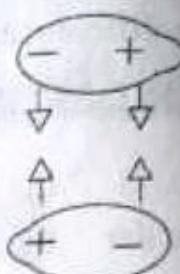


Fig. 3.2

The distance between the two dipoles and their orientation determines the dipole-dipole interaction. All molecules including the polar ones have dispersion forces. In addition to dispersion forces, polar molecules have dipole-dipole forces. These additional forces raise the melting and boiling points of the polar molecules. Non-polar molecules having same molecular weight and shape but lacking the presence of dipole movement has relatively low melting and boiling point. The same is illustrated by comparing Formaldehyde and Ethane in the Table 3.1.

Table 3.1: Comparison of melting &amp; boiling points of Formaldehyde &amp; Ethane

Name	Formula	Molar mass (g/mol)	Boiling Point (°C)	Melting Point (°C)
Formaldehyde (Polar)	CH <sub>2</sub> O	30	-19.5	-92
Ethane (Non-polar)	C <sub>2</sub> H <sub>6</sub>	30.1	-88	-172

Formaldehyde being polar, it shows higher melting point and boiling point than non-polar ethane despite their molecular weights being almost the same.

The polarity of molecules also helps in determining the liquids miscibility i.e. its ability to mix without separating into two phases. Polar liquids are miscible with other polar liquids, but are not miscible with non-polar liquids e.g. water, a polar liquid does not mix with the oil, a non-polar liquid.

### 3.5 HYDROGEN BONDING

Polar molecules containing hydrogen atoms bonded directly to fluorine, oxygen or nitrogen exhibit an additional intermolecular force called a hydrogen bond e.g. HF, NH<sub>3</sub> and H<sub>2</sub>O show hydrogen bonding. The large electronegativity difference between hydrogen and these electronegative elements, as well as the small size of these atoms gives rise to a strong attraction between the hydrogen in each of these molecules and the F, O or N on neighboring molecules. This attraction between a hydrogen atom and an electronegative atom is the hydrogen bond. The example of the same is shown in the Fig. 3.3.

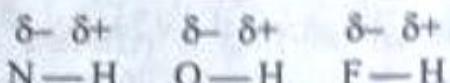


Fig. 3.3

Similarly, the hydrogen atom in each water molecule is hydrogen bonded to the oxygen in four other water molecules as shown in the Fig. 3.4.

As shown in the figure, a normal covalent bond length is  $0.96 \text{ \AA}$  and the hydrogen bond length is  $1.97 \text{ \AA}$ . As the bond length indicates the bond strength, hydrogen bond is weaker than the covalent and the ionic bonds.

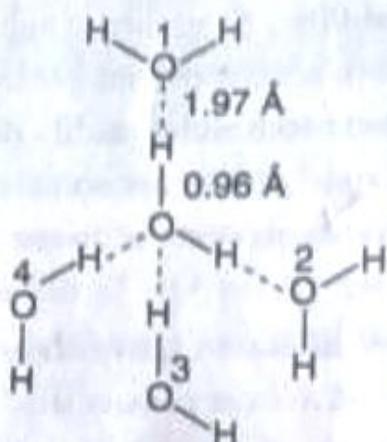


Fig. 3.4: Hydrogen bonding in water molecule

There are two types of hydrogen bonds namely, intramolecular and intermolecular.

#### \* Intramolecular Hydrogen Bond:

The hydrogen bond formed between hydrogen and an electro negative atom (F, O & N) within the same molecule is intramolecular hydrogen bond. It results in the cyclization of the molecules and prevents their association. It does not affect physical properties of the compound. The intramolecular hydrogen bonds present in different molecules is shown in the Fig. 3.5.

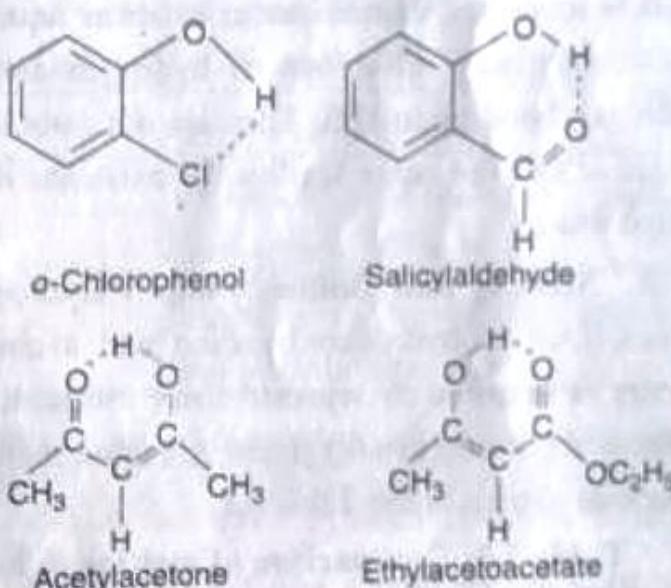


Fig. 3.5: Intramolecular Hydrogen Bonds

The intramolecular hydrogen bonding is important in biological molecules as the shapes of proteins and nucleic acids are largely influenced by it e.g. the two strands of the double helix in DNA are held together by hydrogen bond between hydrogen atoms of one strand with the lone pairs on the nitrogen or oxygen on the other strand.

\* **Intermolecular Hydrogen Bond:** The hydrogen bond formed between the hydrogen atom of one molecule and an electronegative atom of the other molecule is called intermolecular hydrogen bond e.g. Hydrogen Chloride, Water, Ammonia, Alcohol etc.

Effect of intermolecular hydrogen bonding is reflected in many properties of the compounds such as increase in the melting point, boiling point, solubility etc.

#### Effects of hydrogen bonding:

1. **Solubility** : Solubility of substances in certain solvents is influenced by hydrogen bonding. Covalent compounds generally do not dissolve in water. But those which form a hydrogen bond with water readily dissolve in it e.g. Ammonia, Amines, Ethanol, Lower Aldehydes and Ketones are soluble in water due to the formation of hydrogen bonds between hydrogen atom of water molecule and the electronegative atom of these molecules.

2. **Physical State** : Intermolecular hydrogen bonding causes two or more molecules of a compound to exist as associated molecules. This results in an increase in the size and molecular mass of the compound which gets reflected in the physical state of the substance e.g.  $\text{H}_2\text{O}$  is liquid and  $\text{H}_2\text{S}$  is a gas, although oxygen and sulphur belong to the same group. In water, oxygen is highly electronegative and forms intermolecular hydrogen bonds. It results in getting water molecules associated due to which molecular mass is increased. Hence, water exists as liquid at room temperature. On the other hand, electronegativity difference of hydrogen and sulphur is less and there is negligible hydrogen bonding in  $\text{H}_2\text{S}$ . They are not associated and hence  $\text{H}_2\text{S}$  exists as a gas at room temperature. The same applies for existence of HF as liquid and HCl as a gas at room temperature.

3. **Melting and Boiling Point** : Hydrogen bonds are very strong intermolecular forces. Due to hydrogen bonding and a consequent association of molecules, larger energy is required to separate these molecules before they can melt or boil. Therefore these compounds usually show elevated melting and boiling points e.g. methanol and ethane as shown in the Table 3.2.

**Table 3.2: Comparison of melting & boiling points of Methanol & Ethane**

Name	Formula	Molar mass (g/mol)	Boiling Point (°C)	Melting Point (°C)
Methanol	$\text{CH}_3\text{OH}$	32	64.7	-97.8
Ethane	$\text{C}_2\text{H}_6$	30.1	-88	-172

Since Methanol has hydrogen directly bonded to oxygen, its molecule shows hydrogen bonding. This hydrogen is strongly attracted to the oxygen on neighboring molecules. Due to this strong attraction, the boiling point of methanol is higher than ethane.

The melting and boiling points of the hydrides of group 14 increase with increase in molecular weight. However, in case of the hydrides of elements of Groups 15, 16, 17 the melting and boiling points of  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  and  $\text{HF}$  are exceptionally higher than the hydrides of other members of the group because of hydrogen bonding.

### 3.6 ION-DIPOLE FORCE

The ion-dipole force occurs in the mixtures of ionic compounds and polar compounds. It is very important in aqueous solutions of ionic compounds. e.g. When  $\text{NaCl}$  is mixed with water, the sodium and chloride ions interact with water molecules via ion-dipole forces. Ion-dipole forces are the strongest of all types of intermolecular forces. They are responsible for the ability of ionic substances to form solutions with water.

Comparison of different types of intermolecular forces is shown in the Table 3.3.

**Table 3.3: About Intermolecular forces:**

Type of Force	Relative Strength	Present In
Van der Waals force (dispersion force)	weak, but increases with increasing molar mass	all atoms and molecules
dipole-dipole force	moderate	only polar molecules
hydrogen bond	strong	molecules containing H bonded directly to F, O or N
ion-dipole	very strong	mixtures of ionic compounds and polar compounds

### 3.7 EQUATIONS OF STATE OF REAL GASES AND CRITICAL PHENOMENA

The gases which follow the gas laws at a low pressure and a high temperature are called real gases. But their behaviour deviates significantly from that of ideal gas at high pressure and low temperature. The force of attraction between the molecules of real gases cannot be ignored at low pressure and high temperature.

The combination of all the gas laws viz. Boyle's Law, Charles Law and Avogadro's Law gives the ideal gas equation which relates the four parameters – pressure (P), volume (V), absolute temperature (T) and number of moles (n) of ideal gas. This equation is called ideal gas equation. It is expressed as,

$$PV = nRT$$

### Van der Waals equation of State for Real Gases:

The Van der Waals equation of state is the equation that modifies the ideal gas law by disapproving the following points.

1. The force of attraction between gaseous molecules is negligible. The ideal gas law treats gas molecules as point particles that interact with their containers but not with each other.
2. The volume of gaseous molecules is negligible as compared to the total volume of the gas.

The two corrections explained by Van der Waal are as follows.

**Volume Correction:** Since the real gas molecules take up some volume, the actual space available for the movement of gas molecules inside the vessel is not the real volume of the gas. The real volume of the gas is calculated by the following equation:

$$V_{\text{ideal gas}} = V - b$$

Where,

$V$  = Volume of the container

$b$  = Volume occupied by gas molecules

So the ideal gas equation becomes  $P(V - b) = RT$

**Pressure Correction:** The force with which the molecules of the gas inside a container collide with the walls of the container is called the pressure of the gas. According to Van der Waal, the pressure of real gas is the combination of pressure developed due to collision of the molecules of gas with the walls of the container. In addition, in case of real gas, there is pressure loss due to inward pull of adjacent molecules. This inward pull makes the gas molecules striking the walls of the container experience some backward drag. Therefore, the observed pressure is smaller compared to the real gas pressure.

$$P_{\text{ideal gas}} = P + p$$

Where,

$P$  = Observed pressure of the gas.

$p$  = pressure lost by the gas molecules due to molecular attractions

$$= a \frac{n^2}{V^2}$$

$a$  = Van der Waals constant

The value of  $a$  depends on the nature of gas

$n$  = Number of moles of real gas

$V$  = Volume of gas

So the ideal gas equation after correction is rewritten as follows:

$$\left[ P + \frac{a}{V^2} \right] (V - b) = RT \quad (\text{For 1 mol})$$

$$\boxed{\left[ P + a \frac{n^2}{V^2} \right] (V - nb) = nRT \quad (\text{For } n \text{ number of moles})}$$

**Critical Phenomena:** The essential condition for the liquefaction of the gas is described by the study of critical temperature, critical pressure and critical volume and their inter relationships.

When a gaseous system is transformed to its liquid state, there is a tremendous decrease in the volume. This decrease in volume can be effectively brought about by lowering of temperature, or by increasing pressure (or) by both. In both these effects, the gaseous molecules come closer to each other and experience an increase in force of attraction which results in liquefaction of gases. At any constant temperature when pressure is increased volume is decreased and vice versa. Such P-V curves at constant temperature are known as isotherms.

The continuous decrease in pressure with increase in volume is seen in both ideal and real gases. There is a definite deviation exhibited by the real gas from ideal gas behaviour at high pressure and low volumes.

**Critical Temperature ( $T_c$ ):** It is defined as the characteristic temperature of a gas at which increase in pressure results in liquefaction of gas. But above this temperature, there will be no liquefaction even by increasing the pressure. For instance,  $T_c$  of  $\text{CO}_2$  is  $31.1^\circ\text{C}$ . This means that it is not possible to liquefy  $\text{CO}_2$  by applying pressure when its temperature is above  $31.1^\circ\text{C}$ .

**Critical Pressure ( $P_c$ ):** It is defined as the minimum pressure at which a gas can be liquefied at its critical temperature.

**Critical volume ( $V_c$ ):** The volume occupied by 1 mole of a gas at its critical pressure and at critical temperature is the critical volume of the gas.

A gas is said to be at its critical state when its pressure, volume and temperature are  $P_c$ ,  $V_c$  and  $T_c$ .

Let us derive the values of critical constants  $T_c$  (critical temperature),  $V_c$  (critical volume) and  $P_c$  (critical pressure) in terms of the Van der Waal's constants 'a' and 'b'.

The Van der Waal's equation is given by

$$T_c = \frac{8a}{27Rb}$$

Hence the critical constants can be calculated using the values of Van der Waals constants of a gas and vice versa. Since  $P_c$  and  $T_c$  can often be determined experimentally, these values may be employed to calculate the constants  $a$  and  $b$ .

$$a = 3Vc^2Pc$$
$$b = \frac{Vc}{3}$$

Based on the critical temperature values, gases are categorised as "permanent" and "temporary" gases.  $H_2$ ,  $N_2$ ,  $He$  gases having very low critical temperature belong to the permanent type. Gases like  $NH_3$ ,  $CO_2$ ,  $SO_2$ ,  $HCl$  etc. having critical temperature in the ordinary range of temperatures belong to the temporary gases type.

# PHASE RULE – GIBB'S PHASE RULE

## SYLLABUS

- Statement of Gibbs' Phase Rule, Terms involved with examples
- One Component System (Water)
- Reduced Phase Rule
- Two Component System (Pb- Ag)
- Advantages and Limitations of Phase Rule
- Numerical problems on Phase Rule

### 4.1 INTRODUCTION

Phase equilibrium deals with the study of equilibrium conditions of heterogeneous systems. Substances are present in different phases in heterogeneous systems. Such a system can be conveniently studied with the help of a generalization called Phase Rule. This rule was deduced on the basis of Thermodynamic principles by Willard Gibbs (1876) and was later developed by Ostwald, Van't Hoff, H.W.B. Roozeboom and many more. Phase rule is an important tool in the study of heterogeneous equilibrium. It relates the conditions which must be specified to describe the state of a system at equilibrium. The plot indicating the relationships between various phases under different temperature, pressure and concentration is known as phase diagram. Phase rule, with the help of a phase diagram, is useful in predicting the effects of temperature, pressure and concentration on the equilibrium of heterogeneous systems.

A substance can exist in various states depending on the external conditions. For example, water can exist in the form of solid, liquid and vapour. A change in the state of a substance is called phase transition. Equilibrium in a system in which phase transitions occur in addition to a chemical process is called phase equilibrium.

### 4.2 GIBB'S PHASE RULE

Gibb's phase rule states that in every heterogeneous system in equilibrium, the sum of the number of phases and degree of freedom is greater than the number of components by 2.

- This is mathematically expressed as

$$P + F = C + 2$$

or

$$F = C - P + 2$$

Where  $P$  is the number of phases present in equilibrium,  $C$  is the number of components for the system and  $F$  is the number of degrees of freedom for the equilibrium. This rule is valid for any system at equilibrium at definite temperature and pressure provided the equilibrium between any number of phases is not influenced by gravity, by electrical or magnetic forces or by surface action; and is only influenced by temperature, pressure and concentration.

For an accurate and effective interpretation of the phase rule, it is important to understand clearly the meaning of the terms involved in the phase rule.

### 4.2.1 Phase

A phase is defined as any homogeneous, physically distinct, mechanically separable portion of the system which is separated from other parts of the system by definite boundary surfaces.

We all know that a homogeneous system is the one in which both the reactants and products are of one phase (i.e. solid, liquid, gas) and a heterogeneous system is one in which they are in different phases.

A homogeneous system is one which is uniform throughout in physical and chemical properties e.g. a solution of salt in water. A heterogeneous system comprises of two or more different parts, each of which is homogeneous in itself and is separated from others. These homogeneous, physically distinct and mechanically separable parts of a heterogeneous system existing in equilibrium are called phases.

Common example that describe phase are,

- (1) In a freezing water system, ice, liquid water and water vapour constitute three phases. Each of the phases is distinct, homogeneous and mechanically separable.  
 $\text{Ice (s)} \rightleftharpoons \text{water (l)} \rightleftharpoons \text{water vapour (g)}$ .
- (2) A gaseous mixture, being thoroughly miscible in all proportions, constitutes one phase only. Thus, a mixture of  $\text{N}_2$  and  $\text{H}_2$  forms one phase only.
- (3) Two miscible liquids form one liquid phase only.

For example: ethyl alcohol and water.

- (4) Two immiscible liquids form two different phases and can be separated by boundary surfaces.

For example: kerosene and water or benzene and water

(5) A solution of a substance in a solvent consists of one phase.

For example: glucose solution in water.

(6) A system containing  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$  has three phases – two solid phases and one gaseous phase.



(7) A homogeneous solid solution of salt constitutes a single phase.

For example: Mohr's salt  $[\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$  solution constitutes a single phase although it consists of  $\text{FeSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ .

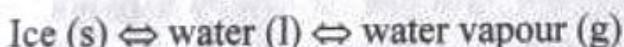
(8) Each solid makes up a separate phase except in the case of a solid solution. For example, many forms of sulphur can exist together and all are separate phases.

#### 4.2.2 Component

The components of the system do not represent the number of the constituents or chemical individuals present in the system. As given in the statement of phase rule, the number of components of a system at equilibrium is the smallest number of independently variable constituents by means of which the composition of each phase present can be expressed, either directly or in the form of chemical equation.

This concept of component can be explained in connection with phase rule with the help of the following examples,

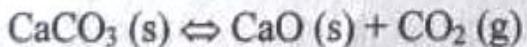
(1) In the water system,



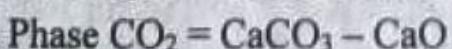
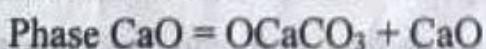
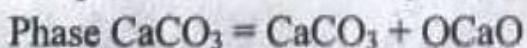
The composition of each one of the solid, liquid and vapour can be expressed using one constituent, namely  $\text{H}_2\text{O}$ . Hence, it is one component system.

(2) The sulphur system consists of four phases rhombic, monoclinic, liquid and vapour, the chemical composition of all the phase is sulphur. Hence, it is one component.

(3) In the thermal decomposition of  $\text{CaCO}_3$ ,

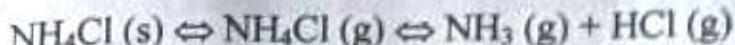


The composition of each of the three phases can be expressed in terms of at least any two of the independently variable constituents,  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$ . Suppose  $\text{CaCO}_3$  and  $\text{CaO}$  are chosen as the two components, then the composition of different phases is represented as follows:



Thus it is a two component system.

- (4) In the dissociation of  $\text{NH}_4\text{Cl}$  in a closed vessel



The proportions of  $\text{NH}_3$  and  $\text{HCl}$  are equivalent and hence, the composition of both phases (solid and gaseous) can be expressed in terms of  $\text{NH}_4\text{Cl}$  alone. Hence, the number of component is one. However, if  $\text{NH}_3$  or  $\text{HCl}$  is in excess, the system becomes a two component system.

- (5) The acetic acid system is a one component system because the composition of each phase can be expressed in terms of each phase of  $\text{CH}_3\text{COOH}$ , although it exists in the form of double molecules entirely in the solid state, to a great extent in the liquid state and only to a smaller extent in the vapour state.

There may be equilibrium such as:



in the solid and liquid phases due to association, but the only independent species in all the three phases is  $\text{CH}_3\text{COOH}$ .

- (6) In the equilibrium,



The minimum components required to express the composition of each phase is three. So it is three component system.

- (7) A salt solution is a two component system.

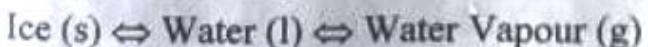
### 4.2.3 Degree of Freedom of Variance

The 'Degree of Freedom' means the minimum number of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to describe completely the state of the system.

A system having one, two, three or zero degrees of freedom are usually called univariant, bivariant, trivariant and invariant respectively.

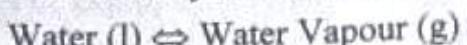
Common examples include,

- (1) In case of water system,



No specification of conditions is necessary because the three phases can occur in equilibrium only at a particular temperature and pressure. This situation exists only at triple point; hence this system does not have any degree of freedom (invariant). If condition (e.g. pressure or temperature) is altered, three phases will not remain in equilibrium and one of the phases disappears.

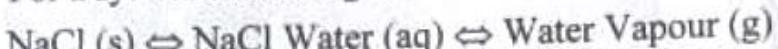
- (2) Consider a system containing water in contact with its vapour.



The vapour will exert a certain pressure at a particular temperature. Hence, it is enough if we fix the temperature of the system. Then, the pressure that would be exerted by the vapour is automatically fixed. Hence of the two variable factors of temperature and pressure, it is enough if we fix one. Therefore this system has only one degree of freedom or it is univariant.

- (3) A system of a pure gas should satisfy the gas equation  $PV = RT$ . If we assign values arbitrarily for any two of the three variables, the value of the third gets automatically fixed and the system is completely defined. This system has two degrees of freedom or it is bivariant.

- (4) For a system consisting of



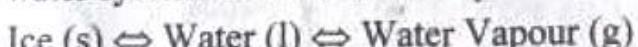
is completely defined if the temperature or pressure is specified. The saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

### 4.3 APPLICATION OF PHASE RULE TO ONE COMPONENT SYSTEM

#### The Water System:

Water is the most common example of one component system.

The water system consists of three phases, namely, ice, water and water vapour.



The three phases may occur in four possible combinations in equilibrium as follows :

- (i) Liquid  $\rightleftharpoons$  Vapour
- (ii) Liquid  $\rightleftharpoons$  Solid
- (iii) Solid  $\rightleftharpoons$  Vapour
- (iv) Solid  $\rightleftharpoons$  Liquid  $\rightleftharpoons$  Gas.

As water ( $H_2O$ ) is the only compound involved in the system, therefore, it is single or one component system. From the phase rule, when  $C = 1$ ,

$$F = C - P + 2 = 1 - P + 2 = 3 - P$$

The degree of freedom depends on the number of phases present at equilibrium. Three different cases are possible.

- (i)  $P = 1$ ;  $F = 2$  (bivariant system)
- (ii)  $P = 2$ ;  $F = 1$  (univariant system)
- (iii)  $P = 3$ ;  $F = 0$  (invariant system)

It is clear that for any one component-system the maximum number of degrees of freedom is two. Therefore, such a system can be represented completely by a two-dimensional diagram.

On the basis of experimental data obtained for the water system, a plot of relationships between the various phases (ice, water and vapour) under different conditions of temperature and pressure. (Temperature on x-axis and pressure on y-axis) is drawn and resulting phase diagram is shown in Fig 4.1.

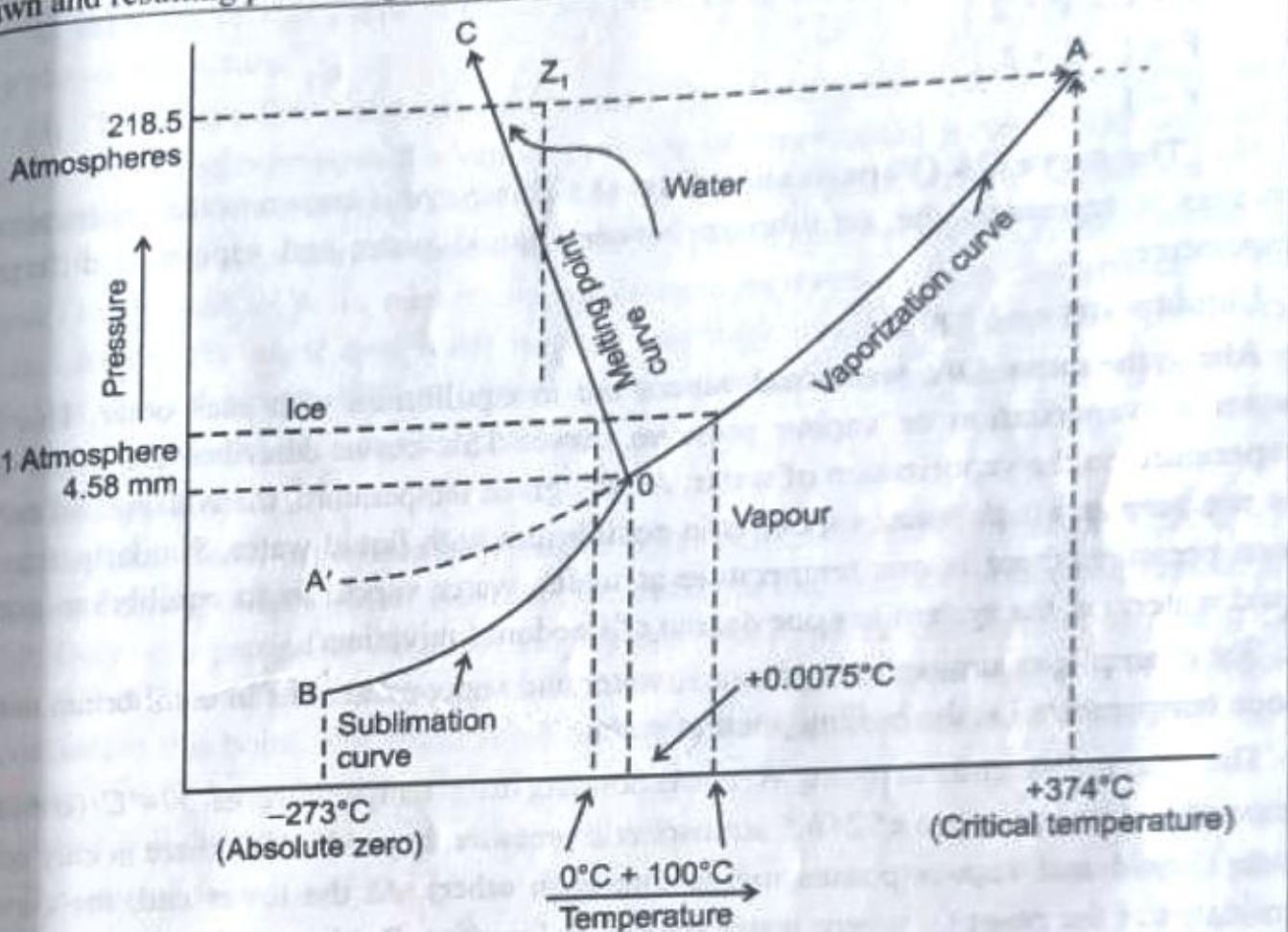


Fig. 4.1 : The Phase Diagram of Water System

#### (A) Area :

As can be seen from the diagram, there are three areas namely BOC (ice), COA (water) and AOB (vapour). In any area, only one of the phases is present. To define the system completely at any point in an area, both temperature and pressure should be fixed. So the system in an area has two degrees of freedom (bivariant). The same conclusion is drawn by substituting the values of  $C = 1$  and  $P = 1$  in the phase rule equation

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

**(B) Boundary Lines :**

Separating the areas are lines OA (vaporization curve), OB and OC, which connect the point at which two phases can co-exist in equilibrium. In order to locate any point on the particular line, either temperature or pressure co-ordinate should be known. In other words, if the value of either the temperature or the pressure is fixed, the value of the other is automatically fixed and the system is completely defined. Any point on the boundary lines has one degree of freedom or is univariant.

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

**(1) The curve OA (Vaporization Curve) :** This curve is known as the vaporization curve as it represents the equilibrium between liquid water and vapour at different temperatures.

Liquid water  $\leftrightarrow$  Vapour

Along the curve OA, water and vapour are in equilibrium with each other. This is known as vaporization or vapour pressure curve. This curve describes the effect of temperature on the vaporization of water. At any given temperature, there is one and only one pressure at which water vapour is in equilibrium with liquid water. Similarly at any given pressure, there is one temperature at which water vapour is in equilibrium with liquid water. i.e. the system has one degree of freedom (univariant).

For example, at atmospheric pressure, water and vapour can exist in equilibrium only at one temperature i.e. the boiling point of water.

The curve OA ends at point A corresponding to a temperature of  $374^{\circ}\text{C}$  (critical temperature) and pressure of 218.5 atmospheric pressure, beyond which there is only one phase (liquid and vapour phases merge into each other). At the lower end, the curve terminates at the point O, where water freezes to form ice. But by careful elimination of solid particles which induce crystallization, water may be cooled far below its freezing point, without the crystallization of ice. Dotted curve OA' shows the vapour pressure of super cooled water. It represents a meta-stable equilibrium and is situated above the sublimation curve, OB. The vapour pressure of the meta-stable phase at any point is greater than that of the stable phase. The super cooled water will at once change into solid ice even with the slightest disturbance.

**(2) The curve OB (Sublimation Curve) :** Along the curve OB, ice and vapour are in equilibrium with each other. It is known as sublimation curve. It is seen that the curve OB terminates at the lower end at absolute zero ( $-273^{\circ}\text{C}$ ) where no vapour can be present and only ice exists.

(3) **The curve OC (Melting Point Curve)** : Along the curve OC, two phases, namely ice and water, are in equilibrium with each other. This is known as melting point or freezing point curve. This curve describes the effect of pressure on the melting point of the ice. The slope of the curve shows that

- (a) Increase of pressure decreases the melting point of ice.
- (b) Ice melts with decrease of volume.

At any point on this curve, if either the pressure or the temperature is changes one of the phases disappears.

(4) **The curve OA' (Metastable Curve)** : The dotted curve OA' is a continuation of the OA curve and represents the vapour pressure of supercooled water. With due care, it is possible to cool water (any liquid) below its freezing point without separation of ice and the water is then said to be super cooled. The liquid  $\leftrightarrow$  vapour system along the curve OA' is said to be in metastable equilibrium as even a slight disturbance in this phase changes the super cool water into ice and the curve merges into OB. This curve OA' lies above the curve OB and shows that the metastable has a higher vapour pressure than the stable one at the same temperature.

#### (C) Triple Point :

It has been found experimentally that the curves OA, OB and OC meet in a point 'O'. This is called the '**triple point**' where all the three phases, viz., ice, water and vapour co-exist. Only at a particular value of temperature and pressure represented by the triple point, all the three phases can co-exist. So, the system has no degrees of freedom (invariant) at this point. The triple point corresponds to a temperature of  $0.0075^{\circ}\text{C}$  and a pressure of 4.58 mm. At this point, if we change either temperature or pressure, one of the phases will disappear.

The salient features of the phase diagram of the water system are summarized in Table 4.1.

**Table 4.1 : Water System**

Number of components = 1

Name of the system as represented in the phase diagram	Phase in equilibrium	Degree of freedom or variance $F = C - P + 2$
Areas		
(1) BOC (ice)	Ice	Two
(2) COA (water)	Water	(Bi-variant)
(3) AOB (vapour)	vapour } vapour	$F = 1 - 1 + 2 = 2$

Curve		
(1) OC (Melting point curve) (2) OA (Vaporization curve) (3) OB (Sublimation curve)	Ice and water Water and vapour Ice and vapour	One (univariant) $F = 1 - 1 + 2 = 1$
Point	Ice, water and vapour	Zero (Invariant) $F = 1 - 3 + 2 = 0$
(1) O (Triple point)		

#### 4.4 APPLICATION OF THE PHASE RULE TO TWO COMPONENT SYSTEMS

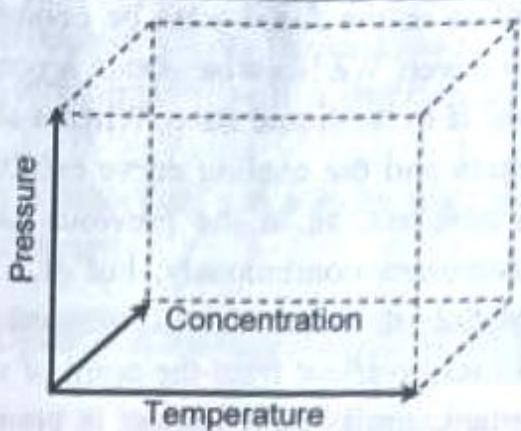


Fig. 4.2 : Three dimensional space model of a two component system

To simplify the diagram, one of the variables is kept constant. If the pressure is kept constant, the diagram is called isobaric; if temperature is kept constant it is called isothermal and if composition is kept constant, the diagram is called isoplethal.

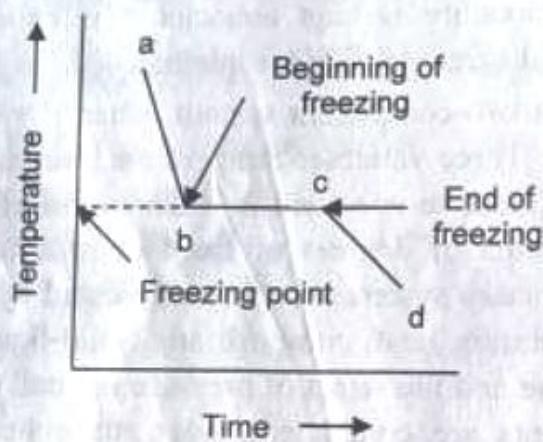
**Phase rule for two component system :** In a two-component system, when  $P = 2$ , degree of freedom ( $F$ ) has the highest value i.e. 3. Three variables temperature, pressure and concentration of one of the two components must be specified in order to describe the system completely. Since the maximum number of degrees of freedom in a two component system is 3, the phase behavior of a binary system may be represented by a three dimensional diagram of pressure, temperature and composition. Solid-liquid equilibrium of an alloy has practically no gas phase and the effect of pressure is small on this type of equilibrium. Usually the experiments are conducted under atmospheric pressure. Thus keeping the pressure constant of a system, in which vapour phase is not considered, is known as condensed system. It will reduce the degrees of freedom of the system by one. For such a system the phase rule becomes  $F = C - P + 1$ . This is known as the reduced or condensed phase rule, having only two variables, temperature and concentration (composition) of the constituents.

#### 4.4.2 Thermal Analysis

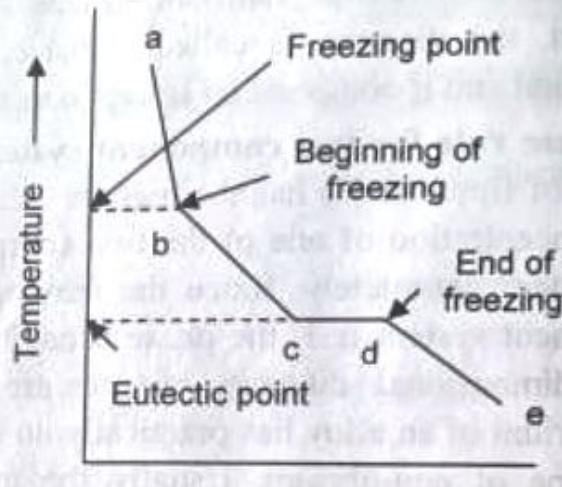
Thermal analysis is the study of the cooling curves of various compositions of a system during solidification. Basically, the form of the cooling curve depicts the composition of the solid. It can be understood from the following considerations:

- (1) When a pure substance in the fused or liquid state is allowed to cool slowly and the temperature noted at definite times, the graphic representation of the rate of cooling will be continuous curve (see Fig. 4.3 (a)). When the freezing point is reached and the solid makes its appearances, it is indicated by a break in the continuity of the cooling curve and the temperature will remain constant, until the liquid is completely solidified. Thereafter, the fall in temperature will again become continuous.

(2) If a mixture of two solids in the fused state be cooled slowly and the cooling curve is obtained in a similar manner. We likewise obtain a continuous cooling curve, so long as the mixture (or solution) is in the liquid state. When a solid phase begins to form, the rate of cooling abruptly alters and the cooling curve exhibits a break. However, the temperature does not remain constant, as in the previous case of cooling of a pure substance. The temperature decreases continuously, but at a different rate and if the mixture forms a *eutectic*, the fall of temperature continues, till the eutectic point is reached. The system now becomes invariant from the point of view of the phase rule and the temperature remains constant, until solidification is complete. (See Fig 4.3 (b)). Thereafter, the fall of temperature becomes uniform, but the rate of fall is quite different from the previous one.



(a)



(b)

Fig. 4.3 : Cooling Curves

Using the cooling curve for any mixture of a definite composition, it is possible to obtain its: (i) freezing point, and (ii) eutectic temperature.

- The freezing point varies with the composition of the system, but the eutectic point remains constant for a given system.
- The nearer the composition of the system to the eutectic, the shorter is the portion bc and the more prolonged is the halt cd.
- If the mixture coincides with the eutectic compositions, the curve shows no break corresponding to bc, but the break appears only at the eutectic point c.
- If the cooling curves of a series of alloys of known compositions are worked out and their freezing points are noted, by plotting freezing point against composition. It is known as the T – C curve for the alloy system. However, in order to complete the diagram, it is necessary to know the freezing points of the pure components also.

- (e) Now the cooling curve of an alloy of the same metals, but of unknown composition is determined and its freezing point located in the T – C diagram. The composition corresponding to this freezing point yields the composition of the alloy.
- (f) The thermal analysis procedure can also be used to derive the phase diagram of any two component system.

#### 4.4.3 Eutectic System

A binary system consisting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically, is known as the "eutectic system", for example, a mixture of lead and silver comprises of such a system.

**Eutectic mixture** is a 'solid solution' of two or more substances having the lowest freezing point of all the possible mixture of the components. This is taken advantage of in "alloying of low melting point", which are generally eutectic mixtures.

**Eutectic point:** Two or more solid substances capable of forming solid solutions with each other have the property of lowering each other's freezing point; and the minimum freezing point attainable corresponding to the eutectic mixture, is termed the **eutectic point** (means lowest melting point).

**Application of eutectics:** Low melting alloy are used in safety devices (for example, as plugs in automobiles), fire-sprinklers and as 'fail safe' device in boilers). By suitable choice of metals, very low melting alloys can be obtained, for example, wood's metal (alloy containing 50% Bi, 25% Cd and 12.5% Cd) melts at 65°C only.

#### 4.4.4 The Lead Silver System

It is a two-component system with four possible phases- solid Ag, solid Pb, solution of Ag + Pb and vapour. Since the pressure has nearly no effect on equilibrium, so the system can be conveniently represented by a temperature- concentration diagram (see Fig. 2.4) at constant atmospheric pressure. As the gaseous phase is practically absent and one variable pressure is neglected, the **condensed phase rule**:  $F = C - P + 1 = 3 - P$  will be applicable.

(1) **Curve AO** (freezing point curve of Ag) shows the effect on freezing point of Ag on addition of lead in small quantities. The curve starts from A (961°C), the melting point of Ag, where pure Ag co-exists as solid and liquid (vapour being neglected). The curve indicates that the melting point of Ag falls gradually on adding Pb, along AO, till the lowest point O (303°C) is reached, where the solution gets saturated with respect to lead. At O, no more lead can go in solution and consequently, melting point of Ag does not fall any further; and if any lead is added, it separates as the solid phase. Along this curve,

solid Ag and solution (vapour being negligible) co-exists and hence, according to reduced phase rule equation:  $F = 3 - P = 3 - 2 = 1$  i.e., the system is univariant. The point O ( $303^{\circ}\text{C}$ ) corresponds to a fixed composition of 2.6% Ag and 97% Pb and is known as eutectic composition. On cooling, the whole mass crystallizes out as such.

(2) **Curve BO** (freezing point curve of Pb). It represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead ( $327^{\circ}\text{C}$ ). Along BO, the melting point gradually falls on the addition of Ag, till lowest point O is reached, where the solution gets saturated with respect to Ag and the melting point of lead does not fall any more. On cooling, the whole mass (having eutectic composition) crystallizes out. The system is univariant like AO.

(3) **Point O** (eutectic point). The two curves AO and BO meet at O, where three phases (solid Ag, solid Pb and their solution) co-exists and according to condensed phase rule, the system will be invariant ( $F = 3 - P = 3 - 3 = 0$ ). The point O ( $303^{\circ}\text{C}$ ) represents a fixed composition ( $\text{Ag} = 2.6\%$ ,  $\text{Pb} = 97.4\%$ ) and is called eutectic composition. No mixture of lead and silver has a melting point lower than the eutectic temperature. At this point, the temperature remains constant, until the whole of the melt solidified en-block to become solid of eutectic composition. However, further cooling results in the simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O. Below the temperature line of eutectic temperature, we have two regions in the diagram, viz.,

- The region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable and
- The region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

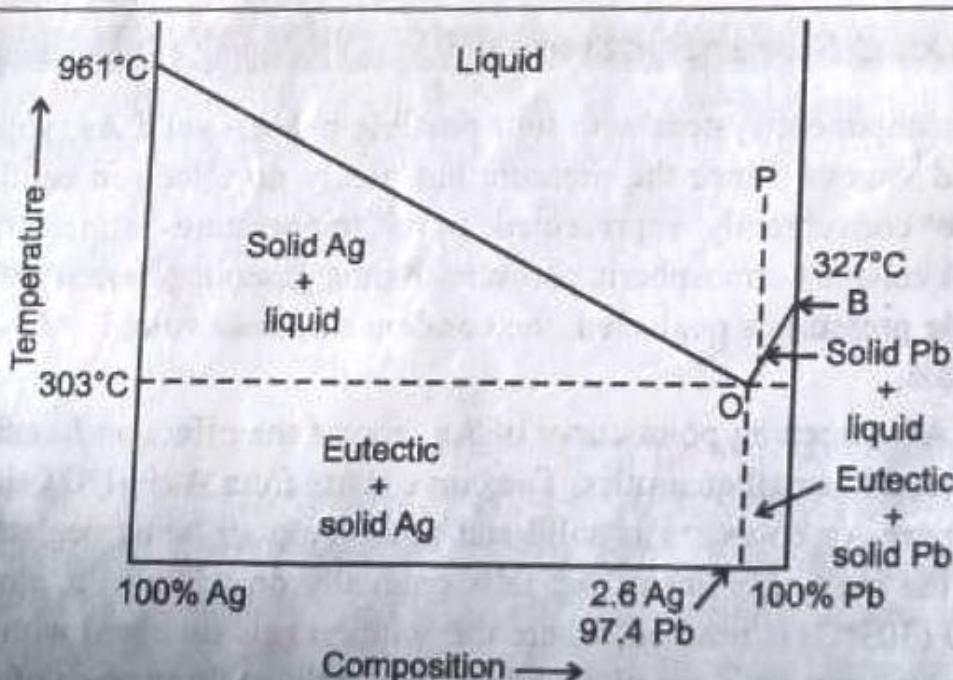


Fig. 4.4 : T – C diagram of Pb-Ag system

(4) Area AOB represents solution of Pb-Ag. If a sample of lead containing less than 2.6% Ag is taken, say P. On allowing the mass to cool, the temperature gradually falls without any change in composition, till point P' is reached on the curve BO. On lowering the temperature, lead begins to separate out and the composition varies along P'O, till point O is reached. On further cooling, the whole mass solidifies en-block to the eutectic composition (2.6% Ag; 97.4% Pb.)

**Application to Pattinson's Process :** The above principle is utilized in the Pattinson's process of desilverization of lead. If a sample of argentiferous lead, containing less than 2.6% Ag, is allowed to cool gradually, lead will separate out and the solution will become progressively richer in Ag, till the percentage 2.6 of Ag is reached; and on further cooling, the whole mass will solidify as such. On the other hand, if lead-silver alloy containing Ag greater than 2.6% is allowed to cool, then pure silver separate along the curve AO, till the eutectic composition at O is reached.

**NUMERICALS BASED ON PHASE RULE**

**(i) Thermoplastics:** They may be defined as those which can be softened on heating hot. On cooling, they soften on heating and remain in the same state till cooling process are purely of the physical nature. The chemical nature of the material is not affected. These plastics have linear polymer chains or negligibly branched chains. They are obtained by addition polymerization.

Mechanically these plastics are soft. They have lesser tensile strength, better flexibility and poor abrasion resistance. Their molecular weight is relatively less and are soluble in certain organic solvents. Some of the examples are polyethene, PVC, polystyrene, polyvinyl acetate, polyacrylonitrile, styrene acrylonitrile co-polymer, nylons, polyesters etc.

**(ii) Thermosets or Thermosetting plastics:** Thermosetting plastics are those which set up on heating and can not be reformed once they are set. In general, they are the plastics which are formed by condensation. They have three dimensional network structures and have high molecular weights. They have predominant covalent cross links between the long chains which are responsible for the three dimensional network structure.

When they are moulded, additional cross-linking are formed between the long chains leading to increase in molecular weight. Due to the cross-linkings formed, they acquire properties as hardness, toughness, brittleness, non-swelling and non-softening etc. The strength of bonds are retained on heating and they can be softened or reclaimed once they are cured.

Some of the examples of thermosetting plastics are phenol formaldehyde, polyurethanes, melamine formaldehyde, urea formaldehyde etc.

#### Comparison between Thermoplastics and Thermosetting:

Thermoplastics (TP)	Thermosetting (TS)
(1) Softens on heating and stiffen on cooling, reversibly, by the action of heat.	(1) On heating, they are converted into an infusible mass and once set, can't be reshaped.
(2) They are formed by addition polymerization.	(2) They are formed by condensation polymerization.
(3) Contain long chains with negligible cross links.	(3) Contains three dimensional array of network.
(4) They can be remoulded, reshaped and can be used.	(4) They can not be remoulded and reused.

(5) They are usually soluble in organic solvents; some swell up in solvent.	(5) They are usually insoluble in any solvents.
(6) They can be reclaimed from the wastes.	(6) They can not be reclaimed.
(7) They are usually soft, weak and less brittle.	(7) They are usually hard, strong and more brittle.
(8) They have low molecular weight as compared to thermosetting.	(8) They have high molecular weight as compared to thermoplastics
(9) Neighbouring polymeric chains are held together by weak Vander Waal's forces.	(9) Neighbouring polymeric chains are held together by strong covalent bonds in the form of crosslinks.
(10) Heating and cooling do not alter chemical nature. Only physical changes are involved on heating.	(10) Chemical changes occur on heating.
(11) For example, polyethylene, polystyrene, PVC, Teflon, nylon etc.	(11) For example, polyurethane, phenol formaldehyde, urea formaldehyde.

## 5.9 COMPOUNDING OF PLASTICS

In order to impart certain definite properties to finished products, plastic is compounded with other ingredients. These ingredients either discharge a useful function during moulding or imparts some useful property to the finished product. This is called a mixture. The various constituents added are –

- (1) Binders, (2) Fillers, (3) Plasticizers, (4) Dyes and pigment, (5) Lubricants, (6) Catalyst, (7) Stabilizers.

**(1) Binders:** Usually plastic is classified depending on the type of binder used for its manufacture. As the name implies, the main purpose of binder is to hold the other constituents of the plastic together. It also determines the type of treatment needed to mould the articles from the plastic material. A binder may compose of 30 to 100% of the plastics.

The binders used may be natural or synthetic resins or cellulose derivatives. In presence of catalyst they get converted into infusible cross link form. They also influence the properties of the plastic. e.g. If low molecular weight binder is used, the plastic gets moulded very easily.

- (2) Fillers:** Fillers are the substance added to plastic to serve the following purposes:
- (a) They reduce the cost of the plastic.
  - (b) They reduce shrinkage on setting and brittleness

- (c) They impart better tensile strength, hardness of the plastic, opacity, finish and workability. Fillers are added to impart special characters to the finished products. For example, (i) Barium salts make plastic impervious to X-rays. (ii) Asbestos provide corrosion and heat resistances. (iii) Carborundum, quartz, mica provide extra hardness. (iv) Addition of carbon black increases tensile strength. (v) Shredded textiles increase tensile impact strength.

In addition to above, the other materials in common use as fillers are cotton, corn husks, graphite, clay, paper pulp, wood flour, pumice, metallic oxides (e.g. ZnO, PbO), saw dust and metal powders (such as Fe, Cu, Pb and Al). The proportion of the filler added can reach as high as 50% of the plastic.

**(3) Plasticizers:** The important function of plasticizer is to improve plasticity and flexibility, so as to reduce the temperature and pressure required for moulding. They play very important role in determining the properties of finished product and hence are chosen accordingly. Their plasticizing properties are believed to be mainly due to the partial neutralization of the intermolecular forces of attraction in the resin molecules. They impart greater freedom of movement between the polymeric macromolecules of the resin. (thus increases flexibility and plasticity). At the same time, it reduces its strength and decreases its chemical resistance.

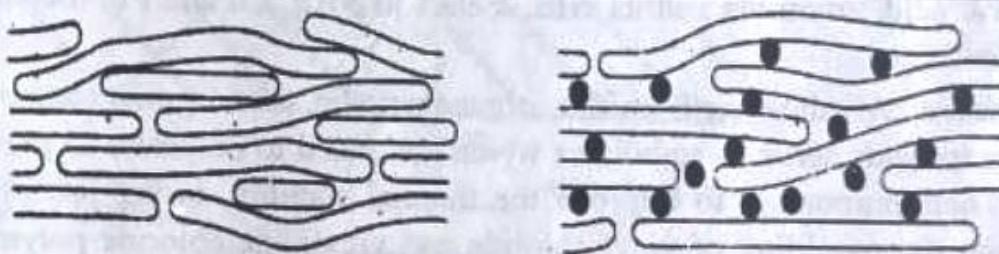


Fig. 5.3 : Action of plasticizer in plastics

The proportion of plasticizer can be up to 60% of the plastics. They are often used with thermosetting plastics. For instance, cellulose derivatives has the tendency to discolour when moulded unless moulding temperature is reduced by the addition of suitable plasticizer.

Most commonly used plasticizers are vegetable oils, camphor, esters of oleic, stearic or phthalic acids, tributyl phosphate, triphenyl phosphate, triacetin etc. When used with cellulose acetate, camphor increases surface hardness; tributyl phosphate and triphenyl phosphate impart flame proofness; triacetin and tributyl phosphate improves toughness.

**(4) Dyes and pigment:** Colour appeal is often of prime importance in high polymer artifacts. Thus they are meant for providing decorative colours to the plastic. The main colouring materials are organic dyestuffs and opaque inorganic pigments.

**Table 5.1 : Materials used as colourants**

<b>Colorants</b>	<b>Imparted colour</b>
Ultramarine	Blue
Carbon black	Black
Calcium carbonate	White
Zinc oxide	White
Chromium trioxide	Green
Ferric oxide	Red
Antimony sulphide	Crimson red

**(5) Lubricants:** These additives promote a good finish to the plastic materials, in addition to improving the flow characteristics and friction reduction in the processing machines. Waxes, oils, stearates, oleates and soaps are employed to make the moulding of the plastics easier and help in providing a glossy finish to the products.

**(6) Catalyst:** Accelerators are added in case of thermosetting plastics to accelerate the polymerization of fusible resin during moulding process, into crosslinked infusible form. Catalysts which are used for this purpose are hydrogen peroxide, benzoyl peroxide, acetyl sulphuric acid, ammonia and its salts, metals like Ag, Cu and Pb; metallic oxides such as zinc oxide etc.

**(7) Stabilizers:** Alkaline earth oxides, organometallic salts, epoxy compounds and amine type compounds serve as stabilizers which are added to polymers to prevent their degradation. Their purpose is to improve the thermal stability during processing. For example, during the moulding of vinyl chloride and vinylidene chloride polymers, heat stabilizers are used, as these polymers show a tendency to undergo decomposition and discolouration at the moulding temperature. Lead salts like white lead, lead chromate, litharge, red lead serve as opaque moulding compounds. Stearates of lead, cadmium and barium are transparent moulding compounds.

## **5.10 MOULDING OR FABRICATION OF PLASTICS**

Fabrication of plastic or moulding is the technique of giving desired shape to the plastic with the help of a mould. This technique involves fabrication of plastic under severe heat and pressure and is applicable to both the types of resins i.e. thermosetting and thermoplastic. Before moulding, it is essential to dry the resins in order to achieve optimum performance of finished product. If moisture is present during moulding, it generally lowers the density and impairs mechanical and optical properties. The moulding process involves different techniques which are described below:

- (A) Compression Moulding
- (B) Injection Moulding
- (C) Transfer Moulding
- (D) Extrusion Moulding.

**(A) Compression Moulding:** This method is applicable to both thermoplastics and thermosetting resins.

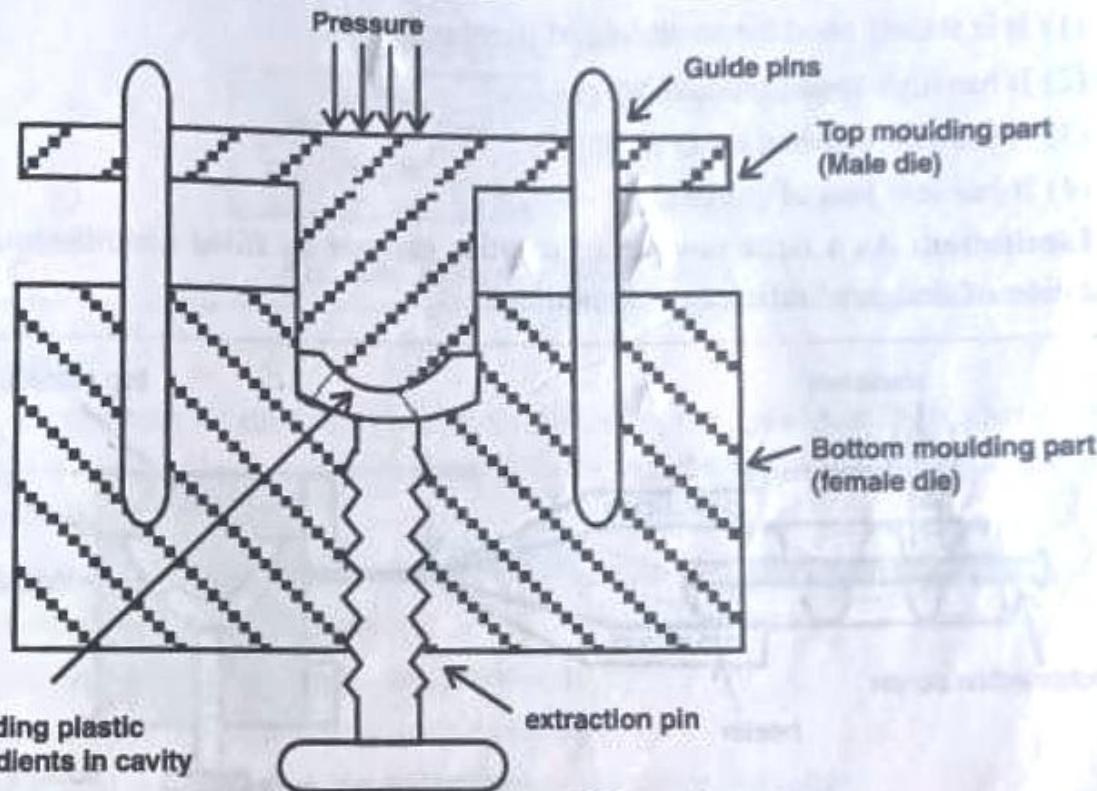


Fig. 5.4 : Compression moulding of plastics

In this method, a synthetic plastic material that has to be moulded is mixed with filler and the other ingredients in proper proportions and then placed in the mould. The mould is closed under low pressure. Then it is heated with simultaneous application of the pressure according to specifications (high pressure of the order of 100 to 500 Kg/cm<sup>2</sup> and temperature of the order of 100 to 200°C). The cavities get filled with fluidized plastic. Once the moulding is over, the material is withdrawn after cooling. Finally curing is done either by heating (in case of thermosetting) or cooling (in case of thermoplastics). After this process is over, the moulded article is taken out by opening the mould parts. Currently fully automatic moulding presses are available to quicken the process. Door handles, handles of electrical iron, bottle caps, screw caps are obtained by this method.

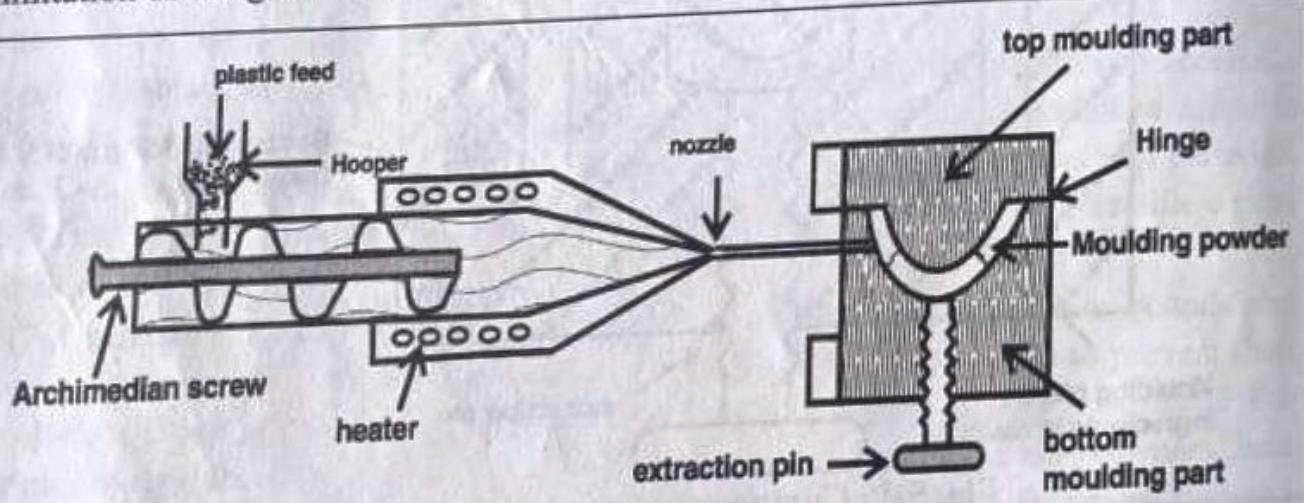
**(B) Injection Moulding:** This method is applicable to thermoplastic resins. The plastic in the form of powder is fed into a hot cylinder through hopper. The hot softened

plastic is forced at a controlled rate into a tightly locked mould by means of screw arrangement or piston. The temperature at the nozzle is increased (between 130°-260°C) which makes plastic fluidized and is injected in the mould. The mould is kept cooled to enable the hot plastic to be cured and become rigid. Moulded object is ejected mechanically without any deformation. Telephones, buckets, dustbins are made by this technique.

#### **Advantages:**

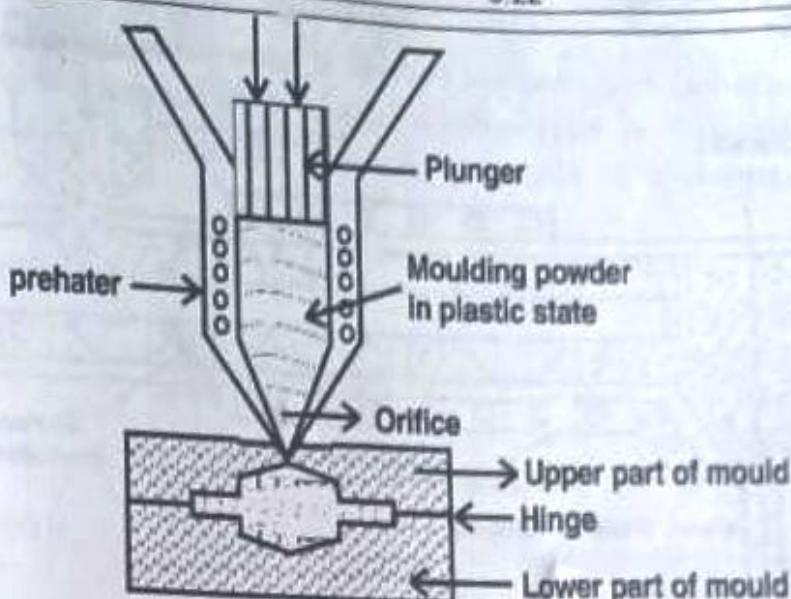
- (1) It is widely used for moulding of thermoplastics.
- (2) It has high speed production.
- (3) It has low finished cost.
- (4) It has low loss of material.

**Limitation:** As a large number of cavities can not be filled simultaneously, there is limitation of design of articles to be moulded.



**Fig. 5.5 : Injection Moulding**

**(C) Transfer Moulding:** This method is used for thermosetting materials. In this process, the principle of injection moulding is operative. In this the moulding powder is placed in a heated chamber, maintained at the minimum temperature at which it begins to become plastic. This plastic material is injected through an orifice, into the mould by a plunger, working at a high pressure. Due to the friction developed at the orifice, the temperature of the material rises to such an extent that the moulded material becomes a liquid and flows into the mould. Curing takes place under the influence of heat and pressure. The moulded article is then ejected mechanically.



**Fig. 5.6: Transfer Moulding**

### Advantages:

- (1) Due to ejection of the material from orifice to the mould at high speed and in highly plasticized condition, delicate articles may be handled without distortion or displacement.
- (2) Intricate shapes not attainable by compression moulding can be produced.
- (3) Blistering is almost eliminated.
- (4) Article free from flow marks are produced.
- (5) Thick pieces cure completely and uniformly.
- (6) Mechanical strength and density of fabricated piece is higher.
- (7) Finished cost of fabrication article is eliminated.

### (D) Extrusion Moulding :

Extrusion moulding is applicable to thermoplastic resins. It is mainly used for continuous moulding of thermoplastic materials into articles of uniform cross section. The thermoplastic ingredients are heated to plastic condition and then pushed by means of a screw conveyor into a die, having the required outer shape of the article to be manufactured. The finished product extruding out is cooled by atmospheric exposure or by blowing air or by spraying water. A long conveyor carries away continuously the cooled product.

The articles of uniform cross section like tubes, rods, strips insulated electric cables are manufactured by this technique.

As per the requirement, extrusion moulding can be carried out in two ways:

- (a) Vertical extrusion moulding.
- (b) Horizontal extrusion moulding.

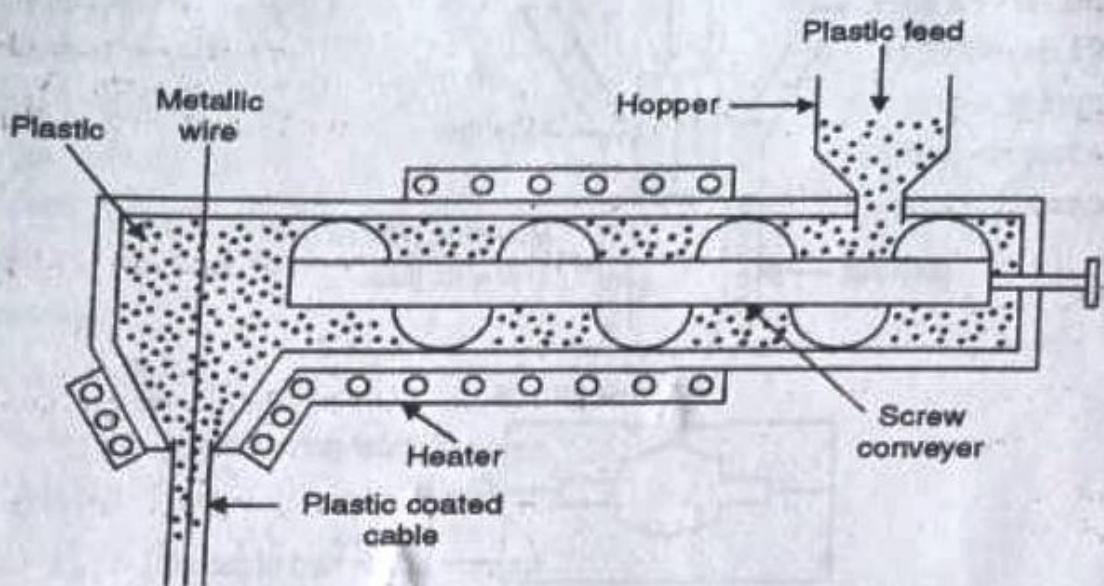


Fig. 5.7 (a) Vertical extrusion moulding

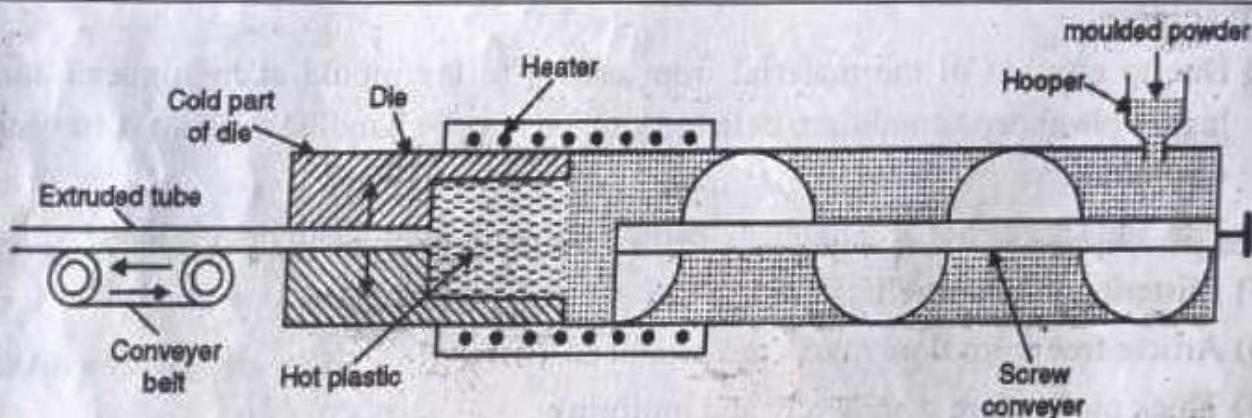
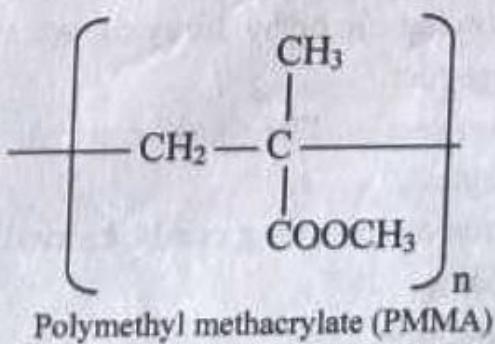


Fig. 5.7 (b) Horizontal extrusion moulding

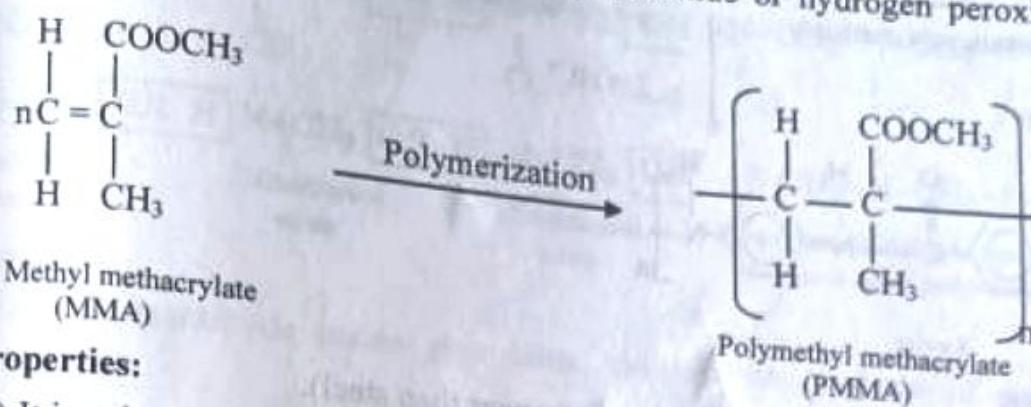
## 5.11 SOME INDIVIDUAL PLASTICS

### 1. Polymethyl methacrylate (PMMA) or Lucite or Plexiglass:

Polymethyl methacrylate is the best known plastic from the acrylates because of its outstanding optical properties. This polymer has the following structure.



**Preparation:** The monomer used is methyl methacrylate (an ester of methyl acrylic acid is produced from acetone). Polymethyl methacrylate is obtained by polymerization of methyl methacrylate in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer.



### Properties:

- (1) It is colourless, transparent, hard and fairly rigid material.
- (2) It is amorphous because of the presence of bulky side groups in the molecules.
- (3) It has high softening point of about  $130^\circ\text{C}$  to  $140^\circ\text{C}$  and becomes rubber like at a temperature above  $65^\circ\text{C}$ .
- (4) It has high optical transparency.
- (5) It has high resistance to sunlight and ability of transmitting light accurately, even in curved sections.
- (6) It has low chemical resistance to hot acids and alkalies.
- (7) It has low scratch resistance.

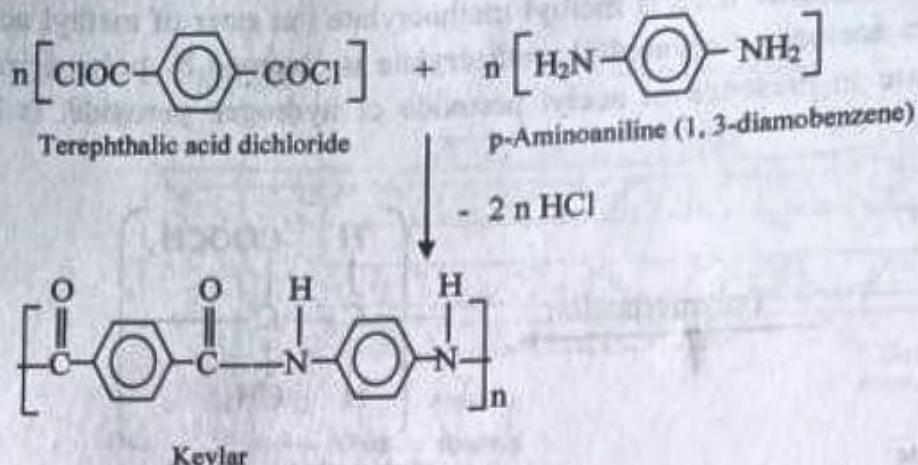
### Uses:

- (1) It is used for automotive applications such as in tail and signal light lenses, dials, medallions etc.
- (2) For making aircraft light fixtures, bomber noses, gun turrets, cockpit canopies, transparent models of complicated mechanisms.
- (3) For making bone splints, artificial eyes, dentures, emulsions, paints, adhesives, wind screens, jewellery, T.V. screens, guards etc.
- (4) Its sheets are used for signs, glazing skylights and decorative purposes.

### 2. Kevlar:

It is an aromatic polyamide with benzene rings linked to the amide groups  $-\text{CONH}-$ .

**Preparation:** It is prepared by poly condensation between aromatic dichloride and aromatic diamines.

**Properties:**

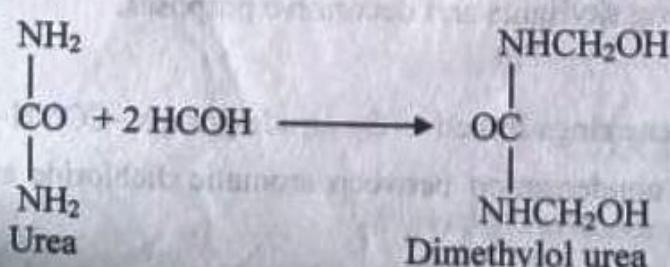
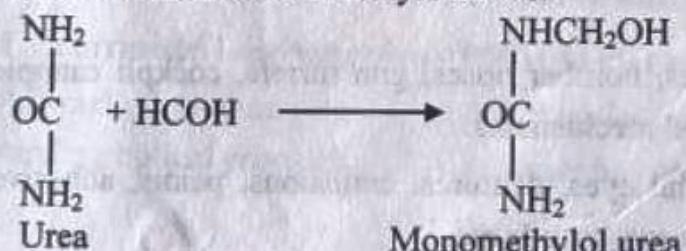
- (i) It is exceptionally strong (five times stronger than steel).
- (ii) It has high heat stability and flexibility.
- (iii) It is more rigid than nylon.

**Uses:**

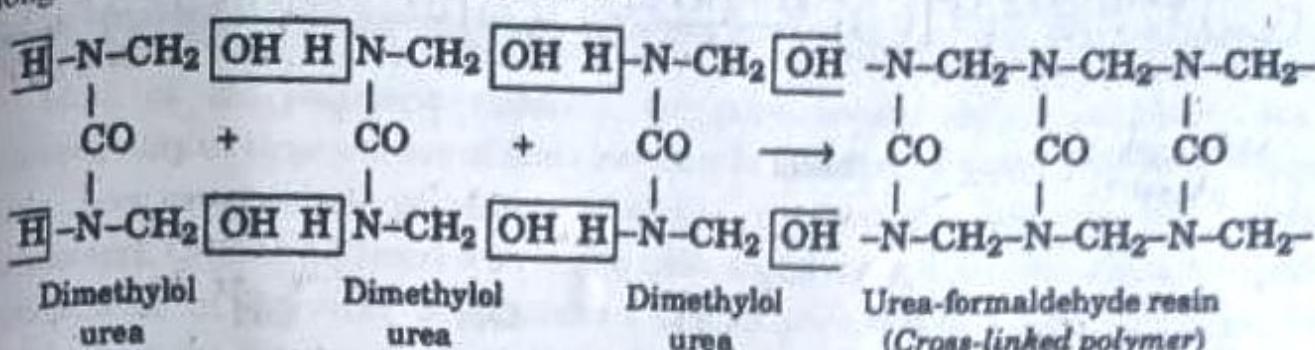
- (i) It is used in the aerospace and aircraft industries.
- (ii) It is used in car parts (tyres, brakes etc.)
- (iii) It is used in ropes, cables, bullet proof vests, motor cycle helmets etc.

**3. Urea formaldehyde resin:**

Amino resins are condensation products, obtained by the reaction of urea or melamine with formaldehyde. Commercially important amino resin is urea-formaldehyde, which is prepared by the reaction between 2 parts of urea and 1 part of formaldehyde, in basic medium, in a stainless steel vessel at about 50°C. Primary products are mono and dimethylol ureas.



For moulding, the methylol derivatives are compounded (with fillers, plasticizers, pigments, and catalyst) and then cured (by applying heat and pressure). During curing, long -C-N-C-N- chains are formed.



#### Properties:

1. Urea formaldehyde resins give clear, water-white products of good tensile strength.
2. It also gives good electrical insulation and good chemical resistance.
3. It gives great hardness, great light-stability and good abrasion resistance.

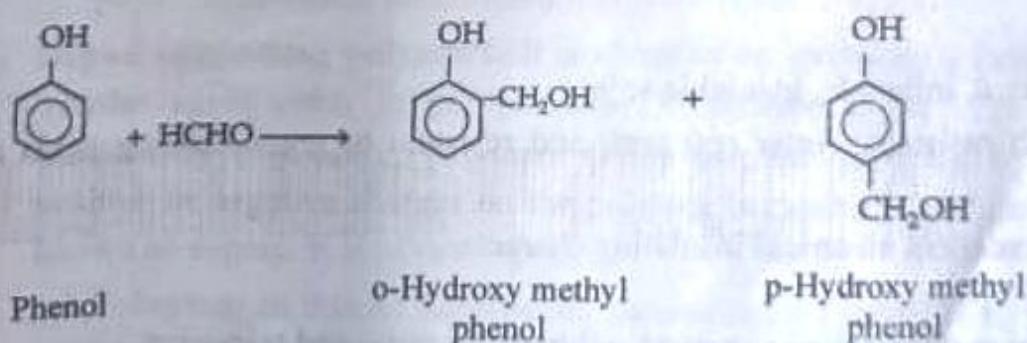
#### Uses:

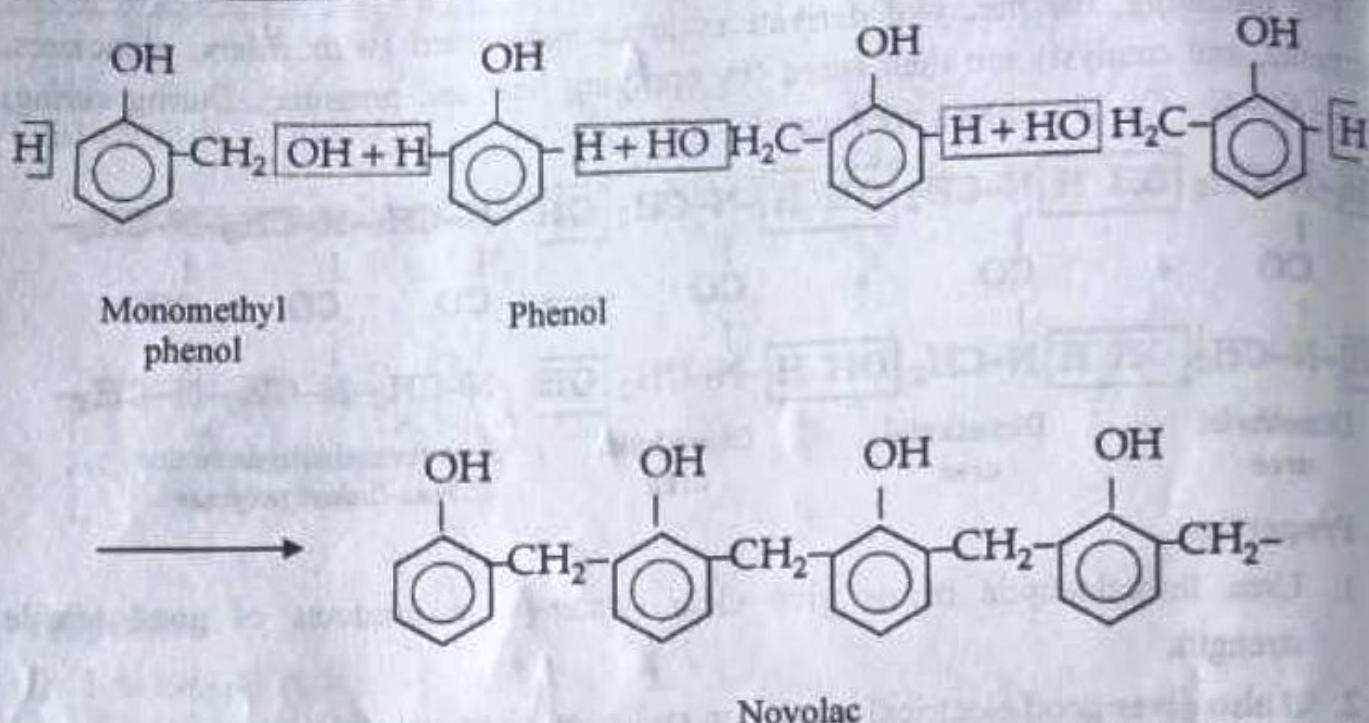
1. It is used for bonding grinding wheels.
2. It is used as binder of glass fibres, rockwool etc., which are used for filtration and insulation purposes.
3. It is used for foundry cores.
4. It is used as electrical insulator.

It is used as decorative articles like plates, drinking glasses, dishes etc.

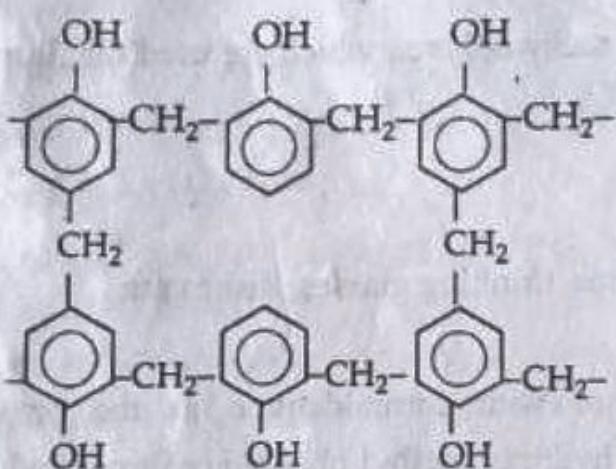
#### 4. Phenol formaldehyde resin:

It is prepared by condensing phenol with formaldehyde in the presence of acidic/alkaline catalyst. Initially, o- and p-hydroxy methyl phenol are formed which react to form linear polymer novolac.





Hexamethylene tetramine is added to novolac which provides formaldehyde. This converts the soluble and fusible novolac into a hard infusible and insoluble solid of cross-linked bakelite.



Cross-linked polymer bakelite

### Properties:

1. It is rigid, hard, infusible, insoluble solid.
2. It is scratch resistant, water resistant, and resistant to non-oxidizing acids and salts.
3. Possesses excellent electrical insulating character.

### Uses:

1. It is used for making telephone parts, cabinets for radio and television.
2. It is used for making bearings used in propeller shaft in paper industry.
3. It is used for making switches, plugs, switch boards etc.

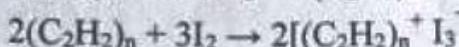
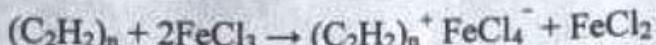
4. It is used in paints and varnishes.
5. It is used as adhesive for grinding wheels.

## 5.12 CONDUCTING POLYMERS

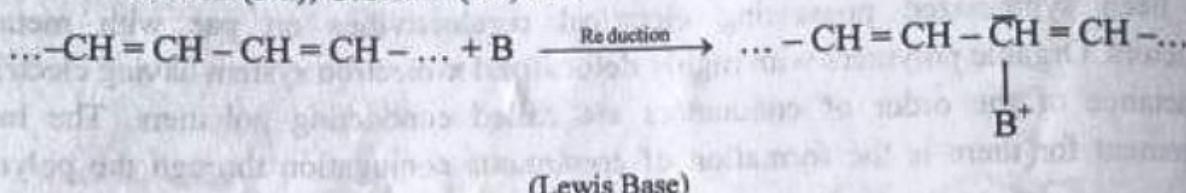
Most of the polymeric materials are poor conductors of electricity due to unavailability of large number of free electrons. In past several years, polymeric materials have been synthesized possessing electrical conductivities on par with metallic conductors. Organic polymers with highly delocalized  $\pi$ -electron system having electrical conductance of the order of conductors are called conducting polymers. The basic requirement for them is the formation of continuous conjugation through the polymer chain.

Different types of conducting polymers are as follows.

1. **Intrinsically conducting polymers:** It is a polymer whose backbone or associated groups consists of delocalized electron pair or residual charge. In an electric field, conjugated  $\pi$ -electron of the polymer get excited, and hence can be transported through the solid polymeric materials. Overlapping of orbitals over the entire backbone results in the formation of valence bands as well as conduction bands. Some common examples are polyacetylene polymers, polyaniline, polyanthrylene, polypyrrole, polythiophene, polyazomethine etc.
2. **Extrinsically conducting polymers:** It is a polymer whose conductivity is due to the presence of externally added ingredient in them. They are of two types:
  - (a) **Conductive elements-filled polymers:** It is a resin filled with conducting elements such as carbon black or metal oxides, in which the polymer acts as a binder to hold the conducting elements. Along with conductivity these polymers are low in cost, light in weight, mechanically durable and strong.
  - (b) **Blended conducting polymer:** It is a polymer obtained by blending a conventional polymer with conducting polymer. Such polymers possess better physical, chemical and mechanical properties.
3. **Doped conducting polymers:** It is obtained by exposing a polymer to a charge transfer agent either in gas phase or in solution phase. The conductivity of intrinsically conducting polymers (ICP) can be increased by creating either positive or negative charges on the polymer backbone by oxidation or reduction known as doping. It is of two types:
  - (a) **P-doping:** In this an intrinsically conducting polymer (ICP) is treated with a Lewis acid where oxidation process takes place and positive charges on the polymer backbone are created. Commonly used p-dopants are  $I_2$ ,  $Br_2$ ,  $AsF_5$ ,  $PF_6$ , naphthylamine, etc.



**(b) N-doping:** In this an intrinsically conducting polymer (ICP) is treated with a Lewis base where reduction takes place and negative charges are created on the polymer backbone. Commonly used n-dopants are Lithium (Li), Sodium (Na), Calcium (Ca) etc.



**4. Co-ordination conducting polymer:** It is a charge transfer complex containing polymer obtained by combining a metal atom with a poly dentate ligand.

#### Applications:

- (1) In rechargeable light weight batteries based on perchlorate doped polyacetylene-lithium system. These are about 10 times lighter than conventional lead storage batteries.
- (2) In wiring in aircrafts and aerospace components.
- (3) In electronic devices such as transistors and diodes and in telecommunication systems.
- (4) In antistatic coating for clothing.
- (5) In electromagnetic screening materials.
- (6) In photovoltaic devices.
- (7) In molecular wires and molecular switches.

### 5.13 POLYMERS IN MEDICINE AND SURGERY

Biomaterials are materials that can be implanted in the body or used in diagnostic, surgical and therapeutic applications without causing adverse effect on blood and other tissues. They are developed from metals, ceramics and polymers. Use of biomaterials made from polymers is increasing day-by-day. Their appeal and acceptability is mainly due to versatility and the fact that they can be modified at will to suit specific body functions.

#### Characteristics of biomedical polymers:

- (1) It should be bio compatible.
- (2) It should be fabricated into the desired shape or form without being degraded.
- (3) It should have purity and reproducibility.
- (4) They can be easily sterilized with no alteration in properties.

- (5) They should have optimum physical and chemical properties.
- (6) They should not destroy cellular elements of blood, enzyme or produce toxic or allergic reactions.
- (7) They should not deplete electrolytes in the body.

**Table 5.2: Applications of biomedical polymers:**

Polymer	Applications
1. Polyethylene	Disposable syringe
2. Polypropylene	Heart walls, blood filters
3. Polyvinylchloride	Disposable syringe
4. Acrylic Hydrogels	Grafting
5. PMMA	Contact lenses
6. Polyalkyl sulphone	Membrane Oxygenator
7. Silicone Rubber	Heart walls, drain tubes
8. Polyurethane	Heart wall, blood filters, artificial heart

#### 5.14 REVIEW QUESTIONS

# CONCEPT OF ELECTROCHEMISTRY

## SYLLABUS

- *Introduction, concept of electrode potential, Nernst equation, types of electrochemical cells, concept of standard electrode with examples*
- *Electrochemical series, simple numericals.*

### 3.1 INTRODUCTION

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (the electrode) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte. Chemical reactions where electrons are transferred between molecules are called oxidation/reduction (redox) reactions. In general, electrochemistry deals with the study of electrodes, electrochemical cells, conversion of chemical energy into electrical energy and vice versa.

### 3.2 ELECTRO CHEMICAL CELL

An electrochemical cell is a device consisting of two electrodes, each in contact with a solution of its own ions and transforms the free energy change of the redox reaction at the electrodes into electrical energy. In a redox reaction, the energy released in a reaction due to the movement of charged particles gives rise to a potential difference. The maximum potential difference is called the electromotive force (EMF) in volts. It should be apparent from the above that the potential difference between the electrodes of a cell is the major factor of the tendency for the cell reaction to take place. The more positive is the cell potential, the greater is the tendency for the reaction to proceed to spontaneity.

The electrochemical cells are classified as, (i) Voltaic cell (Galvanic cell), (ii) Electrolytic cell, (iii) Concentration cell, (iv) Fuel cell.

### (i) Voltaic cell (Galvanic cell) :

The free energy change in a galvanic cell must be negative and the potential difference of the electrodes (cell voltage) must be positive. Energy is released from spontaneous redox reaction. System does work on load/surrounding. In galvanic cell the free energy change of electrode redox reaction is converted into electric energy; that is  $\Delta G = -nFE$ . The examples of galvanic cells are primary irreversible cells (dry cells) and secondary cells (lead storage batteries).

Dissimilar metals

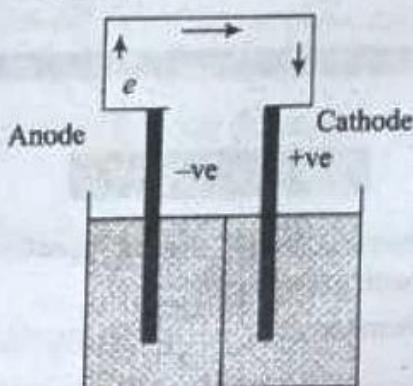


Fig. 3.1 : A galvanic cell

### (ii) Electrolytic cell :

It is device in which electrical energy from an external source can be used to produce chemical reactions. Energy is absorbed to drive non-spontaneous redox reaction. Surroundings (power supply) do work on system (cell). In electrolytic cells, the reaction is being driven in the non-spontaneous direction by external electrical force and free energy change is positive.

Power source

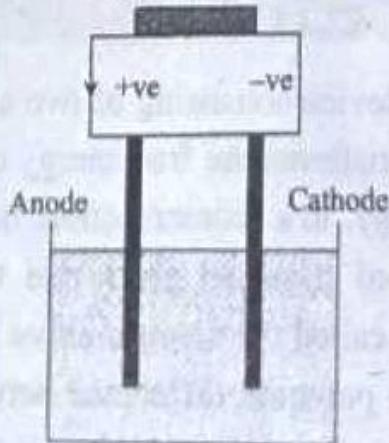
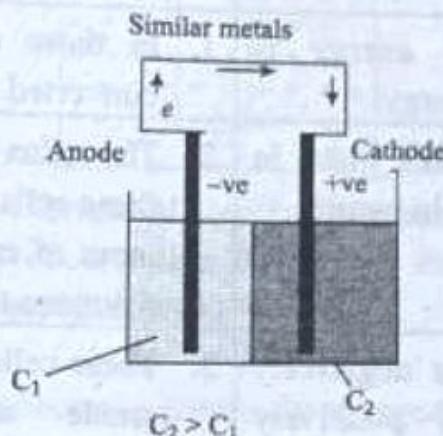


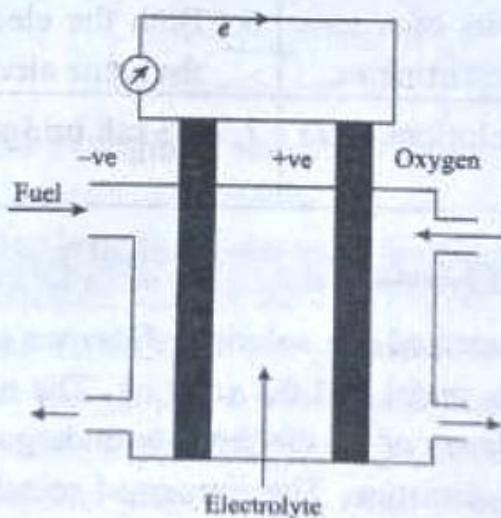
Fig. 3.2 : An electrolytic cell

**(iii) Concentration cell :**

A concentration cell is also an electrochemical device that generates electrical energy when two electrodes of the same metal are in contact with solutions of its ions at different concentrations. In a concentration cell, too, the free energy change of electrode reactions is converted into electric energy.

**Fig. 3.3 : A concentration cell****(iv) Fuel cell :**

A fuel cell is also an electrochemical device, which operates with continuous replenishment of the fuel at the electrode and no charging is required. In a fuel cell, the free energy change of electrode redox reactions is converted into electric energy.

**Fig. 3.4 : A fuel cell****Applications of Electrochemical cells :**

- They are used in electro-refining of many non-ferrous metals. They are used in electro-winning of these metals.
- The production of high purity lead, zinc, aluminium and copper involves their use.
- Metallic sodium can be extracted from molten sodium chloride by placing it in an electrolytic cell and passing an electric current through it.

- Many commercially important batteries are made up of galvanic cell.
- Fuel cells are an important class of electro chemical cells that serve as a source of clean energy in several remote locations.

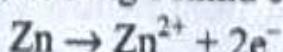
### Comparison :

Galvanic Cell	Electrolytic Cell
1. In these cells, chemical energy is converted into electrical energy.	1. In these cells, electrical energy is converted into chemical energy.
2. The redox reactions that take place in these cells are spontaneous in nature.	2. The redox reactions that take place in these cells are non-spontaneous. An input of energy is required for redox reactions to proceed in these cells.
3. In these cells the anode is negatively charged and cathode is positively charged.	3. These cells feature positively charged anode and negatively charged cathode.
4. The electrons originate from the species that undergoes oxidation.	4. Electrons originate from an external source.
5. Electrodes are of dissimilar metals.	5. Electrodes used may be of dissimilar or same metals.
6. Electrode is immersed in its own ions and both have separate compartments.	6. Both the electrodes are immersed in the same electrolyte solution.
7. The two electrolyte solutions are connected by a salt bridge.	7. No salt bridge is required.

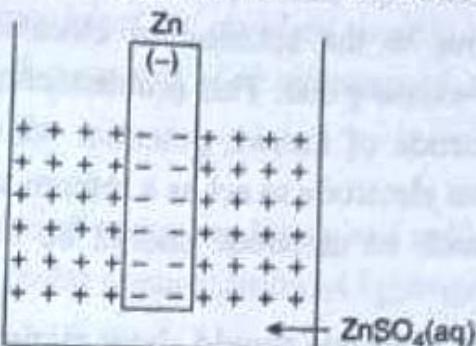
### 3.3 ELECTRODE POTENTIAL

When a piece of metal is immersed in a solution of its own ions, a potential difference is created at the interface of the metal and the solution. The magnitude of the potential difference is a measure of the tendency of the electrode to undergo oxidation or reduction or the tendency to lose or gain electrons. The immersed metal is an electrode and the potential due to reaction at the interface of the electrode and the solution is called the electrode potential.

In order to understand the origin of electrode potential, consider a zinc electrode consists of zinc strip dipped in  $\text{ZnSO}_4$ . Nernst proposed that in the electrode there will be two tendencies – oxidation and reduction. If oxidation tendency occurs then  $\text{Zn}$  atoms on the metal surface undergo oxidation, leaving behind electrons on the surface.

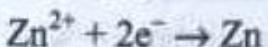


The  $Zn^{2+}$  ions pass into the solution and the metal strip becomes negatively charged. The positively charged metal ions accumulate around the metal as shown in the Fig. 3.5.

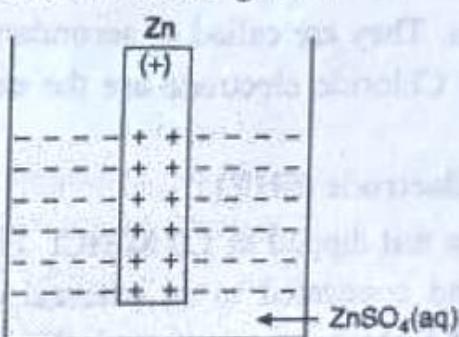


**Fig. 3.5 : Origin of electrode potential (oxidation)**

If the reduction tendency occurs, then  $Zn^{2+}$  ion in the solution undergo reduction by accepting electrons from the metallic surface.



Thus the metallic surface becomes positively charged and the negatively charged ions accumulate around the metal as shown in the Fig. 3.6.



**Fig. 3.6 : Origin of electrode potential (reduction)**

The two tendencies happen simultaneously on the same electrode. Hence, an electrical double layer called Helmboltz electrical double layer (HED) is established at the metal-aqueous solution interface. Across the HED layer, there is movement of charges. This results in the potential called electrode potential. It is defined as the potential that exists between the metal or the gas and its ions in aqueous solution, at their equilibrium when they are in contact with each other. The electrode potential of a metal is thus a major of its tendency to lose or gain electrons when in contact with a solution of its own salt.

### Standard Electrode Potential ( $E^\circ$ ) :

It is defined as the potential that exists between the metal or the gas and its aqueous solution of unit concentration at  $298^\circ K$  when the sum of all partial pressures of the gaseous reactants and products, if any, is equal to 1 atm pressure. This value is considered to compare the relative abilities of different electrodes to undergo oxidation or reduction.

### 3.4 REFERENCE ELECTRODE

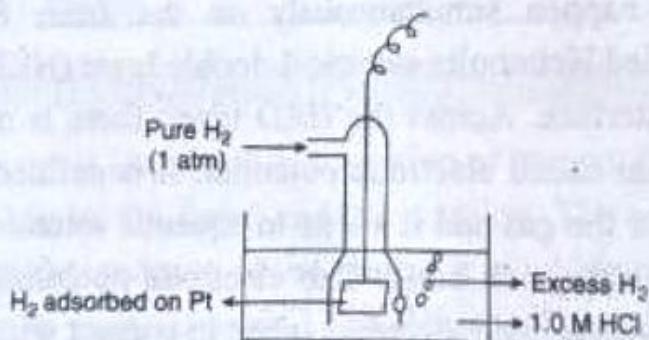
The potential of an electrode cannot be accurately measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. This problem can be overcome if the electrode is connected to another electrode of known potential which can be termed as reference electrode. The criteria for an electrode to act as a reference electrode are:

1. The potential of such an electrode should be known, under the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

The most commonly used reference electrode is the hydrogen electrode. The potential of all other electrodes are measured with respect to the hydrogen electrode which is also called a primary reference electrode. There are few more reference electrodes which are standardized using standard hydrogen electrodes and then can be used as reference electrodes. They are called as secondary reference electrodes. Calomel electrode and Silver-Silver Chloride electrode are the examples of secondary reference electrodes.

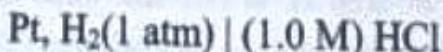
#### [A] Standard Hydrogen Electrode (SHE) :

It consists of a platinum foil dipped in 1.0 M HCl. The platinum foil is enclosed in a thick walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 atm pressure through the inlet at the top. Excess hydrogen leaves the electrode through the outlet at the bottom as shown in the Fig. 3.7

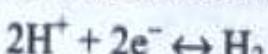


**Fig. 3.7 : Standard Hydrogen Electrode**

Pure hydrogen gets adsorbed on the platinum surface and is in contact with  $H^+$  ions in the solution. It forms a reversible electrode and can be represented as:



If reduction occurs at the electrode, the reaction will be:



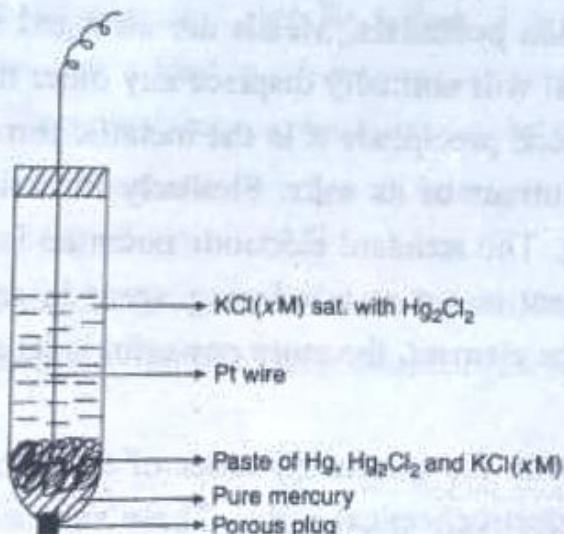
As the potential cannot be measured directly, it is assumed to be zero at 298K. Since  $E^{\circ}$  of SHE is assumed to be zero, the potential of the second electrode can be obtained. The potential of an electrode measured at standard condition is known as standard electrode potential. The electrode potential is a measure of reduction potential of an electrode with respect to SHE.

### **Limitations of SHE :**

1. SHE cannot be used in presence of strong oxidizing and reducing agents.
2. It is difficult to maintain unit molar concentration of hydrogen throughout and to pass hydrogen at 1 atm pressure.
3. Presence of arsenic compounds would get adsorbed on platinum foil and poisons the surface thereby affecting equilibrium of the reaction.

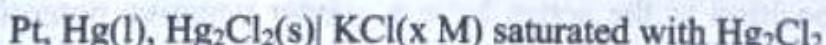
### **[B] Calomel Electrode :**

It consists of a thin layer of pure mercury at the bottom of the container. It is covered with a paste of Hg,  $Hg_2Cl_2$  and KCl of known concentration. The rest of the container is filled with KCl solution of known concentration, saturated with  $Hg_2Cl_2$  as shown in the Fig. 3.8.



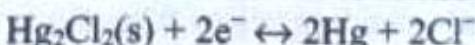
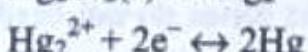
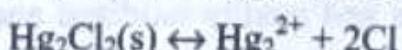
**Fig. 3.8: Calomel Electrode**

The electrode can be represented as:



The potential of this electrode depends on the concentration of KCl. It is a reversible electrode.

If reduction occurs at this electrode, the reaction can be shown as:



Nernst's equation for the Calomel electrode is:

$$E_{\text{Hg/Hg}_2\text{Cl}_2} = E^{\circ}_{\text{Hg/Hg}_2\text{Cl}_2} - \frac{2.303RT}{nF} \log [\text{Cl}]^2$$

Calomel electrode with saturated KCl and 1.0 M KCl have potential values of 0.2412V and 0.28V respectively.

### Advantages of Calomel Electrode:

1. It is used in corrosion studies.
2. It is easy to construct and easy to transport.
3. It provides constant potential value with varying temperature.
4. It finds application in laboratories for measuring potential of an electrode.

## 3.5 ELECTRO CHEMICAL SERIES

The standard electrode potential for all metals can be obtained by preparing the cells in which one electrode is standard hydrogen electrode while the other is metal immersed in a solution of its ions of normal activity. The standard electrode potentials are also known as standard oxidation potentials. Metals are arranged in the increasing order of electrode potential. A metal will normally displace any other metal below it in the series from solutions of its salts and precipitate it in the metallic form. Thus, Mg, Al, Zn or Fe will displace Cu from solutions of its salts. Similarly Pb will displace Cu, Hg or Ag; while Cu will displace Ag. The standard electrode potential is a quantitative measure of the readiness of the element to act as a reducing agent in aqueous solution; the more negative the potential of the element, the more powerful is its action as a reducing agent. (Table 3.1)

The elements arranged in the increasing order of their standard electrode potential constitute a series called electrochemical series. These values are measured with respect to standard hydrogen electrode at 25°C. The greater the negative value of the potential, the greater is the tendency of the metal to pass into solution in the ionic state. Elements occupying higher position in the series have a greater negative potential are said to be highly electropositive and those placed lower in the series are said to be highly electronegative. Metals occupying top positions in the series hold their valence electrons rather loosely and hence exhibit greater tendency to lose electrons. Consequently such metals are highly electropositive and readily oxidized and corroded. On the other hand metals occupying lower positions in the series do not easily lose electrons and hence not corroded easily. All metals standing above in the electrochemical series will have a tendency to displace all metals standing below from dilute solutions containing their ions.

**The characteristics of electrochemical series:**

1. Lithium is the first member of the series.
2. Highly reactive metal systems which are good reducing agents are at the top of the series.
3. Good oxidizing agents are at the bottom of the series.
4. Hydrogen system is at the middle of the series. All the elements which displace hydrogen from dilute acids are placed above it.

**The applications of electrochemical series:**

1. Higher the reduction potential, greater is the tendency of the element to get reduced. Hence the relative oxidizing and reducing abilities of the elements can be compared easily. For instance, among Zn and Cu systems, zinc system has lower reduction potential ( $-0.76$  V) than Cu ( $+0.34$  V). So, zinc system has more reducing ability than Cu. Lower the reduction potential, greater is the reducing ability.
2. A metal placed higher in the series is anodic to other metals which lie below it. An element can displace all elements that lie below it in the series, from their salt solutions. For example, zinc added to a hot saturated solution of  $\text{CuSO}_4$  can displace copper from the salt. Thus displacement reactions can be predicted.
3. Knowledge of electrochemical series helps in selection of electrode assemblies, to construct the galvanic cells of desired EMF.
4. The polarity of the electrode system and electrode reaction can be easily predicted.
5. Spontaneity and feasibility of the cell under construction can be easily predicted.

**Table 3.1 : Standard electrode potentials of metals**

(The values given refer to the normal activity of ions at a standard temperature of 25°C)

Metal ion electrode system	Electrode reaction (Acid solution)	Standard electrode potential ( $E_0$ ) in volts
Li / Li <sup>+</sup>	Li <sup>+</sup> + e <sup>-</sup> = Li	-3.045 (Reactive metals)
K / K <sup>+</sup>	K <sup>+</sup> + e <sup>-</sup> = K	-2.925
Ca / Ca <sup>++</sup>	Ca <sup>+2</sup> + 2e <sup>-</sup> = Ca	-2.866
Na / Na <sup>+</sup>	Na <sup>+</sup> + e <sup>-</sup> = Na	-2.714
Mg / Mg <sup>++</sup>	Mg <sup>+2</sup> + 2e <sup>-</sup> = Mg	-2.363
Al / Al <sup>++++</sup>	Al <sup>+3</sup> + 3e <sup>-</sup> = Al	-1.662
Mn / Mn <sup>++</sup>	Mn <sup>+2</sup> + 2e <sup>-</sup> = Mn	-1.180
Zn / Zn <sup>++</sup>	Zn <sup>+2</sup> + 2e <sup>-</sup> = Zn	-0.763
Cr / Cr <sup>+++</sup>	Cr <sup>+3</sup> + 3e <sup>-</sup> = Cr	-0.744
Fe / Fe <sup>++</sup>	Fe <sup>+2</sup> + 2e <sup>-</sup> = Fe	-0.0441
Cd / Cd <sup>++</sup>	Cd <sup>+2</sup> + 2e <sup>-</sup> = Cd	-0.441
Co / Co <sup>++</sup>	Co <sup>+2</sup> + 2e <sup>-</sup> = Co	-0.277
Ni / Ni <sup>++</sup>	Ni <sup>+2</sup> + 2e <sup>-</sup> = Ni	-0.25
Sn / Sn <sup>++</sup>	Sn <sup>2+</sup> + 2e <sup>-</sup> = Sn	-0.136
Pb / Pb <sup>++</sup>	Pb <sup>2+</sup> + 2e <sup>-</sup> = Pb	-0.126
H <sub>2</sub> / 2H <sup>+</sup>	2H <sup>+2</sup> + 2e <sup>-</sup> = H <sub>2</sub>	0.00 Reference
Cu / Cu <sup>++</sup>	Cu <sup>+2</sup> + 2e <sup>-</sup> = Cu	0.337
Cu / Cu <sup>+</sup>	Cu <sup>+</sup> + e <sup>-</sup> = Cu	0.522
Hg / Hg <sup>+</sup>	Hg <sup>+</sup> + e <sup>-</sup> = Hg	0.799
Ag / Ag <sup>+</sup>	Ag <sup>+</sup> + e <sup>-</sup> = Ag	0.80
Hg / Hg <sup>++</sup>	Hg <sup>++</sup> + 2e <sup>-</sup> = Hg	0.854
Pd / Pd <sup>++</sup>	Pd <sup>++</sup> + 2e <sup>-</sup> = Pd	0.987
Pt / Pt <sup>++</sup>	Pt <sup>++</sup> + 2e <sup>-</sup> = Pt	1.2
Au/Au <sup>+++</sup>	Au <sup>+++</sup> + 3e <sup>-</sup> = Au	1.42 (Noble metals)

### 3.6 GALVANIC SERIES

**Table 3.2 : Galvanic series (on the basis of relative oxidation potentials in sea water)**

More Anodic or Active (or Corroded end)	
Magnesium	
Magnesium alloys	Active or more anodic
Zinc	
Aluminium	
Aluminium alloys	
Low carbon steel	
Cast iron	
Stainless steel (active)	
Lead-tin alloys	
Lead	
Tin	
Brass	
Copper	
Bronze	
Copper-Nickel alloys	
Inconel	
Silver	
Stainless steel	
Monel	
Graphite	
Titanium	Noble (cathodic)
Gold	
Platinum	

Although electrochemical series gives very useful information regarding chemical reactivity of metals, it may not be able to provide sufficient information in predicting the corrosion behavior in a particular set of environmental conditions. However, in practical situations many side reactions may take place which influence the corrosion reactions. In view of this, oxidation potential measurements of various metals and alloys in common use have been made using standard calomel electrode as the reference electrode and

immersing the metals and alloys in sea water. These are arranged in decreasing order of their activity and this series is known as 'galvanic series'. (Table 3.2)

Where as in the electrochemical series, metals are arranged from top to bottom in increasing order of their reduction potential. A metal high in the series is more anodic and undergoes corrosion faster than metal below it. However, some exceptions to this generalization are known. For example, in Zn – Al couple, Zn (below than Al) corrodes as Al develops oxide layer and resists corrosion. Such a behavior is well explained by considering the positions of these metals in galvanic series. The galvanic series provide more accurate information regarding the relative tendency of common metals and alloys to undergo corrosion and is more reliable than those based on electrochemical series. In the galvanic series more active metals are given higher place and corrode readily. The metals at the lower end do not easily react and therefore do not corrode so easily under atmospheric condition. When two metals are in electrical contact and an electrolyte is present, the one higher up in the galvanic series corrodes and the other is protected. The greater the difference in their positions in the galvanic series the faster will be the corrosion. Metals close to each other in the galvanic series show less tendency to corrode when in contact with each other.

### Comparison :

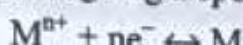
Electrochemical series	Galvanic series
1. Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration, without any oxide film on them.	1. This series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films, if any removed.
2. The position of a given metal in electrochemical series is fixed.	2. The positions of given metal may shift in galvanic series.
3. It gives no information regarding positions of alloys.	3. Since alloys are included in galvanic series so their corrosion can be studied from this series.
4. The position of a metal in this series is permanently fixed.	4. The position of a metal when present in the form of an alloy, is different from pure metal.
5. This series comprises of metals and non-metals.	5. This series comprises of metals and alloys
6. It predicts the relative displacement tendencies.	6. It predicts the relative corrosion tendencies.

### 3.7 NERNST EQUATION

In an electrochemical cell, the electrode potential depends on the nature of the electrode, concentration of the electrolyte and temperature. Nernst derived a fundamental equation relating the free energy change of any electrode processes to the potential developed at the electrode along with the concentration of ions in the solutions and its temperature.

#### Derivation :

Consider an electrode assembly undergoing a spontaneous reaction.



The equilibrium constant (K) for this system in equilibrium can be evaluated as

$$K = \frac{[M]}{[M^{n+}]}$$

Some amount of electrical work is done and is maximum at equilibrium referred to as  $W_{\max}$ .

$W_{\max}$  = (Number of Coulombs of charge flowing across the HED) × (Energy available per Coulombs of charge)

$$W_{\max} = nEF$$

As the reaction is spontaneous, there is decrease in the free energy. Also the decrease in free energy appears as work done ( $W_{\max}$ ).

Therefore,

$$-\Delta G = W_{\max} = nEF$$

Under standard conditions,  $-\Delta G^0 = nE^0 F$

The decrease in free energy change for the above mentioned reaction can be expressed as,

$$\Delta G = \Delta G^0 + 2.303 RT \log_{10} \frac{[M]}{[M^{n+}]}$$

Substituting the values of  $\Delta G$  and  $\Delta G^0$ ,

$$-nEF = -nE^0 F + 2.303 RT \log_{10} \frac{[M]}{[M^{n+}]}$$

Dividing by  $-nF$  we get,

$$E = E^0 - \frac{2.303 RT}{nF} \log_{10} \frac{[M]}{[M^{n+}]}$$

For a Galvanic cell the EMF is given as,

$$E_{cell} = E_{cell}^0 - \frac{2.303 RT}{nF} \log_{10} K$$

Where, K is the equilibrium constant for the reaction.

**Applications of Nernst Equation:**

1. The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
2. The concentration of the reactants can be calculated by knowing the potential of an electrode.
3. The pH of a solution can be calculated by measuring the EMF.
4. The concentration of a solution in the galvanic cell can be determined.

**NUMERICALS ON NERNST EQUATION**

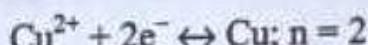
1. Calculate the electrode potential of copper, if the concentration of  $\text{CuSO}_4$  is 0.206 M at  $23.1^\circ\text{C}$ . Given that  $E^{\theta}_{\text{Cu}^{2+}/\text{Cu}} = +0.34\text{V}$ .

**Solution :**

Given that

$$[\text{CuSO}_4] = 0.206; T = 296.1^\circ\text{K}$$

The reaction taking place is



According to Nernst's equation,

$$\begin{aligned} E_{\text{Cu}^{2+}/\text{Cu}} &= E^{\theta}_{\text{Cu}^{2+}/\text{Cu}} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Cu}^{2+}]} \\ &= +0.34 - \frac{2.303 \times 8.314 \times 296.1}{2 \times 96500} \times \log_{10} \frac{1}{0.206} \\ &= 0.31984\text{V} \end{aligned}$$

$$\text{Ans. : } E_{\text{Cu}^{2+}/\text{Cu}} = 0.31984\text{V}$$

2. Calculate the concentration of  $\text{NiCl}_2$  in the nickel electrode having a potential of  $-0.16942\text{ V}$  at  $24.9^\circ\text{C}$ . Given that  $E^{\theta}_{\text{Ni}^{2+}/\text{Ni}} = -0.14\text{V}$ .

**Solution :**

According to Nernst's equation,

$$E_{\text{Ni}^{2+}/\text{Ni}} = E^{\theta}_{\text{Ni}^{2+}/\text{Ni}} - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Ni}^{2+}]};$$

Here  $n = 2$ , So,

$$-0.16942 = -0.14 + \frac{2.303 \times 8.314 \times 297.9}{2 \times 96500} \times \log_{10}(x);$$

Where  $x = [\text{Ni}^{2+}]$ . So,

$$\begin{aligned}-0.16942 &= -0.14 + (0.02955) \times \log_{10} x \\ -0.02942 &= 0.02955 \times \log_{10} x\end{aligned}$$

We get  $x = [\text{NiCl}_2] = 0.1010 \text{ M}$

**Ans. : Concentration of  $\text{NiCl}_2 = 0.1010 \text{ M}$**

3. Calculate the standard electrode potential of lead electrode, if the electrode potential is  $-0.18025 \text{ V}$  at  $301 \text{ K}$  and a concentration of  $\text{Pb}^{2+}$  solution is  $0.0096 \text{ M}$ .

**Solution :**

Given  $[\text{Pb}^{2+}] = 0.0096 \text{ M}$ ;  $E_{\text{Pb}^{2+}/\text{Pb}} = -0.18025 \text{ V}$ ;  $T = 301 \text{ K}$ .

According to Nernst's equation,

$$\begin{aligned}E_{\text{Pb}^{2+}/\text{Pb}} &= E_{\text{Pb}^{2+}/\text{Pb}}^0 - \frac{2.303RT}{nF} \log_{10} \frac{1}{[\text{Pb}^{2+}]} \\ E_{\text{Pb}^{2+}/\text{Pb}}^0 &= E_{\text{Pb}^{2+}/\text{Pb}} - \frac{2.303RT}{nF} \log_{10} [\text{Pb}^{2+}] \\ &= -0.18025 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \times \log_{10}(0.0096) \\ &= -0.18025 - 0.02986 \times (-2.0177) \\ &= 0.1200 \text{ V}\end{aligned}$$

**Ans. :  $E_{\text{Pb}^{2+}/\text{Pb}}^0 = 0.1200 \text{ V}$**