A textbook of

Engineering Chemistry - I

Common to All Engineering Branches

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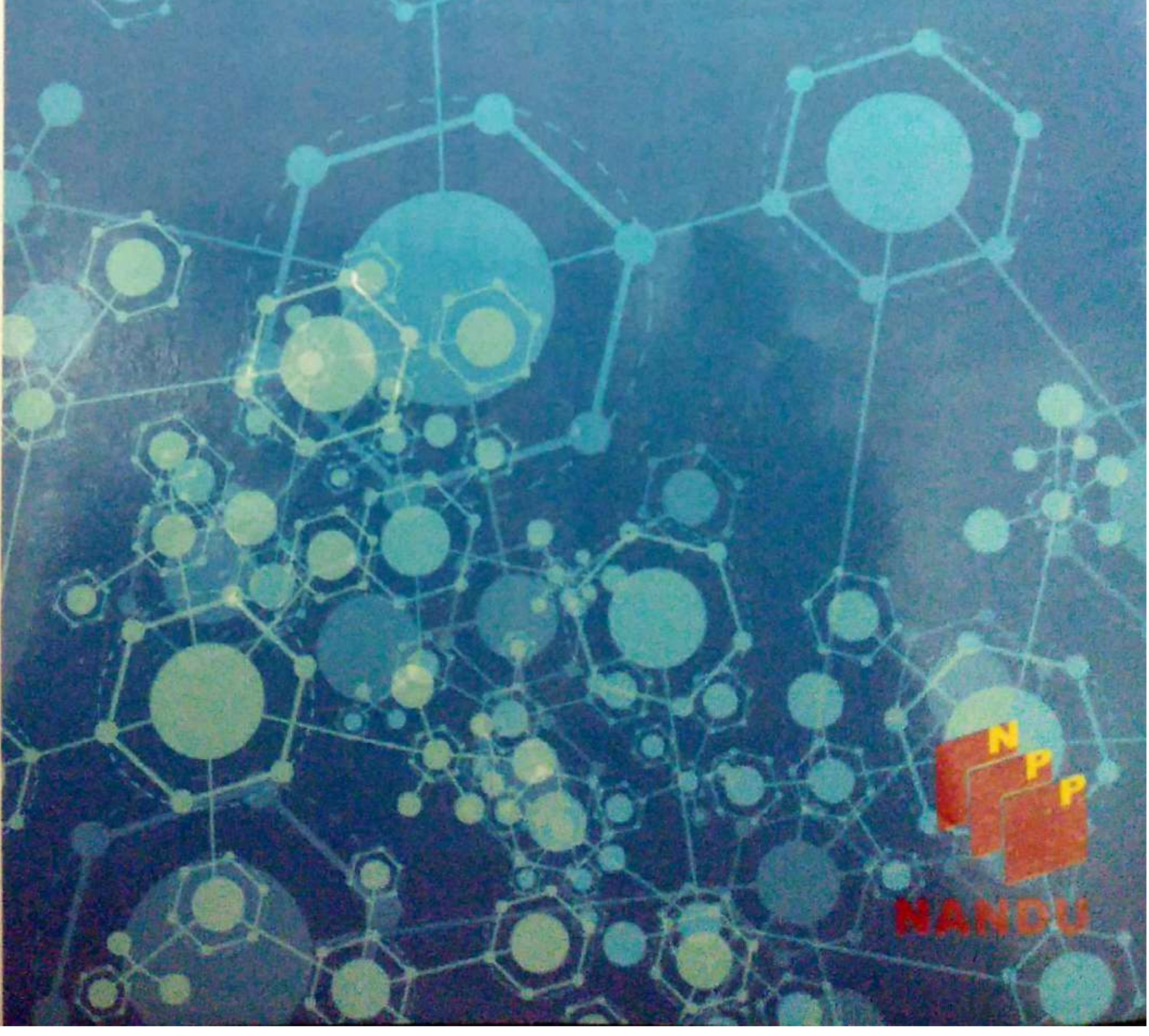

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A textbook of
ENGINEERING CHEMISTRY - I

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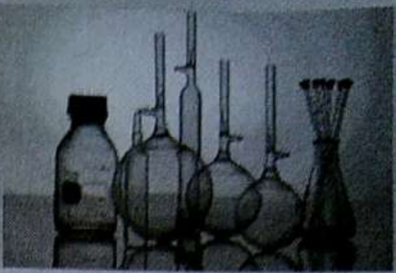
CONTENTS



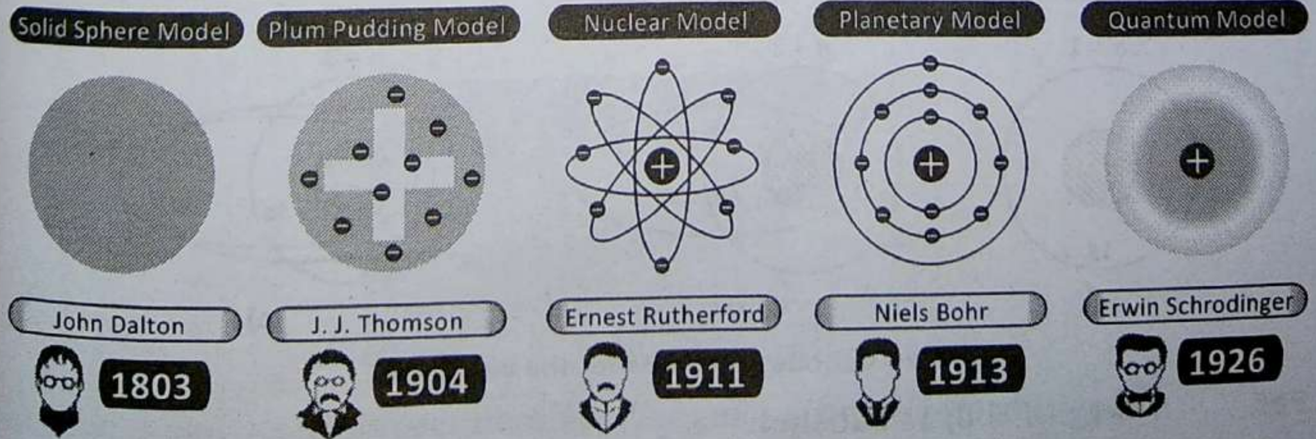
CHAPTER 1

ATOMIC AND MOLECULAR STRUCTURE

1.1 Introduction

Today our knowledge on the atomic structure has evolved due to the tireless efforts of numerous scientists since past 200 years. A word for the tiniest particle at that time was coined by Greeks, called atom *meaning indivisible*. As per their belief particles can be broken down into very tiny invisible particles called atom. Atom as a concept was put forth by the Greek philosophers Democritus and John Dalton. Democritus explained nature of matter and proposed that all substances are made up of matter. Further he also proposed that atoms are constantly moving, invisible, minuscule particles that are different in shape, size, temperature and cannot be destroyed. Ever since Democritus coined atom, atomic theory seemed to be more relevant to philosophy and physics but not very useful in explaining chemical properties of matter. In the early 19th century Lavoisier's theory and Proust's law of constant proportion of chemical compounds set a foundation for Dalton's atomic theory in 1803. Road map for atomic discovery is given below,

A History of the Atom : Theories and Models



According to Sommerfeld, an electron revolving around a central positively charged nucleus is influenced by the nuclear charge that it is set into motion in elliptical orbits with the nucleus situated at one of the foci as shown in the Fig. 1.1. In this case, there will be a major axis and a minor axis having different lengths. As the orbit broadens, the lengths of the two axes become closer and they become equal when the orbit becomes circular.

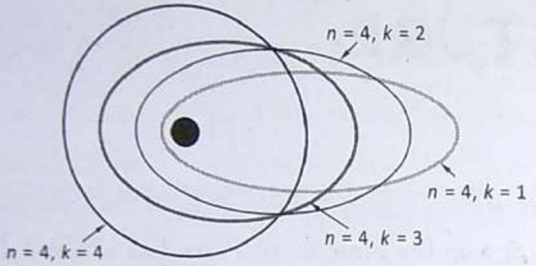


Fig. 1.1 : Sommerfeld's elliptical electron orbits for $n = 4$

The electrons travelling in an elliptical orbit will have its angular momentum. The angular momentum of electron moving in an elliptical orbit is $k\,h/2\pi$, where k is an integer except zero.

Value of $k = 1, 2, 3, 4$.....

$$\frac{n}{k} = \frac{\text{length of major axis}}{\text{length of minor axis}}$$

With increase in value of k, ellipticity of the orbit decreases. When $n = k$, then orbit is circular.

Further, Sommerfeld suggested that orbits are made up of sub-energy levels. These are *s, p, d, f*. These subshells possess slightly different energies.

Bohr gave a quantum number '*n*', which determines the energy of electron. Sommerfeld introduced a new quantum number called *orbital* or *azimuthal quantum number* (l) which determines the orbital angular momentum of electron. Values of $l = 0$ to $(n - 1)$ (Fig. 1.2)

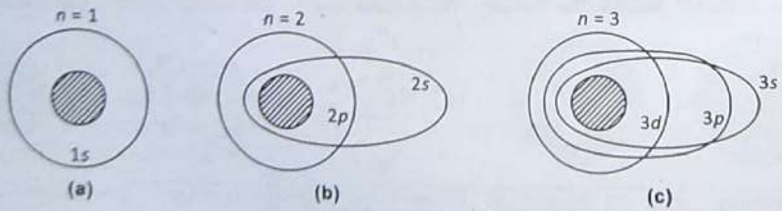


Fig. 1.2 : Various subshells for the electrons

For, $n = 1$; $l = 0$; 1s subshell

$n = 2$; $l = 0, 1$; 2s, 2p subshell

$n = 3$; $l = 0, 1, 2$; 3s, 3p, 3d subshell

$n = 4$; $l = 0, 1, 2, 3$; 4s, 4p, 4d, 4f subshell

1.2 Shapes of Atomic Orbitals and Electron Distribution

In quantum mechanics, an atomic orbital is a mathematical function that describes the wave-like behaviour of either one electron or a pair of electrons in an atom. The three coordinates that come from solving Schrodinger's wave equations are the principal (n), angular (l) and magnetic (m) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals on an atom. The shape of this region gives the shape of the orbital basically determined by azimuthal quantum number (l), while the orientation of orbital depends on the magnetic quantum number (m). Each orbital is denoted by a number (energy level) and a letter (shape of orbital).

Four quantum numbers are

(1) The principle quantum number designated by n, is the principle shell or main energy level of the electron. It describes the distance of the electron from the centre of the nucleus. Larger the value of n, more is the distance of an electron from the nucleus. n is any positive integer starting from 1, $n = 1, 2, 3, 4$..

When an electron jumps from lower level to higher, it absorbs energy whereas when an electron jumps from higher energy to lower energy it emits energy.

(2) The azimuthal quantum number also known as the orbital angular momentum quantum number designated by l. It determines *s, p, d, f* energy subshells and the shape of orbitals. The value of l is dependent on the principal quantum number n.

Since $l = n - 1$, it can have values from 0 to $n - 1$.

Name of subshell	Value of l
s	0
p	1
d	2
f	3

(3) The magnetic quantum number designated by m determines the number of orbitals and their orientation within a subshell. Its values depend upon l. $m = -l$ to $+l$

(4) The spin quantum number is independent of the other three quantum numbers. It is designated by s. It takes the value of +1/2 or –1/2 and describes the direction of the electron spin, +1/2 means upwards spin represented by upward arrow ↑ and –1/2, means downwards spin represented by downward arrow ↓. Fig. 1.3 describes the significance of the four quantum numbers.

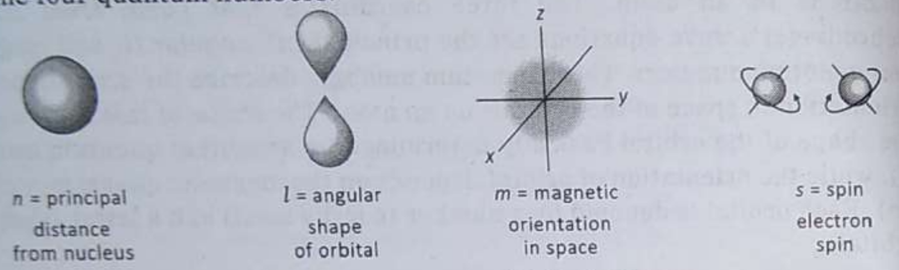


Fig. 1.3 : Quantum numbers and their significance

1.2.1 Electronic Configuration of Atom

Electron configuration of an atom represents how the electrons are distributed among the orbits (shells) and subshells in its ground state. For the electronic configuration of an atom we have to follow certain rules given by Aafbau principle, Pauli's exclusion principle and Hund's rule. Let us now see the shapes of orbitals in the various subshells.

1.2.1.1 Aafbau Principle

Aafbau principle states that in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels (Fig. 1.4).

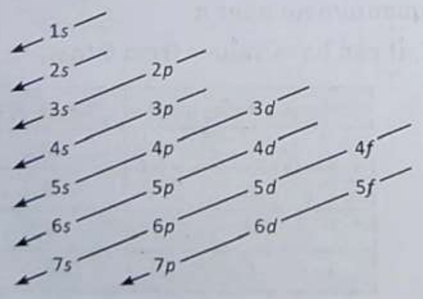


Fig. 1.4 : Occupancy of electrons in orbitals by Aafbau principle

1.2.1.2 Pauli's Exclusion Principle

The Pauli exclusion principle states that no two electrons can have the same four quantum numbers. Every orbital occupies two electrons, both of this electrons should have opposite spins, electrons with same spins occupying same orbital is forbidden (Fig. 1.5).

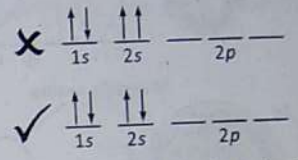


Fig. 1.5 : Pauli's exclusion principle

1.2.1.3 Hund's Rule

When assigning electrons in orbitals, each electron will first fill all the orbitals with similar energy (also referred to as degenerate) before pairing with another electron in a half-filled orbital (Fig. 1.6).

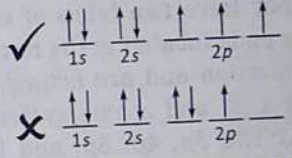


Fig. 1.6 : Representation of Hund's rule

(i) **s-orbital :** An s-orbital is spherically symmetric around the nucleus of the atom, like a hollow ball made of rather fluffy material with the nucleus at its centre. Every s-orbital has two electrons. As the energy levels increase, the electrons are located further from the nucleus, so the orbitals get bigger. The size of orbitals depends on principle quantum number n, as n goes on increasing, size of orbitals also goes on increasing. The order of size is $1s < 2s < 3s < \ldots$, as shown below in Fig. 1.7(a) and 1.7(b).

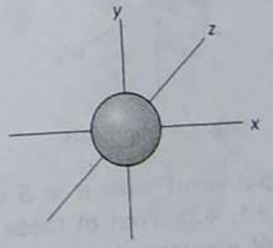


Fig. 1.7(a) : s-orbital in x, y, z coordinates

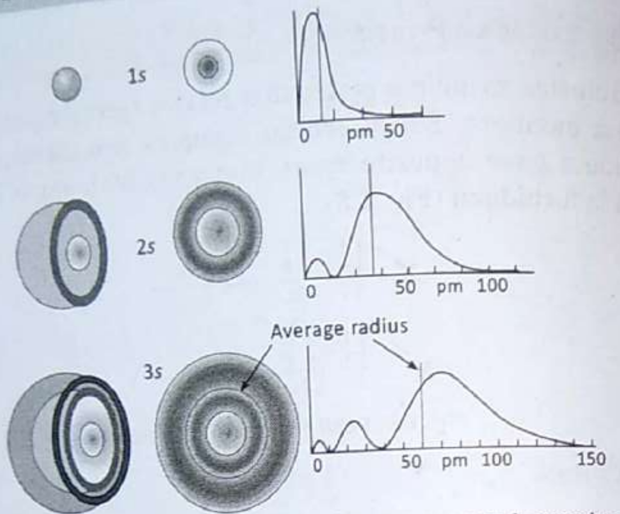


Fig. 1.7(b) : s-orbitals in increasing size as *n* goes on increasing

(ii) **p-orbital :** Any principal level with $n = 2$ or higher contains three *p* orbitals ($m = -1, 0, +1$). The *p* orbitals are not spherical symmetrical like the *s* orbital, but they have two lobes of electron density on either side of the nucleus and a node located at the nucleus. The three *p* orbitals differ only in their orientation and are orthogonal to one another. It is convenient to define an *x*, *y*, and *z* axis system and then label each *p* orbital as p_x, p_y and p_z. The 3*p*, 4*p*, 5*p*, and higher *p* orbitals are all similar in shape to the 2*p* orbitals, but they contain additional nodes (same as higher *s* orbitals) and are progressively larger in size.

Each *p* orbital can contain 2 electrons, so it can contain 6 electrons in total. All these three orbitals belonging to a particular energy shell have equal energies and are called degenerate orbitals (Fig. 1.8).

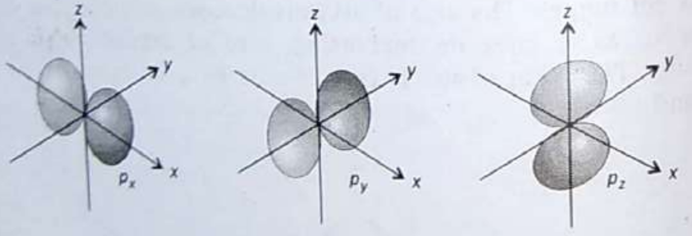


Fig. 1.8 : *p*-orbitals

(iii) ***d*-orbital :** Each principal level with $n = 3$ or greater contains five *d* orbitals ($m = -2, -1, 0, +1, +2$). Four of these orbitals have a cloverleaf shape, with four lobes of electron density around the nucleus and two perpendicular nodal plates. The d_{xy}, d_{xz} and d_{yz} orbitals are oriented along the *xy*, *xz* and *yz* planes, respectively, and their lobes are oriented between the corresponding axes. The $d_{x^2-y^2}$ lie along *x*-*y* axis and d_{z^2} along *z* axis. The 4*d*, 5*d*, 6*d*, and higher *d* orbitals are all similar in shape to the 3*d* orbitals, but they contain additional nodes and are progressively larger in size. There are total five *d* orbitals containing 10 electrons. Shapes of *d*-orbitals are shown below in Fig. 1.9.

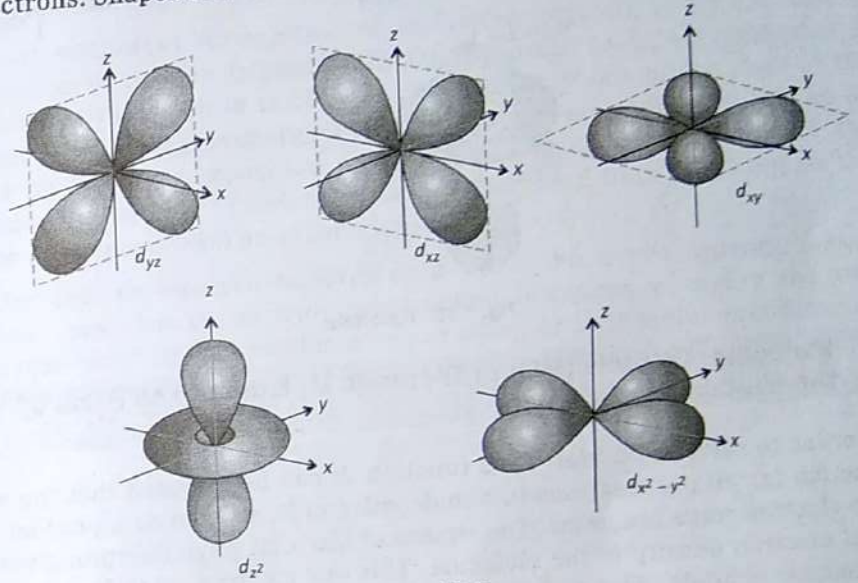
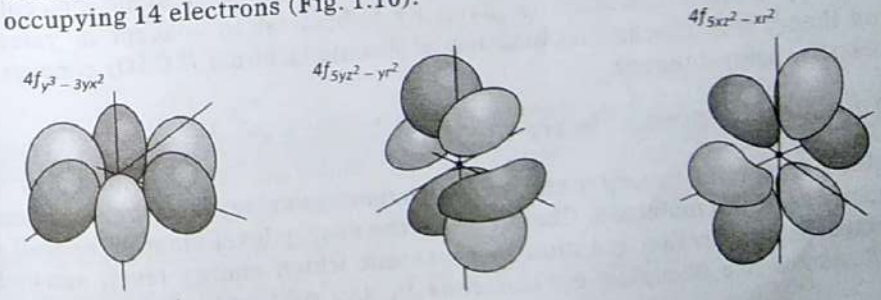


Fig. 1.9 : *d*-orbitals

(iv) ***f*-orbitals :** Each principal level with $n = 4$ or higher contains seven *f* orbitals ($m = -3, -2, -1, 0, +1, +2, +3$). These *f* orbitals have more lobes and nodes than *d* orbitals. There are total seven *f*-orbitals and capacity of occupying 14 electrons (Fig. 1.10).



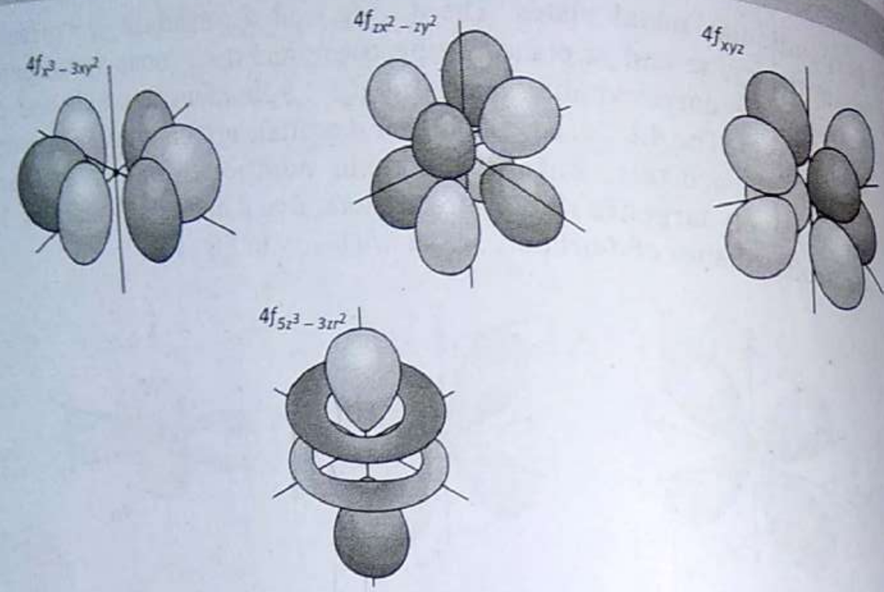


Fig. 1.10 : *f*-orbitals

1.3 Molecular Orbitals (MO) of Diatomic Molecules and Plots of the Multicentre Orbitals

In order to solve molecular wave function, it can be assumed that the wave function for all the electrons in a molecule can be written as a product of n one-electron wave functions. The square of the total wave function gives the total electron density in the molecule. This one electron wave functions are molecular orbitals. The molecular orbital has the same formulation as an atomic orbital does in a many electron atoms. The square of the molecular orbital gives the probability density for the electron. Molecular orbitals are delocalised. An electron wave function extends throughout the molecule, and is not confined to a bond between two atoms, except in diatomic molecules. Molecular orbital formation is given by hybridization concept in valence bond theory and Linear Combination of Atomic Orbitals (LCAO) concept in molecular orbital theory.

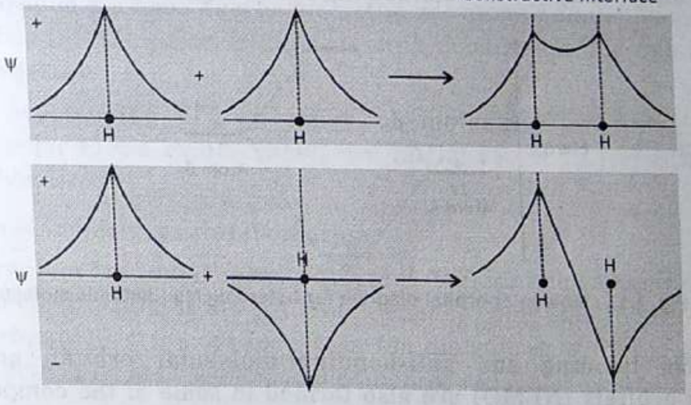
1.3.1 Molecular Orbital Theory

Molecular orbital theory uses quantum mechanics to describe electronic structures of the molecule. Chemists use the energy level diagram as well as electron configuration notation to represent which energy level, subshell, and orbital are occupied by electrons in any particular atom. In atoms, electrons occupy atomic orbitals, but in molecules they occupy similar molecular orbitals (MO). Electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. Molecular orbital describes a region of space around two or more atoms inside which electrons are likely to be found. Molecular orbital of a molecule is represented by molecular orbital diagram for qualitative description explaining chemical bonding in molecules.

The most simplified formulation of molecular orbitals is by the Linear Combination of Atomic Orbitals (LCAO) approach. In LCAO method it is assumed that the electron is close to the nucleus of one of the atom of the molecule. Hence, approximation can be made that molecular orbital can be formed by the superimposition of an atomic orbital of each atom of the molecule. The number of molecular orbitals obtained from LCAO equals the number of atomic orbital basis functions.

Consider that an electron behaves as a wave; when two separate waves combine, they can do so with *constructive interference*, where the two amplitudes build up and reinforce one another, or *destructive interference*, where the two amplitudes cancel one another as shown in the Fig. 1.11.

Constructive interface



Destructive interface

Fig. 1.11 : Constructive and destructive interference of waves

For example, H_2 orbitals which overlap constructively concentrate their charge in the internuclear region and are bonding.

Bonding wave function $\psi_1 = \psi_a + \psi_b$

Charge density is $(\psi_1)^2 = (\psi_a + \psi_b)^2 = (\psi_a)^2 + (\psi_b)^2 + 2\,\psi_a\,\psi_b$

Orbitals which overlap destructively depletes or have no charge in the internuclear region and are anti-bonding.

Anti-bonding wave function $\psi_2 = \psi_a - \psi_b$

Charge density is $(\psi_2)^2 = (\psi_a - \psi_b)^2 = (\psi_a)^2 + (\psi_b)^2 - 2\,\psi_a\,\psi_b$

Energy level diagram for constructive and destructive interference for H_2 molecule is shown in Fig. 1.12.

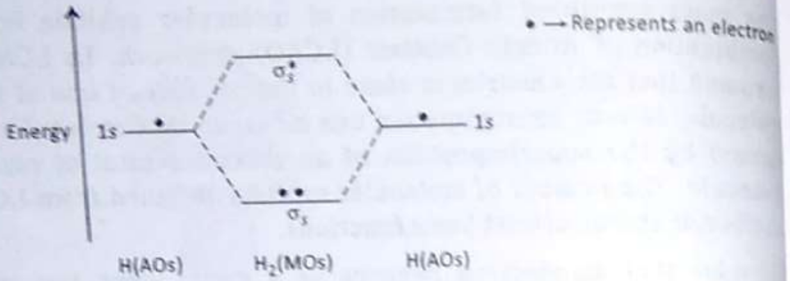


Fig. 1.12 : Molecular orbital diagram for H_2 molecule

When two atoms are different i.e. when atomic orbital have difference in energy overlaps, bonding molecular orbital will be much lower in energy whereas anti-bonding will be much high in energy (Fig. 1.13).

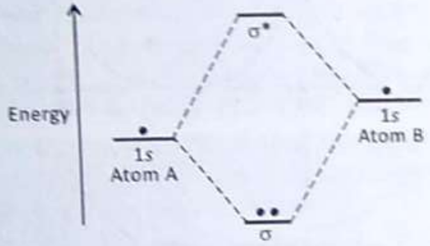


Fig. 1.13 : Molecular orbital diagram for heteronuclear diatomic molecule

Apart from bonding and anti-bonding molecular orbital, non-bonding molecular orbitals (NBMO) are also formed in some of the compounds as a result of no interaction between atomic orbitals due to lack of compatible symmetries needed for overlapping. Energy level of non-bonding molecular orbitals is often quite similar to or close to its constituent atomic orbital, thus not contributing to bonding energetics. Electrons in non-bonding orbitals tend to be associated with atomic orbitals that do not interact positively or negatively with one another, and electrons in these orbitals neither contribute nor detract from bond strength.

Atomic and molecular orbitals formed by Linear Combination of Atomic Orbitals (LCAO)

Sr.No	Atomic orbitals	Molecular orbitals
(1)	1sA + 1sB	$\sigma 1s$
(2)	1sA − 1sB	$\sigma^* 1s$
(3)	2sA + 2sB	$\sigma 2s$
(4)	2sA − 2sB	$\sigma^* 2s$
(5)	$2p_xA + 2p_xB$	$\sigma 2p_x$
(6)	$2p_xA - 2p_xB$	$\sigma^* 2p_x$
(7)	$2p_yA + 2p_yB$	$\pi 2p_y$
(8)	$2p_yA - 2p_yB$	$\pi^* 2p_y$
(9)	$2p_zA + 2p_zB$	$\pi 2p_z$
(10)	$2p_zA - 2p_zB$	$\pi^* 2p_z$

Following interactions take place during the bond formation by molecular orbital,

(1) A bond involving molecular orbitals which are symmetric with respect to rotation around the bond axis between the two atomic nuclei forms sigma bond (σ-bond), this region is high electron density holding two nuclear centers together.

(2) Lateral overlapping of two lobes of molecular orbital that are perpendicular to the axis between two nuclei result in formation of pi bond (π-bond).

Construction of molecular orbital diagram

While constructing molecular orbital diagram it should be remembered that bonding molecular orbital is always less in energy compared to anti-bonding molecular orbital. Electron occupation in the molecular orbital is governed by Aufbau's principle, Pauli's exclusion principle and Hund's rule.

The factors upon which relative energies of molecular orbitals depend are,

(i) Energies of the atomic orbital combining to form molecular orbital.

(ii) The extent of overlapping between the atomic orbitals. The greater the overlap, more is the bonding orbital lowered in energy and more is the anti-bonding orbital raised in energy relative to atomic orbitals.

(iii) Type of overlapping. Axial overlapping gives strong σ-bond whereas lateral overlapping gives weaker π-bond.

Postulates of molecular orbital theory

(1) When two atoms approach each other, they mutually overlap to form molecular orbitals and lose their identity. The molecular orbitals are obtained by the Linear Combination of Atomic Orbitals (LCAO).

(2) The number of molecular orbitals formed are same as the number of atomic orbitals combining, half of which are bonding and half anti-bonding.

(3) Only valence shell orbitals take part in the formation of molecular orbitals. Inner orbitals do not interact appreciably and hence remain practically non-bonding (denoted by KK).

(4) All the electrons originally occupying the atomic orbitals are accomodated in the molecular orbitals according to Aufbau principle, Pauli's exclusion principle and Hund's rule.

(5) The order of the energy levels of these molecular orbitals is as follows,

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p < \pi 2p = \pi 2p < \pi^* 2p = \pi^* 2p < \sigma^* 2p$$

It should be noted that, out of three *p* orbitals, one *p* orbital forms σ-bond and the other two form π bonds. In other words, *p* orbitals which are closer overlap axially to form σ-bond and have lower energy compared to other two *p* orbitals that overlap laterally forming π bonds possessing higher energy. Hence, those differences in relative proximity is why the *p* orbitals have different energies in a molecular orbital context.

Advantages of molecular orbital theory

(1) Molecular orbital theory is useful to calculate the bond order. It is the number of bonds formed between two atoms. It is given by the equation,

$$\text{Bond order} = \frac{1}{2}\left[\begin{array}{c}\text{Electrons in bonding}\\ \text{molecular orbitals}\end{array} - \begin{array}{c}\text{Electrons in anti-bonding}\\ \text{molecular orbitals}\end{array}\right]$$

Bond order informs about bond length and bond strength. Generally, higher bond order is associated with a shorter bond length because of greater number of bonds between the atoms, which in turn increases the strength of the bond.

(2) Molecular orbital theory successfully explains the magnetic behaviour of molecules. In molecular orbitals, if a molecule contains one or more electron pair, then it is paramagnetic and if it contains no electron, then it is diamagnetic.

Comparison between bonding and anti-bonding molecular orbitals

Sr. No	Bonding Molecular Orbitals	Anti-bonding Molecular Orbitals
(1)	They are formed by in-phase combination of atomic orbitals.	They are formed by out-of-phase combination of atomic orbitals.
(2)	They are formed by the additive effect of atomic orbitals.	They are formed by the subtractive effect of the atomic orbitals.
(3)	They are formed when the lobes of the combining orbitals have the same sign.	They are formed when the lobes of the combining orbitals have opposite sign.
(4)	They take part in the formation of a chemical bond as they contain electrons inside the region between two atomic nuclei.	They do not take part in the formation of a chemical bond as they contain electrons outside the region between two atomic nuclei.
(5)	They contribute to the shape of the molecule.	They do not contribute to the shape of the molecule.
(6)	The geometry of a molecule is represented by the spatial arrangement of bonding molecular orbitals.	They are not involved in the representation of the geometry of the molecule.
(7)	The electron density in bonding molecular orbitals is higher.	The electron density in anti-bonding molecular orbitals is low.
(8)	The energy of bonding molecular orbitals is lower than both anti-bonding molecular orbitals and parent atomic orbitals.	The energy of anti-bonding molecular orbitals is comparatively higher than both bonding molecular orbitals and parent atomic orbitals.
(9)	The addition of electrons to bonding molecular orbitals results in stabilization of the molecule.	The addition of electrons to anti-bonding molecular orbitals results in destabilization of the molecule.
(10)	Bonding molecular orbitals are more stable than both anti-bonding molecular orbitals and parent atomic orbitals.	Anti-bonding molecular orbitals are less stable than both bonding molecular orbitals and parent atomic orbitals.

Drawbacks of molecular orbital theory

(1) Molecular orbital theory is successful in explaining bonding for simple homonuclear and heteronuclear diatomic molecules such as dihydrogen, dioxygen and carbon monoxide but it becomes more complex when discussing even comparatively simple polyatomic molecules such as methane.

(2) Molecular theory explains whether a molecule will exist or not on the basis of bond order.

(3) Concept of bond order is not feasible and appropriate to explai existence of polyatomic molecules.

(4) It does not give any idea about molecular geometry and shape o molecule.

1.3.2 Building Molecular Orbital Diagrams for Homonuclear and Heteronuclear Diatomic Molecules

By following the steps below, molecular orbital diagram for a molecule can be constructed.

Step 1 : Writing electronic configuration. Find number of valence electrons taking part in molecular orbital formation.

Step 2 : Number of atomic orbitals should be equivalent to number of molecular orbitals. Formed molecular orbitals will have equal numbers of bonding and anti-bonding orbital i.e. if two molecular orbitals are formed; one is bonding and other is anti-bonding. Bonding molecular orbital is placed lower compared to anti-bonding molecular orbital in the diagram.

Step 3 : Check whether the molecule is homonuclear or heteronuclear. Accordingly, for homonuclear molecule, the atomic orbitals will be symmetric and for heteronuclear molecule atomic orbitals will be slightly different because the more electronegative atom will be placed lower on the diagram. This is due to lone pairs of electrons being more stable on more electronegative elements leading them to be lower in energy. For e.g. in HCl, Cl will be placed lower in the molecular orbital diagram than H.

Step 4 : Fill molecular orbital with electrons as per Aufbau's principle, Pauli's exclusion principle and Hund's rule.

Step 5 : Using diagram, predict properties of a molecule like bond order, magnetism, etc.

Bond order can be calculated by the formula,

$$\frac{1}{2}\left[\begin{array}{l}\text{Electrons in bonding}\\ \text{molecular orbital}\end{array} - \begin{array}{l}\text{Electrons in anti-bonding}\\ \text{molecular orbital}\end{array}\right]$$

Bond order is half the difference between the number of electrons occupying bonding and anti-bonding orbitals in a molecule. A bond order of unity corresponds to a conventional "single bond".

1.3.2.1 Why Beryllium Molecule (Be_2) is not Formed?

Step 1 : $Be^4 = 1s^2 2s^2$ (2 valence electrons from both Be atoms will be used)

Step 2 : 1 atomic orbital from each Be overlaps, hence 2 molecular orbitals are formed, one is bonding and other is anti-bonding.

Step 3 : Homonuclear molecule with each atomic orbital of Be will be equivalent in energy hence symmetrical diagram will be obtained.

Step 4 : Filling one electron from each Be atomic orbital into molecular orbital.

Step 5 : Magnetic property cannot be predicted.

If Be_2 molecule is formed, it will have eight electrons. According to molecular orbital theory, the 1*s* and 2*s* orbitals of one beryllium atom will overlap with the corresponding orbitals of other beryllium atom to form molecular orbitals. In each case, two molecular orbitals are formed, of which one is bonding and other is anti-bonding. Thus, two atomic orbitals of each atom form two molecular orbitals. Since each atom contributes four electrons, eight electrons will be distributed in the molecular orbitals.

The overlap of the 1*s* atomic orbitals of the two beryllium atoms to produce molecular orbitals ($\sigma 1s$, $\sigma^* 1s$) does not contribute to bond formation. Thus, they remain effectively non-bonding orbitals. Therefore, according to Aufbau's principle, out of eight electrons in a beryllium molecule, four electrons occupy $\sigma 1s$ and $\sigma^* 1s$ non-bonding molecular orbitals.

The valence shell of beryllium atom includes 2*s* orbital. The overlap of 2*s* atomic orbitals of the two beryllium atom produces molecular orbitals ($\sigma 2s$, $\sigma^* 2s$), which accommodate the remaining four electrons. As bonding ($\sigma 2s$) as well as anti-bonding ($\sigma^* 2s$) molecular orbitals contain two electrons each, these anti-bonding molecular orbitals also do not contribute in the bonding.

Molecular orbital diagram

Since beryllium molecule is a homodiatomic molecule, atomic orbitals of the two beryllium atoms are at the same energy levels (Fig. 1.14).

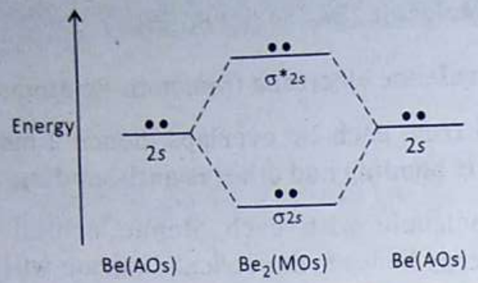


Fig. 1.14 : Molecular orbital diagram for Be_2 molecule

Molecular orbital electronic configuration can be represented as,

$$KK < \sigma 2s^2 < \sigma^* 2s^2$$

Bond order can be calculated as follows,

Electrons present in bonding molecular orbitals = 2

Electrons present in anti-bonding molecular orbitals = 2

Bond order = ½ (2 – 2) = 0

As bond order is zero, no bond can be formed between two beryllium atoms. Thus, Be_2 molecule formation is not possible. Since Be_2 does not exist magnetic property cannot be predicted.

1.3.2.2 O_2 Molecule

Step 1 : $O^8 = 1s^2\, 2s^2\, 2p_x^{\ 2}\, 2p_y^{\ 1}\, 2p_z^{\ 1}$ (6 valence electrons from both O atoms wil be used)

Step 2 : 4 atomic orbitals from each O atom overlaps, one is bonding and other is anti-bonding, hence 8 molecular orbitals are formed .

Step 3 : Homonuclear molecule with each atomic orbital of O atom will be equivalent in energy hence symmetrical diagram will be obtained.

Step 4 : Filling one electron from each O atomic orbital into molecular orbital.

Step 5 : All the spins are paired in O_2 molecule; it is diamagnetic in nature.

Atomic number of oxygen is 8. Electronic configuration is $1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}$ $2p_z^{\ 1}$. Thus, the oxygen molecule has sixteen electrons. According to molecular orbital theory, the 1*s*, 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals of one oxygen atom overlap with the corresponding orbitals of other oxygen atom to form molecular orbitals. In each case, two molecular orbitals are formed, of which one is bonding and other is anti-bonding. Thus, two atomic orbitals of each atom form two molecular orbitals. Since each atom contributes eight electrons, sixteen electrons are distributed in the molecular orbitals.

The valence shell of oxygen atom does not include 1s atomic orbital. Hence, the overlap of the 1s atomic orbitals of the two oxygen atoms to produce molecular orbitals (σ1s, σ*1s) does not contribute to bond formation. Thus, they remain effectively non-bonding orbitals. According to Aufbau principle, out of sixteen electrons in oxygen molecule, four electrons occupy σ1s and σ*1s non-bonding molecular orbitals.

The valence shell of oxygen atom includes 2s and 2p orbitals. The overlap of 2s atomic orbitals of the two oxygen atoms produces molecular orbitals (σ2s, σ*2s), which accommodate the next four electrons. Since bonding (σ2s) as well as anti-bonding (σ*2s) molecular orbitals contain two electrons each, they do not contribute to bonding.

In case of *p*-orbitals, the $2p_x$ orbitals of the two oxygen atoms overlap head-to-head to give $\sigma 2p_x$ and $\sigma^* 2p_x$ orbitals. The $2p_y$ and $2p_z$ orbitals of the two oxygen atoms overlap laterally to give $\pi 2p_y$, $\pi^* 2p_y$, $\pi 2p_z$ and $\pi^* 2p_z$. Out of remaining eight electrons, six electrons are accomodated in $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals according to Aufbau principle. Further, according to Pauli's exclusion principle, $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals accommodate one electron each.

Molecular orbital diagram

Since oxygen molecule is a homodiatomic molecule, atomic orbitals of the two oxygen atoms are at the same energy levels. Molecular orbital diagram is as follows (Fig. 1.15)

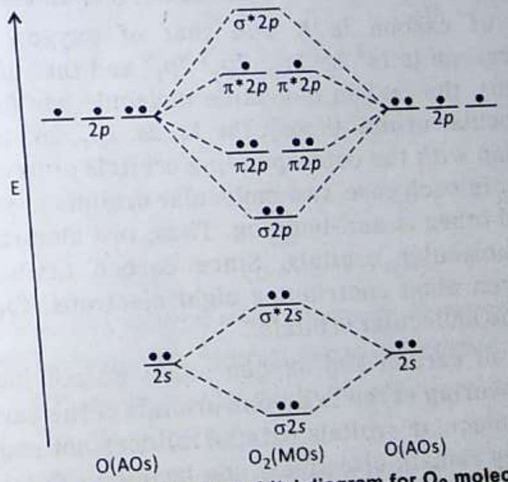


Fig. 1.15 : Molecular orbital diagram for O_2 molecule

Molecular orbital electronic configuration can be represented as,

$$KK < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^{\ 2} < \pi 2p_y^{\ 2} = \pi 2p_z^{\ 2} < \pi^* 2p_y^{\ 1} = \pi^* 2p_z^{\ 1}$$

Bond order can be calculated as follows,

Electrons present in bonding molecular orbitals = 8

Electrons present in anti-bonding molecular orbitals = 4

Bond order = ½ (8 – 4) = 2

It implies that there are two bonds between two oxygen atoms, one is σ-bond and other is π-bond.

Magnetic properties : As π^*2p_y and π^*2p_z molecular orbitals contain one electron each, oxygen molecule is paramagnetic in nature.

1.3.2.3 CO Molecule

Step 1 : $C^6 = 1s^2\,2s^2\,2p_x{}^1\,2p_y{}^1\,2p_z{}^0$ (4 valence electrons)

$O^8 = 1s^2\,2s^2\,2p_x{}^2\,2p_y{}^1\,2p_z{}^1$ (6 valence electrons)

Step 2 : 4 atomic orbitals from each C and O overlaps, hence 8 molecular orbitals are formed.

Step 3 : Heteronuclear molecule with atomic orbital of C and O atoms will be non-equivalent in energy hence unsymmetrical diagram will be obtained.

Step 4 : Filling one electron from each C and O atomic orbital into molecular orbital.

Step 5 : All the spins are paired in CO molecule; it is diamagnetic in nature.

Atomic number of carbon is 6 and that of oxygen is 8. Electronic configuration of carbon is $1s^2\,2s^2\,2p_x{}^1\,2p_y{}^1\,2p_z{}^0$ and that of oxygen is $1s^2\,2s^2$ $2p_x{}^2\,2p_y{}^1\,2p_z{}^1$. Thus, the carbon monoxide molecule has fourteen electrons. According to molecular orbital theory, the 1s, 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of carbon atom overlap with the corresponding orbitals of oxygen atom to form molecular orbitals. In each case, two molecular orbitals are formed, of which one is bonding and other is anti-bonding. Thus, two atomic orbitals of each atom form two molecular orbitals. Since carbon atom contributes six electrons and oxygen atom contributes eight electrons, fourteen electrons are distributed in the molecular orbitals.

The valence shells of carbon and oxygen atoms do not include 1s atomic orbital. Hence, the overlap of the 1s atomic orbitals of the carbon and oxygen atoms to produce molecular orbitals (σ1s, σ*1s) does not contribute to bond formation. Thus, they remain effectively non-bonding orbitals. According to Aufbau principle, out of fourteen electrons in carbon monoxide molecule, four electrons occupy σ1s and σ*1s non-bonding molecular orbitals.

The valence shell of carbon and oxygen atoms includes 2s and 2p orbitals. The overlap of 2s atomic orbitals of carbon and oxygen atoms produces molecular orbitals (σ2s, σ*2s), which accommodate the next four electrons. As bonding (σ2s) as well as anti-bonding (σ*2s) molecular orbitals contain two electrons each, they do not contribute to bonding.

In case of p-orbitals, the $2p_x$ orbitals of carbon and oxygen atoms overlap head-to-head to give $\sigma 2p_x$, and σ^*2p_x orbitals. The $2p_y$ and $2p_z$ orbitals of carbon and oxygen atoms overlap laterally to give $\pi 2p_y$, π^*2p_y, $\pi 2p_z$ and π^*2p_z. The remaining six electrons are accomodated in $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals.

Molecular orbital diagram

Since carbon monoxide molecule is a heterodiatomic molecule, atomic orbitals of carbon and oxygen atoms are at different energy levels. Amongst the two atoms, oxygen atom is more electronegative than carbon atom, hence atomic orbitals of oxygen atoms are at lower energy levels than the corresponding atomic orbitals of carbon atoms. Molecular orbital diagram is as follows (Fig. 1.16)

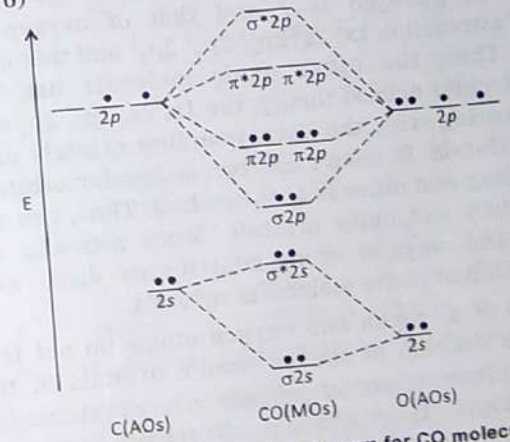


Fig. 1.16 : Molecular orbital diagram for CO molecule

Molecular orbital electronic configuration can be represented as,

$$KK < \sigma 2s^2 < \sigma^*2s^2 < \sigma 2p_x{}^2 < \pi 2p_y{}^2 = \pi 2p_z{}^2$$

Bond order can be calculated as follows,

Electrons present in bonding molecular orbitals = 8

Electrons present in anti-bonding molecular orbitals = 2

Bond order = ½ (8 – 2) = 3

It implies that there are three bonds between carbon and oxygen atoms, on is σ-bond and other two are π-bonds.

Magnetic properties : As $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ molecular orbitals contai paired electrons, carbon monoxide molecule is diamagnetic in nature.

1.3.2.4 NO Molecule

Step 1 : $N^7 = 1s^2\,2s^2\,2p_x^{\ 1}\,2p_y^{\ 1}\,2p_z^{\ 1}$ (5 valence electrons)
$O^8 = 1s^2\,2s^2\,2p_x^{\ 2}\,2p_y^{\ 1}\,2p_z^{\ 1}$ (6 valence electrons)

Step 2 : 4 atomic orbitals from each N and O atoms overlap, hence molecular orbitals are formed.

Step 3 : Heteronuclear molecule with atomic orbital of N and O will be non equivalent in energy hence unsymmetrical diagram will be obtained

Step 4 : Filling one electron from each N and O atomic orbital into molecular orbital.

Step 5 : 1 spin is unpaired in NO molecule; it is paramagnetic in nature.

Atomic number of nitrogen is 7 and that of oxygen is 8. Electronic configuration of nitrogen is $1s^2\,2s^2\,2p_x^{\ 1}\,2p_y^{\ 1}\,2p_z^{\ 1}$ and that of oxygen is $1s^2\,2s^2$ $2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$. Thus, the nitric oxide molecule has fifteen electrons. According to molecular orbital theory, the 1*s*, 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals of nitrogen atom overlap with the corresponding orbitals of oxygen atom to form molecular orbitals. In each case, two molecular orbitals are formed, of which one is bonding and other is anti-bonding. Thus, two atomic orbitals of each atom form two molecular orbitals. Since nitrogen atom contributes seven electrons and oxygen atom contributes eight electrons, fifteen electrons are distributed in the molecular orbitals.

The valence shells of nitrogen and oxygen atoms do not include 1s atomic orbital. Hence, the overlap of the 1*s* atomic orbitals of the nitrogen and oxygen atoms to produce molecular orbitals (σ1*s*, σ*1*s*) does not contribute to bond formation. Thus, they remain effectively non-bonding orbitals. According to Aufbau principle, out of fifteen electrons in nitric oxide molecule, four electrons occupy σ1*s* and σ*1*s* non-bonding molecular orbitals.

The valence shell of nitrogen and oxygen atoms includes 2*s* and 2*p* orbitals. The overlap of 2*s* atomic orbitals of nitrogen and oxygen atoms produces molecular orbitals (σ2*s*, σ*2*s*), which accommodate the next four electrons. As bonding (σ2*s*) as well as anti-bonding (σ*2*s*) molecular orbitals contain two electrons each, they do not contribute to bonding.

In case of *p*-orbitals, the $2p_x$ orbitals of nitrogen and oxygen atoms overlap head-to-head to give $\sigma 2p_x$, and $\sigma^* 2p_x$ orbitals. The $2p_y$ and $2p_z$ orbitals of nitrogen and oxygen atoms overlap laterally to give $\pi 2p_y$, $\pi^* 2p_y$, $\pi 2p_z$ and $\pi^* 2p_z$. Out of remaining seven electrons, six electrons are accomodated in $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals according to Aufbau principle. Further, according to Pauli's exclusion principle, $\pi^* 2p_y$ orbital accommodates one electron.

Molecular orbital diagram

Since nitric oxide molecule is a heterodiatomic molecule, atomic orbitals of nitrogen and oxygen atoms are at different energy levels. Amongst the two atoms, oxygen atom is more electronegative than nitrogen atom, hence atomic orbitals of oxygen atoms are at lower energy levels than the corresponding atomic orbitals of nitrogen atoms. Molecular orbital diagram is as follows (Fig. 1.17)

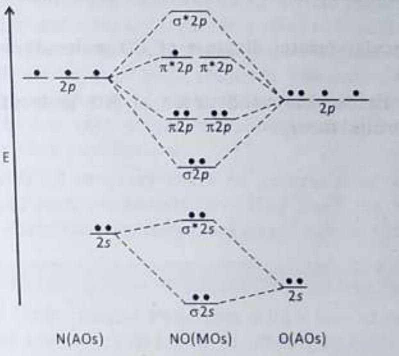


Fig. 1.17 : Molecular orbital diagram for NO molecule

Molecular orbital electronic configuration can be represented as,

$$KK < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_x^{\ 2} < \pi 2p_y^{\ 2} = \pi 2p_z^{\ 2} < \pi^* 2p_y^{\ 1}$$

Bond order can be calculated as follows,

Electrons present in bonding molecular orbitals = 8

Electrons present in anti-bonding molecular orbitals = 3

Bond order = ½ (8 – 3) = 2.5

Experimentally it is found that NO has bond order in between double and triple bond hence calculated bond order is justified. Rounding 2.5 to the nearest whole number gives 3, 1 σ-bond and 2 π-bond formation. NO easil forms NO^+ ion by losing 1 electron and it is isoelectronic to N_2 forming tripl bond. NO molecule exists in canonical forms due to presence of an unpaire electron.

Magnetic properties : As π^*2p_y molecular orbital contains one electron nitric oxide molecule is paramagnetic in nature.

1.4 Review Questions

(1) Give postulates of molecular orbital theory.

(2) Explain usefulness and disadvantages of molecular orbital theory.

(3) Compare bonding and anti-bonding orbitals.

(4) Explain why Be_2 molecule has bond order zero.

(5) Discuss diamagnetism of O_2 molecule on the basis of molecular orbita theory.

(6) Draw molecular orbital diagram of CO molecule and comment on it bond order.

(7) State and discuss the bond order of NO molecule on the basis o molecular orbital theory.

* * *

CHAPTER 2

AROMATIC SYSTEMS AND THEIR MOLECULAR STRUCTURE

2.1 Introduction

The earliest use of the term aromatic was in an article by August Wilhelm Hofmann in 1855. Hofmann used the term for a class of benzene compounds, many of which have odours (aromas), unlike pure saturated hydrocarbons. Remember the smell of a paint or paint thinners. The strong smell of these products is due to the presence of an aromatic compound called toluene. Similarly, moth balls are very strong smelling because they contain an aromatic compound called *naphthalene*.

Aromaticity as a chemical property bears no general relationship with the olfactory properties of such compounds (how they smell) i.e. there are some compounds that are chemically aromatic, but do not have a distinct smell.

2.2 Aromaticity

It is the property of cyclic, planar structures with a ring of resonance bonds that gives increased stability compared to other geometric or connective arrangements with the same set of atoms.

According to James Dewar, aromatic system is a cyclic compound with a large resonance energy, where all the annular atoms take part to form a single conjugate system.

2.3 Huckel's Rule

For a cyclic system to be aromatic, it should contain $(4n + 2)$ π electrons where n is an integer i.e. $n = 0, 1, 2, 3$.

Molecules having 2, 6, 10, 14, 18, 22....... π electrons satisfy the $(4n + 2)$ rule and are therefore aromatic.

2.3.1 Criteria for Aromaticity

A compound is said to be aromatic if it fulfils the following criteria,

(1) The molecule must be cyclic with conjugated π bonds.

(2) Each atom in the ring must have an unhybridized *p*-orbital.

(3) The unhybridized *p*-orbitals must overlap to form a continuous ring o parallel orbitals. The structure must be planar or nearly planar fo effective overlap.

(4) It should obey Huckel's rule.

If any of these conditions are violated, no aromaticity is possible. Some examples are discussed below,

(1) Ethylene ($H_2C{=}CH_2$) obeys Huckel's rule as it contains 2 π electrons Since it is not a cyclic molecule, it is not aromatic.

(2) Cyclopentadiene is non-aromatic since there is no delocalization of electrons due to presence of one sp^3 hybridized carbon atom. Also, it does not obey Huckel's rule as it contains 4 π electrons. However, if a proton is removed from that sp^3 hybridized carbon atom to form cyclopentadienyl anion, the carbon becomes sp^2 hybridized with an unhybridized *p*-orbital. The delocalization of electrons takes place in cyclopentadienyl anion. Secondly, owing to 6 π electrons, it obeys Huckel's rule. Hence, cyclopentadienyl anion is aromatic in nature.

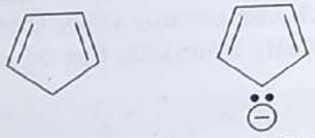


Fig. 2.1 : Cyclopentadiene-Cyclopentadienyl anion

(3) Cycloheptatriene is non-aromatic. It obeys Huckel's rule since it contains 6 π electrons. However, there is no delocalization of electrons due to presence of one sp^3 hybridized carbon atom. If a hydride anion is removed from that sp^3 hybridized carbon atom to form cycloheptatrienyl cation (tropyllium cation), the carbon becomes sp^2 hybridized with an unhybridized *p*-orbital. The delocalization of electrons takes place in cycloheptatrienyl cation. Hence, cycloheptatrienyl cation is aromatic in nature.

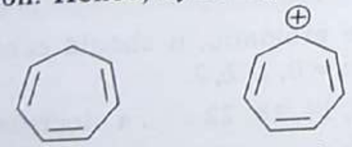


Fig. 2.2 : Cycloheptatriene-Cycloheptatrienyl cation

(4) Cyclooctatetraene is non-aromatic. It does not obey Huckel's rule since it contains 8 π electrons as well as it is non-planar.

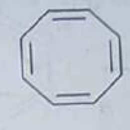


Fig. 2.3 : Cyclooctatetraene

Though unsaturated, aromatic compounds undergo substitution reactions rather than addition reactions, which is the common property of unsaturated compounds. Aromatic compounds resist addition reactions because these reactions involve breaking the delocalization and losing stability of the cyclic system.

2.4 Aromaticity of Benzene

The molecular formula of benzene is C_6H_6. The six carbon atoms are sp^2 hybridized. Each sp^2 hybridized carbon atom forms σ bonds with two carbon atoms and one hydrogen atom. The six remaining electrons (from each carbon atom) are in unhybridized *p*-orbitals. Two neighbouring unhybridized *p*-orbitals each contain one electron overlap above and below the plane of the ring (Fig. 2.4). The planarity of the ring allows maximum overlap of these *p*-orbitals.

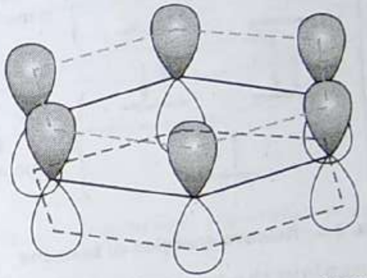


Fig. 2.4 : Overlapping of *p*-orbitals of benzene

Since these *p*-orbitals are out of the plane of the atoms, these orbitals can interact with each other freely and become delocalized. Thus, instead of being localized to one carbon atom, each electron is shared by all six carbon atoms in the ring. Thus, the π electrons strengthen all of the bonds on the ring equally (Fig. 2.5). It can be said that, each carbon is joined to each of its neighbours by a one-and-half bond.

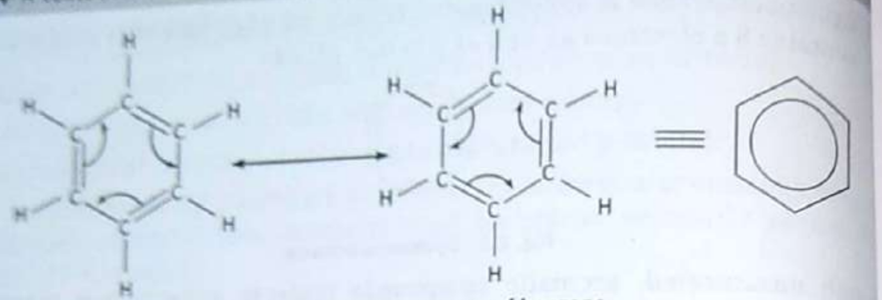


Fig. 2.5 : Resonating structures of benzene

Six delocalized π orbitals are formed of which three are bonding with lowe energy and three are anti-bonding with higher energy. Six electrons ar present in bonding molecular orbitals (Fig. 2.6).

The six carbon atoms form a perfectly regular hexagon where six carbo atoms are 1.397 A° apart from each other. Six hydrogen atoms associated wit each carbon atom and directed outside the ring are at a distance 1.09 A°. A H-C-C and C-C-C bond angles are 120°. Bonds are conjugated, therefor electrons are delocalized above and below the plane of the ring makin benzene stable. The resonance energy of benzene is 36 kcal/mole.

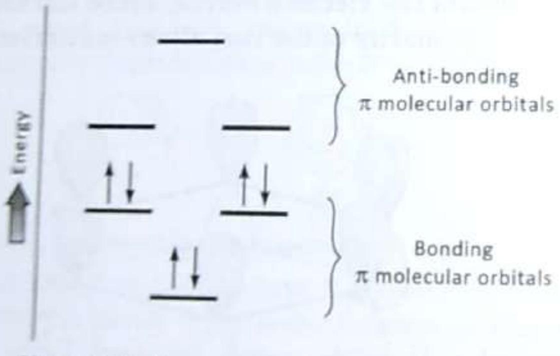


Fig. 2.6 : Relative energies of benzene

The following evidences explain the aromatic character of benzene,

(1) The compound is cyclic with conjugated π bonds.

(2) Each carbon atom is sp^2 hybridized with an unhybridized *p*-orbital containing one electron each. Thus, it obeys Huckel's rule.

(3) It is a planar molecule with delocalization of π electrons.

(4) It exhibits resonance with high resonance energy.

(5) It is resistant to oxidation with reagents like $KMnO_4$ and Br_2 in CCl_4.

(6) It undergoes electrophilic substitution like halogenation, nitration, sulphonation, Friedal-Crafts alkylation and acylation to form the following products,

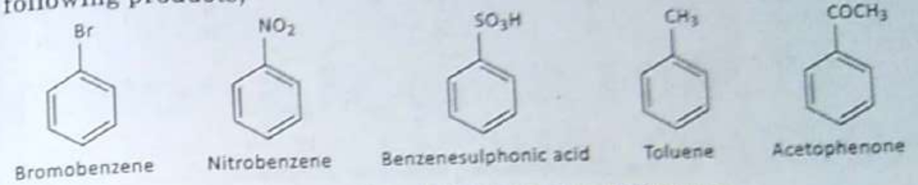


Fig. 2.7 : Electrophilic substitution products of benzene

2.5 Aromaticity of Pyrrole

The molecular formula of pyrrole is C_4H_5N. The four carbon atoms and nitrogen are sp^2 hybridized. Two sp^2 hybridized carbon atoms form σ bonds with two carbon atoms and one hydrogen atom each. The other two sp^2 hybridized carbon atoms form σ bonds with a neighbouring carbon atom, one hydrogen atom and the nitrogen atom. Each carbon atom contains an unhybridized *p*-orbital with one electron each. Four electrons are contributed by the carbon atoms of the ring and two electrons are contributed by the sp^2 hybridized nitrogen to make an aromatic sextet (Fig. 2.8).

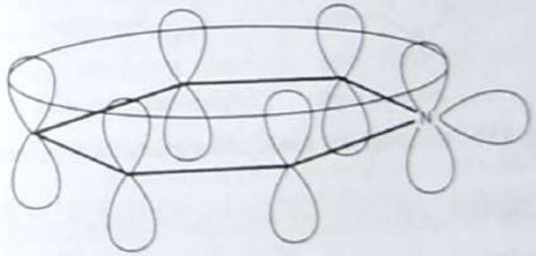


Fig. 2.8 : Overlapping of *p*-orbitals of pyrrole

Pyrrole exhibits resonance (Fig. 2.9), which results in producing negative charges on carbons and positive charge on nitrogen. In pyrrole, both inductive and mesomeric effects are present, but they are opposing each other. However, mesomeric effect predominates.

In pyrrole, the N-C2 and N-C5 bond lengths are 1.38 A°; C2–C3, C4–C5 bond lengths are 1.37 A° and C3–C4 bond length is 1.43 A°. The resonance energy of pyrrole is 22 kcal/mole.

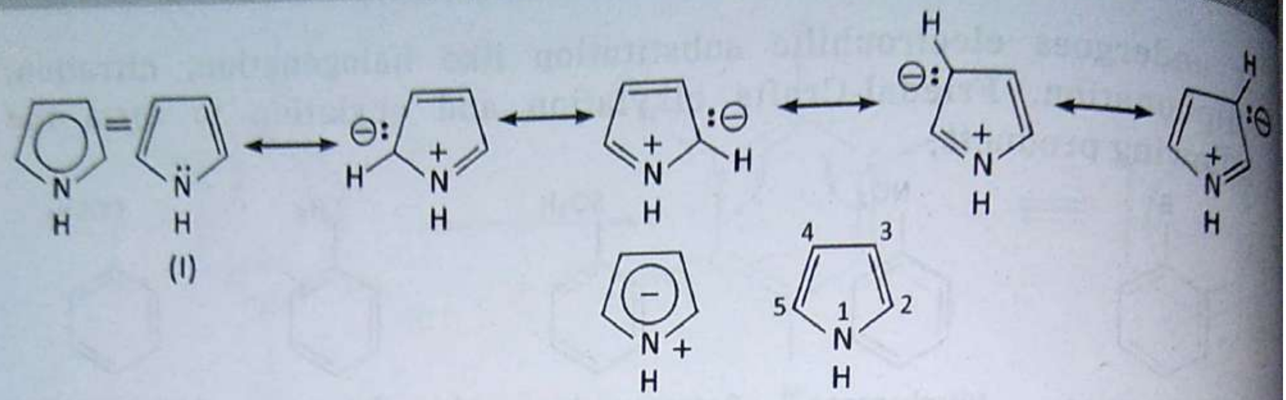


Fig. 2.9 : Resonating structures of pyrrole

The following evidences explain the aromatic character of pyrrole,

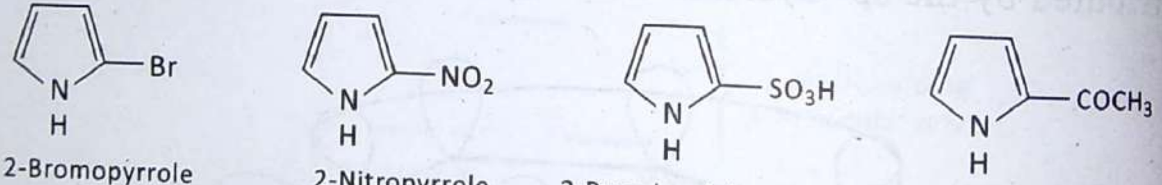
(1) The compound is cyclic.

(2) Each carbon atom is sp^2 hybridized with an unhybridized *p*-orbital containing one electron each. Nitrogen provides unshared pair o electrons to complete the sextet. Thus, it obeys Huckel's rule.

(3) It is a planar molecule with delocalization of π electrons.

(4) It exhibits resonance with high resonance energy.

(5) It undergoes electrophilic substitution like halogenation, nitration, sulphonation and Friedal-Crafts acylation to form the following products,



2-Bromopyrrole 2-Nitropyrrole 2-Pyrrolesulphonic acid 2-Acetylpyrrole

Fig. 2.10 : Electrophilic substitution products of pyrrole

2.6 Review Questions

(1) Define aromaticity.

(2) State Huckel's rule.

(3) Cycloheptatriene is non-aromatic. Explain.

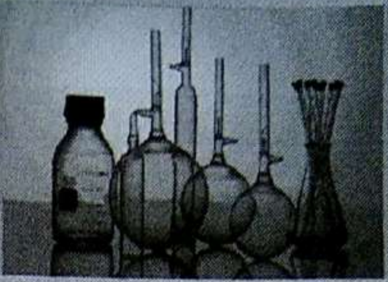
(4) State and explain, whether cyclopentadiene is aromatic or not.

(5) Explain the aromaticity of benzene.

(6) Comment on the aromatic character of pyrrole.

❖❖❖

CHAPTER 3



INTERMOLECULAR FORCES AND CRITICAL PHENOMENON

3.1 Introduction

A chemical bond represents a strong force of attraction between two atoms. According to the Lewis octet rule, atoms of all elements have a tendency to acquire an electronic configuration similar to that of inert gases because it represents the most stable electronic configuration. All atoms having an unstable or incomplete outer shell have a propensity to gain or lose electrons so as to acquire an electronic configuration of the nearest inert gas in the periodic table. It is this tendency of atoms to complete and hence stabilize their outermost orbit of electrons, which is mainly responsible for chemical combination between the atoms.

The requirement of electron pairing are mainly accomplished by the following modes,

(1) By complete transfer of one or more electrons from one atom to another which results in the formation of ions and hence is called ionic bonding.

(2) By sharing of electrons between the two combining atoms, which results in the formation of a covalent bond.

(3) A special type of covalent linkage in which both the shared electrons are contributed by one atom only and not one by each atom as in the case of proper covalent linkage.

3.2 Ionic or Electrovalent Bond

This type of bond is formed by the transference of electrons from one atom to another. Essentially an atom that loses one or more of its electron, and a one that can accept them is required. The metals in group I and group II in the periodic table have the greatest tendency to lose electrons and turn into positive ions. The non-metals of groups VI and VII have the greatest affinity for electrons and readily change into negative ions. The atom which loses electrons acquires positive charge and contracts, while the atom which gains electrons acquires negative charge and increases in size. The cation and anion thus produced are held together by electrostatic lines of force and hence the linkage is called *electrovalent bond* and the compound so produced is called *electrovalent compound*. These are also called polar compounds since their molecule acquires polarity due to the formation of ions by electron transfer. Example: KCl molecule (Fig. 3.1).

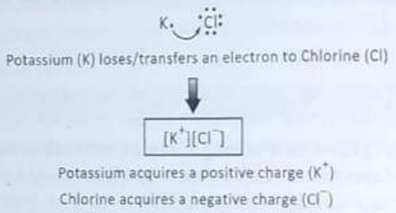


Fig. 3.1 : Formation of ionic bond

3.2.1 Characteristics of Ionic Compounds

The characteristics of ionic compounds are as given below,

(1) They consist of oppositely charged ions held together by electrostatic forces of attraction.

(2) They are generally soluble in water and insoluble in organic solvents.

(3) Due to the powerful electrostatic force between the ions in the crystals, considerable amount of energy is required to separate the molecules from each other. Hence they have high melting and boiling points.

(4) When dissolved in water or in the molten state, they conduct electricity because then the binding forces in the crystal lattice are weakened.

(5) They are crystalline compound.

3.3 Covalent Bond

This type of bond is formed by sharing of one or more electron pairs between the atoms thus, achieving stability by attaining octet or duplet in their outermost shell. The electrons for pair formation are contributed equally by the two participating atoms and become their common property. The covalent linkage can connect similar atoms when both of them are short of a few electrons to achieve their nearest inert gas configuration. Since there is no transference of electrons and ions are not formed, the covalent linkage is also called *non-ionised linkage*. Example: HCl molecule (Fig. 3.2).

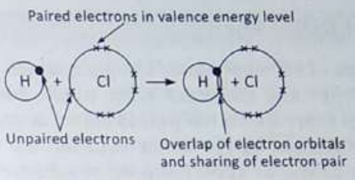


Fig. 3.2 : Formation of covalent bond

3.3.1 Polar and Non-polar Character

Depending upon whether the electron pairs are shared equally or unequally between the bonding atoms, a covalent bond may be non-polar or polar. In homodiatomic molecules like H_2 and Cl_2, the sharing of electron pair is equal between the two atoms and such a bond is called as a non-polar covalent bond. But in heteroatomic molecules like HF or HCl the sharing of electron pair is unequal because, one of the two atoms is likely to attract the electrons more strongly than the other. The atom that attracts the electrons more strongly develops some negative charge; and the other atom develops some positive charge. These fractional charges are designated as δ^+ and δ^-. In HCl, Cl atom is more electron attracting than H atom and hence HCl can be depicted as $H^{\delta+} - Cl^{\delta-}$. Such covalent bonds are said to be polar and the bond is said to have partial ionic character.

3.3.2 Characteristics of Covalent Compounds

The characteristics of covalent compounds are as given below,

(1) The atoms in a covalent molecule are firmly held together by the shared pair of electrons and hence covalent compounds do not dissociate or conduct electricity when put in water or melted.

(2) Covalent compounds are generally insoluble in water and soluble in organic solvents.

(3) A covalent molecule is non-polar and hence do not have external field of force. Due to this they have low melting and boiling points.

(4) Normal covalent compounds are liquids or gases at room temperature. However, covalent compounds with high molecular weights exist as solids.

(5) Covalent compounds in solution react slowly as compared to io compounds.

3.4 Coordinate or Dative Bond

This is a special type of covalent bond. The atom which donates the electr pair is called as *donor* and the other atom which does not contribute electron towards the shared electron pair is called *acceptor*. The pair of t valency electrons possessed by the donor is called the *lone pair*. The bo formed as above is called as *coordinate* or *coordinate covalent* or *dati bond*. Further, since such a bond always renders the molecule polar, it is al called *semi-polar bond*. Compounds containing one or more of su coordinate bonds in their molecules are termed coordination compounds. coordinate bond is usually represented by an arrow pointing from the don to the acceptor atom (Fig. 3.3).

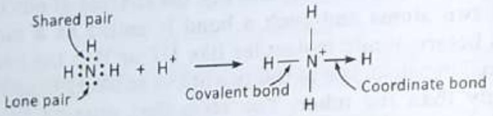


Fig. 3.3 : Representation of coordinate bond

3.4.1 Characteristics of Coordinate Compounds

The characteristics of coordinate compounds are as given below,

(1) The coordinate bond is rigid and directional and hence provid opportunity for exhibiting stereoisomerism of molecules.

(2) These compounds are generally insoluble in water and soluble in organ solvents.

(3) These compounds have relatively higher melting and boiling points tha those of covalent compounds and lower than those of electrovaler compounds.

(4) The coordinate linkage being partly covalent in nature, the atoms ar firmly held by electrons and hence these compounds do not dissociat when placed in water or melted.

(5) The coordinate compounds are stable like covalent compounds.

3.5 Van der Waals Force

Van der Waals force is a general term used to define attraction of intermolecular forces between the molecules. These forces are distance dependent between the atoms or molecules. It is important to remember that van der Waals forces are forces that exist between molecules of the same substance. They are quite different from the forces that make up the molecule. For example, a water molecule is made up of hydrogen and oxygen, which are bonded together by covalent bond. The van der Waals forces are the forces that exist between the millions of separate water molecules, and not between the hydrogen and oxygen atoms in the case of water.

There are three types of vander Waals forces viz.

(1) Weak- London dispersion forces

(2) Strong- Dipole-dipole forces

(3) Weak- Hydrogen bonding forces

3.5.1 London Dispersion Forces

London dispersion forces are type of van der Waals forces. They exist between non-polar molecules. For example, chlorine gas is made up of two chlorine atoms. In this bond, the electrons are equally shared and are not dominant on one side of the molecule as is the case in HCl. The atom looks like this Cl - Cl, no overall charge on either side but, within a bond, electrons are constantly MOVING. They zoom around the atoms really quickly. As a result, there may be a tiny instant in time where the electrons happen to be dominant on one side, creating a situation like, $Cl^{+} - Cl^{-}$. However, this temporary charge disappears as quickly as it appeared because the electrons are moving fast. These temporary dipoles allow the temporarily negative side of one molecule to attract the temporarily positive side of another molecule, which is the intermolecular force.

$$Cl^{+} - Cl^{-} \;.....\; Cl^{+} - Cl^{-} \;.....\; Cl^{+} - Cl^{-}$$

3.5.2 Dipole-dipole Forces

Dipole-dipole forces occur in polar molecules, that is, molecules that have an unequal sharing of electrons. For example, HCl comprising of hydrogen and chlorine is polar molecule. The chlorine atom has an extra electron, donated by the hydrogen atom. Because of this, the chlorine part of the molecule is negatively charged, and the hydrogen side of the molecule is positively charged i.e. $H^{+} - Cl^{-}$. Hence in an aqueous HCl, there are thousands of these molecules around that are slightly charged on each side, the molecules naturally orient themselves as shown below,

$$H^+ : Cl^- \ldots\ldots H^+ : Cl^- \ldots\ldots H^+ : Cl^-$$

The positive part of one molecule will move until it is next to the negative part of a neighbouring molecule. These forces between molecules tend to make them 'stick' together.

3.5.3 Hydrogen Bonding Forces

A hydrogen bond is a dipole-dipole interaction that occurs between any molecule with a bond between a hydrogen atom and any atom of oxygen/fluorine/nitrogen. So, hydrogen fluoride (HF), water (H_2O), ammonia (NH_3) and any other molecule that has a hydrogen bonded to either an oxygen, fluorine or nitrogen atom, exhibits hydrogen bonding [Fig. 3.4(a)].

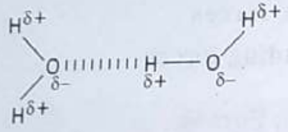


Fig. 3.4 (a) : Hydrogen bonding in H_2O

The hydrogen bond is just a dipole-dipole force but it is extremely strong compared to other dipole-dipole forces like in HCl. It is extremely strong because F, N and O are highly electronegative and H is highly electropositive. So basically, the bond is EXTREMELY a one-sided affair, resulting in an extreme dipole situation, thus named, a hydrogen bond. The extremely positive side of the molecule will orient itself with the extremely negative side of another molecule [Fig. 3.4(b)].

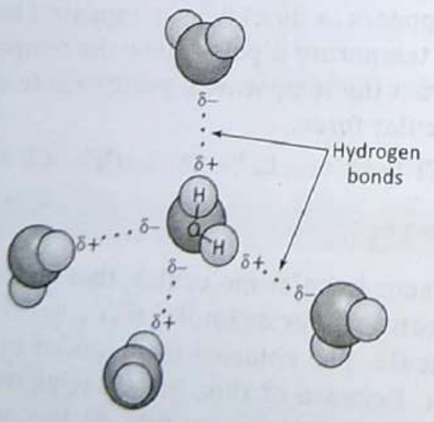


Fig. 3.4 (b) : Hydrogen bonding in H_2O

Types of hydrogen bonding

There are two types of H-bonds, and it is classified as following,

(1) Intermolecular hydrogen bonding : This type of bond formation occurs between the different molecules of same or different compounds. For example : p-nitrophenol. (Fig. 3.5)

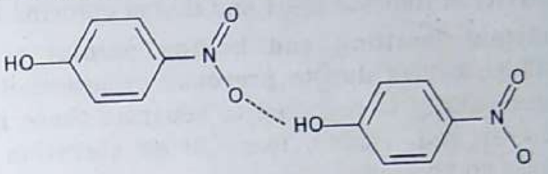


Fig. 3.5 : p-nitrophenol

(2) Intramolecular hydrogen bonding : This type of bond formation occurs when the hydrogen atom lies in between the two electronegative elements present in the same molecule.

For example : o-nitrophenol (Fig. 3.6)

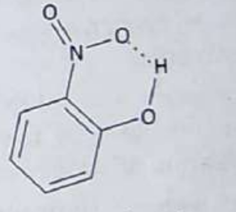


Fig. 3.6 : o-nitrophenol

The consequences of hydrogen bonding on the physical properties of compounds are discussed below.

(1) Physical state : Due to existence of intermolecular hydrogen bonding, molecules of a substance are present as associated or grouped molecules. This results in an increase in the size and the molecular mass of the compound, affecting the physical state of the substance.

Example : At ordinary temperature, H_2O is a liquid whereas H_2S is a gas. The difference in the physical state of two compounds can be explained on the basis of hydrogen bonding.

The electronegativity of hydrogen, oxygen and sulphur are 2.1, 3.5 and 2.5 respectively. Since the difference in the electronegativity of hydrogen and oxygen is remarkable, H_2O molecule exhibits intermolecular hydrogen bonding, resulting in molecular association. Hence, H_2O exists as a liquid at ordinary temperature. Since the difference in t electronegativity of hydrogen and sulphur is less, there is negligib hydrogen bonding in H_2S molecule. Hence, H_2S exists as a gas ordinary temperature. Similar explanation can be given for the existen of HF as a liquid and HCl as a gas under similar condition (Electronegativity of fluorine is 4.1 and that of chlorine is 3.2).

(2) **Physical constant (melting and boiling points) :** Because of th association of molecules due to presence of intermolecular hydroge bonding, larger energy is required to separate these molecules befo they can melt or boil. Hence, there is an elevation in the physic constant of these compounds.

Example : p-nitrophenol has higher boiling point than o-nitrophenol. I p-nitrophenol, molecular association takes place due to intermolecula hydrogen bonding between the molecules. In o-nitrophenol, intra molecular hydrogen bonding takes place.

(3) **Solubility :** The compounds which can form a hydrogen bond with wate readily dissolve in water whereas covalent compounds do not generall dissolve in water. Thus, hydrogen bonding influences the solubility o compounds in specific solvents.

Example : Alcohols, ammonia are soluble or miscible in water due t formation of hydrogen bond between the electronegative atom in thes molecules with hydrogen atom of water molecules.

(4) **Anomalous behaviour of water :** Hydrogen bonding very well explain the anomalous behaviour of water, namely floating of ice over water an higher density of ice than water.

(a) **Floating of ice over water :** The density of the solid form of compound is generally greater than its liquid form and the density o liquids decreases on heating. However, in case of water, the densit of ice is less than that of water because of which ice always float over water and the density of water increases from 0 °C, reaches maximum at 4 °C and then decreases.

The reason is that due to intermolecular hydrogen bonding, th molecules of water are associated in groups (Fig. 3.7).

In the solid state, the tetrahedral arrangement of H_2O molecule extends in three dimensions. Also, the packing of H_2O molecules i not very close as hydrogen bond length (1.76 Å) is longer tha covalent bond (1.00 Å) between oxygen and hydrogen.

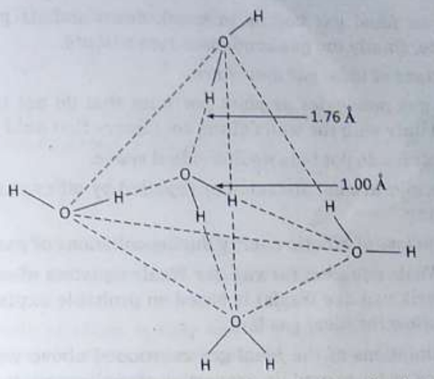


Fig. 3.7 : Tetrahedral arrangement of associated water molecules in ice

Hence, in the open-cage-like crystal structure of ice, vacant space exists, that results in a larger volume for the given mass of water in the solid state i.e. ice. Accordingly, the density of ice is less than water.

(b) **Higher density of ice than water :** With increase in temperature, when ice melts, the open-cage-like crystal structure collapses due to partial breaking of the hydrogen bonds. The H_2O molecules come closer and also fill the vacant spaces in the open-cage structure. This results in decrease in volume. Hence, the density increases on heating above the melting point of ice and becomes maximum at 4 °C.

3.6 Equations of State of Real Gases and Critical Phenomena

The ideal gas law, also known as the general gas equation, is the equation of state of a hypothetical ideal gas. It describes the behaviour of a gaseous state of a chemical substance under ordinary environmental conditions, around 1 atm pressure and a temperature of 300 K. The equation is given as

$$PV = nRT \qquad \text{......(I)}$$

Where P, V and T are the pressure, volume and absolute temperature; n is the number of moles of gas; and R is the ideal gas constant. It is the same for all gases.

But when the temperature is reduced, or the pressure is raised, the above equation of an ideal gas begins to break down and its properties becom unpredictable; finally the gas condenses into a liquid.

The assumptions of ideal gas model are,

- It treats gas molecules as point particles that do not interact with eac other but only with the walls of the containers that hold them.
- Gas molecules do not take up individual space.
- Gas molecules are not attracted or repelled by other gas molecules in th surrounding.
- There is no loss of kinetic energy during collisions of gas molecules.

The van der Waals equation (or van der Waals equation of state; named afte Johannes Diderik van der Waals) is based on probable explanations that rea gases do not follow the ideal gas law.

The basic assumptions of the ideal gas mentioned above were discarded b van der Waals in order to explain properties of real gas such as,

- Gas molecules occupy space.
- There exists interaction between neighbouring gas molecules.
- A gas condenses to a liquid at sufficiently high pressures and low temperatures, as intermolecular attractions become dominant.
- A gas flowing through a pipe gets temporarily held on the pipe surfac and therefore the molecules are affected by the intermolecular attractiv forces. This varies the viscosity of the gas.

3.6.1 Van der Waals Equation

Van der Waals recognized that molecules of a gas occupy their own space tha gets subtracted from the volume of the container. Thus, the "volume of th gas" V in the ideal gas equation is substituted with the term $(V - b)$, in whic b relates to the excluded volume, typically of the order of 20-100 $cm^3\ mol^{-1}$.

The equation now becomes,

$$P(V - b) = n R T \qquad \text{......(II}$$

where, b = the volume occupied by gas molecules

Further, in real gases molecules exert a small cohesive force between them thus helping to hold the gas molecules together and reducing the pressure they exert on the walls of the container. As a consequence, real gases are more compressible than ideal gases.

Hence, equation (II) gets further modified as,

$$\left(P + \frac{a}{V^2}\right)(V - b) = R T \qquad \text{......(III)}$$

where, a = measure of the strength of attraction between the gas molecules.

The above equation can also be written as

$$\left(P + \frac{a n^2}{V^2}\right)(V - n b) = n R T \qquad \text{......(IV)}$$

where, n = the number of moles of gas.

The van der Waals constants a and b must be determined empirically for every gas.

The van der Waals equation is only one of many equations of state for real gases. More elaborate equations are required to describe the behaviour of gases over wider pressure ranges.

3.6.2 Critical Phenomena

On decreasing the temperature and increasing the pressure, real gases cease to exist in gaseous state leading to a decrease in volume. At lower temperature, the gas molecules lose their kinetic energy. The slowed down gas molecules then aggregate due to attractions between them and get converted to a liquid. This implies that the gaseous state vanishes and in its place a new state of matter appears i.e. a liquid state. At one particular temperature and pressure distinction between liquid and gas no longer exists. Such a temperature and pressure are termed as critical temperature and critical pressure respectively (Fig. 3.8). At the critical point, the particles in a closed container are believed to be vaporizing at such a rapid rate that the density of liquid and vapour are equal, and thus form a supercritical fluid.

The critical temperature T_c of a gas is the temperature at and above which vapour of the gas cannot be liquefied, irrespective of the pressure applied.

The critical pressure P_c of a gas is the minimum pressure required to liquefy a gas at its critical temperature.

The critical volume V_c of a gas is the volume occupied by one mole of the gas at T_c and P_c.

The terms T_c , P_c and V_c are together referred to as critical constants of the gas. All real gases have characteristic critical constants.

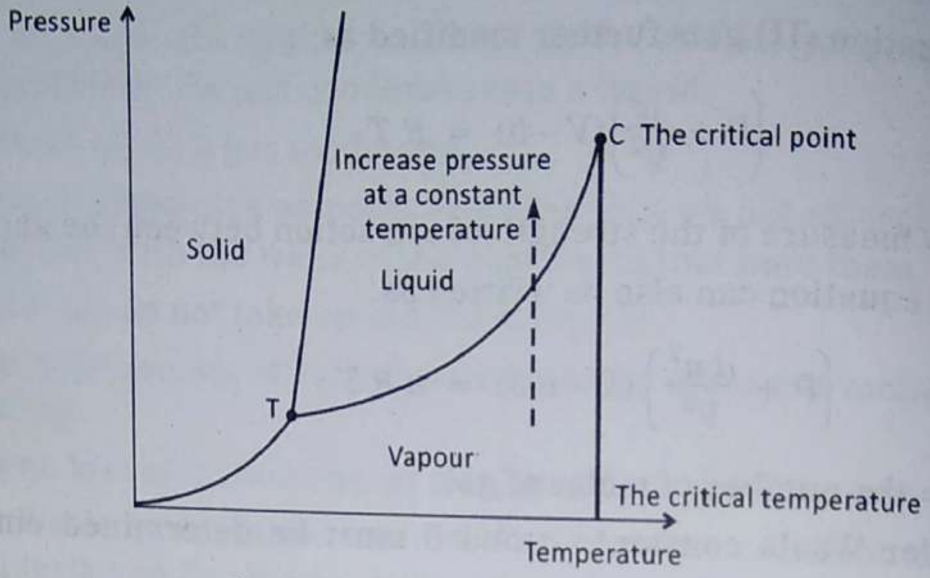


Fig. 3.8 : Critical point of a gas

The actual determination of critical constants of a gas is a very difficul process. However, the T_c and P_c of a gas can be measured relatively easily with the help of Cagniard de la Tour's apparatus.

3.7 Review Questions

(1) What is ionic bond? Give characteristics of ionic compounds.

(2) What is covalent bond? Give characteristics of covalent compounds.

(3) What is coordinate bond? Give characteristics of coordinate compounds.

(4) Write a note on the following

  (i) London dispersion forces

  (ii) Dipole-dipole forces

  (iii) Critical point of a gas

(5) Explain hydrogen bonding with appropriate example.

(6) Discuss van der Waals equation.

(7) Justify : HF is a liquid and HCl is a gas under similar conditions.

(8) Explain with suitable example how hydrogen bonding affects the physical constant of compounds.

(9) How is the anomalous behaviour of water explained on the basis of hydrogen bonding?

(10) What is hydrogen bonding? Discuss the consequences of hydrogen bonding on solubility of a compound in water.

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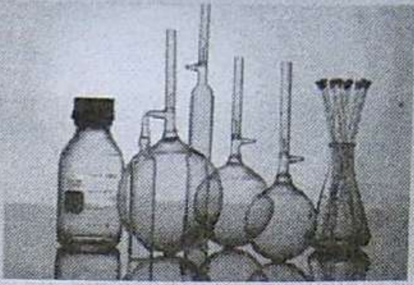


CHAPTER 4

PHASE RULE

4.1 Introduction

The phase rule was invented by J. Willard Gibbs to study the heterogeneous systems in equilibrium. It helps to study the effect of changing temperature, pressure and composition on the behaviour of heterogeneous system in equilibrium by means of a phase diagram.

4.2 Statement

Gibbs' phase rule states that, provided the equilibrium between any number of phases is not influenced by gravity or electrical or magnetic forces or by surface tension but only by temperature, pressure and concentration, then the degrees of freedom (F) of a system is related to the number of components (C) and phases (P) by the phase rule equation,

$$F = C - P + 2$$

4.3 Explanation of the Terms

The terms involved in the phase rule are phase, component and degree of freedom which are explained below,

4.3.1 Phase

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

For a system in equilibrium obeying phase rule, the number of phase cannot be a negative number or zero, i.e. minimum one phase must exist to define a system.

Examples

Each solid phase constitutes a single phase.

(1) At triple point (specific temperature and pressure) in a water system, number of phases is three.

$$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$$

(2) In the thermal decomposition of solid $CaCO_3$,

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$$

number of phases is three viz. two solid phases and a gaseous phase.

Any number of miscible liquids together constitutes a single phase.

(3) A mixture of alcohol and water constitutes a single phase.

Two immiscible liquids constitute two phases.

(4) A mixture of benzene and water constitutes two phases.

Any number of gases together constitutes a single phase.

(5) A mixture of N_2 and H_2 forms a single phase.

(6) When steam is passed over iron,

$$Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2\,(g)}$$

number of phases is three viz. two solid phases and a gaseous phase.

(7) A solid compound such as sugar or salt dissolved in water constitutes a single phase.

4.3.2 Component

A component is defined as the smallest number of independent variable constituent, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of a chemical equation.

For a system in equilibrium obeying phase rule, the number of component cannot be a negative number or zero, i.e. minimum one component must be specified to define a system.

Examples

(1) In a water system, irrespective of the number of phases, the composition of each phase is expressed by a single constituent, H_2O.

$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$; $P = 3$

$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)}$; $P = 2$

Hence, it is a one component system.

(2) In a sulphur system, irrespective of the number of phases, the composition of each phase is expressed by a single constituent, S.

$\text{Monoclinic sulphur}_{(s)} \rightleftharpoons \text{Rhombic sulphur}_{(s)} \rightleftharpoons \text{Vapour sulphur}_{(g)}$; $P = 3$

$\text{Monoclinic sulphur}_{(s)} \rightleftharpoons \text{Rhombic sulphur}_{(s)}$; $P = 2$

Hence, it is a one component system.

(3) In the thermal decomposition of solid $CaCO_3$,

$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)} \; ; P = 3$$

the composition of any single phase cannot be represented by a single constituent. It can be expressed by any two constituents out of three. This can be explained as tabulated below,

Phase	Constituent/s Considered	Composition of Each Phase
Phase 1 : $CaCO_3$	Consider only one constituent, e.g. $CaCO_3$	$CaCO_3 = CaCO_3$
Phase 2 : CaO		Composition of CaO cannot be expressed by only $CaCO_3$
Phase 3 : CO_2		Composition of CO_2 cannot be expressed by only $CaCO_3$
Similarly, it is applicable for other constituents, viz. CaO and CO_2. Hence, it cannot be a one component system.		
Phase 1 : $CaCO_3$	Consider a combination of two constituents, e.g. $CaCO_3$ and CaO	$CaCO_3 = CaCO_3 + 0CaO$
Phase 2 : CaO		$CaO = 0CaCO_3 + CaO$
Phase 3 : CO_2		$CO_2 = CaCO_3 - CaO$
Phase 1 : $CaCO_3$	Consider a combination of two constituents, e.g. CaO and CO_2	$CaCO_3 = CaO + CO_2$
Phase 2 : CaO		$CaO = CaO + 0CO_2$
Phase 3 : CO_2		$CO_2 = 0CaO + CO_2$

Phase 1 : $CaCO_3$	Consider a combination of two constituents, e.g. $CaCO_3$ and CO_2	$CaCO_3 = CaCO_3 + 0CO_2$
Phase 2 : CaO		$CaO = CaCO_3 - CO_2$
Phase 3 : CO_2		$CO_2 = 0CaCO_3 + CO_2$

Since the composition of each phase can be expressed by minimum tw constituents, it is a two component system.

(4) In the dissociation of NH_4Cl in a closed vessel,

$$NH_4Cl_{(s)} \rightleftharpoons NH_4Cl_{(g)} \rightleftharpoons NH_{3\,(g)} + HCl_{(g)}\ ;\ P = 2$$

(i) If the proportions of NH_3 and HCl are equivalent, then th composition of each phase can be expressed in terms of NH_4Cl alone Hence, it is a one component system as composition of any on constituent needs to be known to express the composition of any o the phases.

(ii) If the proportions of NH_3 and HCl are not equivalent, then it is a tw component system as concentration of both constituents needs to b known to express the composition of any of the phases.

4.3.3 Degree of Freedom

Degree of freedom is defined as the minimum number of independentl variable factors such as temperature, pressure and composition of th phases, which may be arbitrarily specified in order to represent perfectly th condition of a system.

For a system in equilibrium obeying phase rule, the number of degree o freedom cannot be a negative number. However, it can be defined wit minimum zero degree of freedom.

Examples

(1) In a water system (one component system), consider the followin conditions,

(i) Ice $_{(s)} \rightleftharpoons$ Water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$; $P = 3, C = 1$

This particular equilibrium exists at a definite temperature and pressure. Thus, to define this system, no parameter needs to be specified. Hence, it is a zero variant or invariant system. It has no degree of freedom.

(ii) Water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$; $P = 2, C = 1$

To define this system, either of the parameters viz. temperature or pressure needs to be specified, the other parameter gets automatically fixed.

Hence, it is a univariant or monovariant system. It has one degree of freedom.

(iii) Ice $_{(s)}$ or Water $_{(l)}$ or Water vapour $_{(g)}$; $P = 1, C = 1$

The system contains only one phase, either solid, liquid or gaseous.

To define this system, both the parameters viz. temperature and pressure needs to be specified. Hence, it is a bivariant system. It has two degrees of freedom.

(2) The system of saturated solution of NaCl in equilibrium with solid NaCl and water vapour exists at a definite temperature.

NaCl $_{(s)} \rightleftharpoons$ NaCl-water $_{(l)} \rightleftharpoons$ Water vapour $_{(g)}$

Hence, this system has one degree of freedom.

(3) For a sample of pure gas obeying the equation, $PV = RT$, if pressure and temperature are specified, the volume gets automatically fixed. Hence, this system has two degrees of freedom.

(4) For a mixture of two or more gases at equilibrium, all the three parameters viz. temperature, pressure and composition need to be specified to define a system. Hence, this system has three degrees of freedom.

4.4 One Component Water System

The water system comprises of three possible phases namely solid (ice), liquid and gaseous (vapour). Since only one constituent H_2O is sufficient to express the composition of each phase, it is a one component system, i.e. $C = 1$.

Substituting for $C = 1$ in Gibbs' phase rule equation, $F = C - P + 2$, we get

$$F = 1 - P + 2$$

$$F = 3 - P$$

The minimum number of degree of freedom can be zero for a system, i.e. when $F = 0$, then $P = 3$. This implies that all the three phases can exist in equilibrium for a water system.

Minimum one phase is required to define the system at equilibrium, i.e. when $P = 1$, $F = 2$. Thus, for water system, the maximum number of degrees of freedom is two. These two degrees of freedom for one component system are pressure and temperature.

The phase diagram for one component system can be represented by plotting a graph of pressure against temperature (Fig. 4.1).

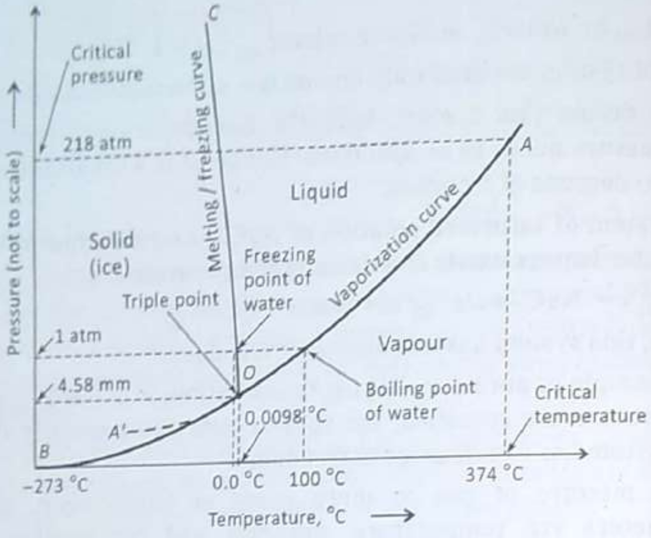


Fig. 4.1 : One component water system

The water system is explained as follows,

(1) **Areas :** In the areas *AOB*, *AOC* and *BOC*, only single phase (namely vapour, liquid and solid respectively) exists and the degrees of freedom are two, i.e. both parameters, temperature and pressure need to be specified in order to define the system.

(2) **Boundary lines :** The boundary lines, namely melting point or freezing or fusion curve (*OC*), vaporization curve (*OA*) and sublimation curve (*OB*) divide the phase diagram into three areas. Along the boundary lines, two phases are in equilibrium and the degree of freedom is one, i.e. either temperature or pressure needs to be specified in order to define the system.

The curve *OC* shows that the melting point of ice is decreased with increase in temperature. *A* point on curve *OC* corresponding to 1 atmosphere pressure and 0 °C temperature is the melting or freezing point of water.

The curve *OA* terminates at point *A*, called critical point corresponding to 218 atmosphere pressure and 374 °C temperature, above which the liquid phase and the vapour phase merge into each other. A point on curve *OA* corresponding to 1 atmosphere pressure and 100 °C temperature is the boiling point of water.

The curve *OB* terminates at point *B*, corresponding to –273 °C temperature, below which the solid phase and the vapour phase merges into each other.

(3) **Triple point :** The curves *OC*, *OA* and *OB* meet at point '*O*' called triple point of water. At triple point, all the three phases, i.e. solid, liquid and gaseous co-exist in equilibrium.

The degree of freedom is zero, i.e. neither temperature nor pressure needs to be specified in order to define the system. The triple point exists at 4.58 mm pressure and 0.0098 °C ≈ 0.01 °C temperature.

(4) **Metastable curve :** The curve *OA'* is called the metastable curve, which is the extension of curve *OA*. At the freezing point, water would normally freeze and form ice. But by careful removal of solid particles, which promote this crystallization, water may be cooled way below its freezing point without forming ice. Thus, by preventing water to freeze at its freezing point, it is possible to extend the vapour pressure curve even below the normal freezing point. It signifies the vapour pressure curve of supercooled water.

The above discussion is tabulated below ($C = 1$)

Name of the System	Phases in Equilibrium	Degrees of Freedom $F = C - P + 2$
Areas		
(1) *BOC*	Solid, $P = 1$	$F = 1 - 1 + 2 = 2$ The systems are bivariant.
(2) *COA*	Liquid, $P = 1$	
(3) *AOB*	Vapour, $P = 1$	
Curves		
(1) *OC* (Melting point curve)	Solid and Liquid, $P = 2$	$F = 1 - 2 + 2 = 1$ The systems are univariant.
(2) *OA* (Vaporization curve)	Liquid and Vapour, $P = 2$	
(3) *OB* (Sublimation curve)	Solid and Vapour, $P = 2$	
Triple point O	Solid, Liquid and Vapour, $P = 3$	$F = 1 - 3 + 2 = 0$ The system is invariant.

4.5 Reduced Phase Rule Equation

For a two component system, when $C = 2$, substituting in Gibbs' phase rule equation, $F = C - P + 2$, we get,

$$F = 2 - P + 2$$

$$F = 4 - P$$

Minimum one phase is required to define the system at equilibrium, i.e. when $P = 1$, $F = 3$. Thus, for two component system, the maximum number of degrees of freedom is three. The phase diagram for two component system can be represented by plotting a three dimensional graph/diagram of temperature, pressure and composition. In practice, one of the three variables is kept constant and a graph of two variables is considered. Hence, in such cases, the number of degree of freedom gets reduced by 1. Thus, phase rule becomes,

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

$$F = C - P + 1$$

This equation is called as *reduced phase rule equation*.

When pressure is kept constant, the system is called *condensed system*. Hence, in such a case, reduced phase rule is also called as *condensed phase rule*.

Two components alloy system follows condensed phase rule. An alloy is a mixture of two metals or of a metal and non-metal, forming a homogeneous mass having unique characteristics. The possible four phases exhibited by an alloy system are two solid phases of two metals or one metal and one non-metal, liquid phase of solution of two solids and gaseous phase of vapours of two solids. However, for an alloy system, gaseous phase is practically absent and effect of pressure is negligible. Thus, an alloy system can be studied by keeping pressure constant. Therefore, reduced or condensed phase rule is applicable for an alloy system.

4.5.1 Phase Diagram of Silver-Lead Alloy System

It is a two component system. It consists of four possible phases, **(i)** Solid silver (Ag), **(ii)** Solid lead (Pb), **(iii)** Liquid of (silver + lead), **(iv)** Vapours of molten silver and lead which contributes gas phase. Since gaseous phase is practically absent and effect of pressure is negligible, reduced or condensed phase rule is applicable.

Substituting for $C = 2$ in reduced phase rule equation,

$$F = C - P + 1$$

$$F = 2 - P + 1$$

$$F = 3 - P$$

The minimum number of degree of freedom can be zero for a system, i.e. when $F = 0$, then $P = 3$. This implies that all the three phases can exist in equilibrium for a silver-lead alloy system.

Minimum one phase is required to define the system at equilibrium, i.e. when $P = 1$, $F = 2$. Thus, for silver-lead system, the maximum number of degrees of freedom is two. These two degrees of freedom are temperature and % composition. The phase diagram for two component system can be represented by plotting a graph of temperature against % composition (Fig. 4.2).

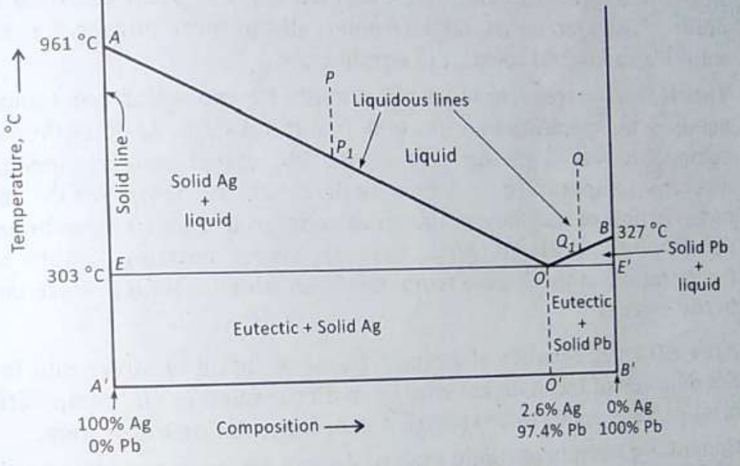


Fig. 4.2 : Two component silver-lead system

The silver-lead system is explained as follows,

(1) Curves

(i) **Curve *AO* :** It is the freezing point curve of silver. The curve starts from point *A*, at 961 °C temperature, which is the melting point of silver. It indicates that on addition of lead to silver, the melting point of silver decreases gradually along *AO* till point *O* is reached. At point *O*, no more lead can go in solution (Point *O* is the lowest limit where lead can be added to solution) and if it is added, it separates out as solid lead.

(ii) **Curve BO :** It is the freezing point curve of lead. The curve star from point B, at 327 °C temperature, which is the melting point o lead. It indicates that on addition of silver to lead, the melting poin of lead decreases gradually along BO till point O is reached. At poin O, no more silver can go in solution (Point O is the lowest limit wher silver can be added to solution) and if it is added, it separates out a solid silver.

Along curve AO, solid silver and liquid are in equilibrium whil along curve BO, solid lead and liquid are in equilibrium. Thus alon both the curves, two phases are in equilibrium and the degree o freedom is one, i.e. either composition or temperature needs to b specified in order to define the system.

(2) **Eutectic point :** The curves OA and OB meet at point O called *eutecti point of the system*. At eutectic point, all the three phases, i.e. solid Ag solid Pb and liquid co-exist in equilibrium.

The degree of freedom is zero, i.e. neither composition nor temperature needs to be specified in order to define the system. At eutectic point, the composition is 2.6% Ag and 97.4% Pb, called *eutectic composition* whereas temperature is 303 °C, called *eutectic temperature*. Eutectic composition of an alloy is the solid solution of fixed proportions of the constituents involved which has the lowest freezing point. Eutectic temperature is the lowest temperature at which a liquid phase can exist in the system.

(3) **Area AOB :** It consists of a single phase of liquid of silver and lead and the degrees of freedom are two, i.e. both parameters viz. composition and temperature needs to be specified in order to define the system.

Consider a sample of liquid melt of Ag and Pb, corresponding to point Q, having a composition less than 2.6% Ag. On cooling the melt, the temperature gradually decreases without any change in composition till point Q_1 is reached on curve BO. Further cooling allows the composition to vary along Q_1O and lead starts separating out till the eutectic composition is obtained. Similarly, if a melt having composition more than 2.6% Ag (at point P) is taken and cooled till P_1, silver gets separated till the eutectic point composition is attained.

The phase diagram also shows following regions,

(i) Region enclosed by AOE shows a stable composition of solid crystalline silver and the liquid melt of silver and lead.

(ii) Region enclosed by BOE' shows a stable composition of solid crystalline lead and the liquid melt of silver and lead.

(iii) Region enclosed by $EOO'A'$ shows a stable composition of silver crystals and solid eutectic crystals.

(iv) Region enclosed by $E'OO'B'$ shows a stable composition of lead crystals and solid eutectic crystals.

4.6 Advantages of Phase Rule

The advantages of phase rule are as given below,

(1) It applies to both, physical and chemical phase reactions.

(2) It provides a suitable basis for classification of equilibrium states of systems by means of phases, components and degree of freedom.

(3) It applies to macroscopic systems, therefore information about molecular structures is not needed.

(4) It does not take into account the nature or amount of substances present in the system.

(5) It specifies that different systems with the same degrees of freedom behave in a similar manner. Moreover, it is useful in predicting the behaviour of a system under different conditions of temperature, pressure and composition.

(6) It helps in deciding whether the given number of substances together would exist in equilibrium under a given set of conditions or whether some of them will have to be inter-converted or eliminated.

4.7 Limitations of Phase Rule

The limitations of phase rule are as given below,

(1) It applies only to systems in equilibrium. It is not much useful in case of systems which attain the equilibrium state very slowly.

(2) It is applicable, provided all the phases of the system are present under the same conditions of temperature, pressure and gravitational force.

(3) It applies to a single equilibrium state only and does not indicate the other possible equilibria in the system.

(4) It considers only the number of phases and not their quantities. Even a minute quantity of the phase, when present, accounts towards the number of phases. Therefore, proper care has to be taken while deciding the number of phases existing in the equilibrium state.

(5) The solid and liquid phases should not be so finely sub-divided as t bring about deviation from their normal values of vapour pressure.

(6) It takes into account only the intensive variables such as temperature pressure and composition. It does not consider other factors such a influence of electric or magnetic field.

4.8 Numerical Problems

Example 1 : An alloy of zinc and cadmium contains 83.5% zinc. Find the mass of eutectic in 1 kg of solid alloy if the eutectic contains 67% of zinc.

Solution : 1 kg of alloy contains 835 g (0.835 kg) zinc and 165 g (0.165 kg) cadmium.

It is given that, in the eutectic composition, zinc is 67% that means cadmium is 33%.

The amount of zinc corresponding to 165 g of cadmium

$$= \frac{(165 \times 67)}{33} = 335 \text{ g}$$

$\therefore$ Total amount of eutectic in alloy = 165 + 335 = 500 g

Example 2 : An alloy of silver and copper contains 84% silver. Find the mass of eutectic in 2 kg of solid alloy if the eutectic contains 71.8% of silver.

Solution : 2 kg of alloy contains 1680 g (1.680 kg) silver and 320 g (0.320 kg) copper.

It is given that, in the eutectic composition, silver is 71.8% that means copper is 28.2%.

The amount of silver corresponding to 320 g of copper

$$= \frac{(320 \times 71.8)}{28.2} = 814.75 \text{ g}$$

$\therefore$ Total amount of eutectic in alloy = 320 + 814.75 = 1134.75 g

Example 3 : 1300 kg of a sample of argentiferous lead containing 0.4% silver is melted and then allowed to cool. If eutectic contains 2.6% silver, what amount of eutectic will be formed? How much amount of lead will separate out?

Solution : Amount of silver in 1300 kg argentiferous lead

$$= \frac{0.4}{100} \times 1300 = 5.2 \text{ kg}$$

Since eutectic contains 2.6% silver, amount of eutectic

$$= \frac{(5.2 \times 100)}{2.6} = 200 \text{ kg}$$

$\therefore$ Amount of lead separated out = 1300 – 200 = 1100 kg

Example 4 : An alloy of zinc and aluminium weighing 2390 kg, containing 2% zinc is melted and then allowed to cool. If eutectic contains 95.6% zinc, what amount of eutectic will be formed? How much amount of aluminium will separate out?

Solution : Amount of zinc in 2390 kg alloy

$$= \frac{2}{100} \times 2390 = 47.8 \text{ kg}$$

Since eutectic contains 95.6% zinc, amount of eutectic

$$= \frac{(47.8 \times 100)}{95.6} = 50 \text{ kg}$$

$\therefore$ Amount of aluminium separated out = 2390 – 50 = 2340 kg

Example 5 : An alloy of *AB* of 10 g weigh contained *A* at 30%. The molten *AB* on cooling gave out *B* and an eutectic alloy with *A* and *B* at equal percentage. What is the amount of *B* that has formed?

Solution : Since alloy contains 30% of *A*, in 10 g alloy, weight of $A = 3$ g and weight of $B = 7$ g

It is given that, on cooling, equal amounts of *A* and *B* separate.

On cooling, 3 g of each *A* and *B* will separate out.

$\therefore$ The amount of *B* formed = Original amount – Amount in eutectic

= 7 – 3 = 4 g

4.9 Review Questions

(1) State Gibbs' phase rule.

(2) Define - (i) Phase, (ii) Component, (iii) Degree of freedom.

(3) Give number of phases and component involved in the following systems:

   (i) $CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)}$
   (ii) A mixture of water and alcohol
   (iii) A mixture of water and oil
   (iv) $Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Water\ vapour_{(g)}$

(v) $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(g)}$

(vi) A mixture of H_2 and N_2

(4) Draw a phase diagram for water system.

(5) Explain the application of Gibbs' phase rule to water system.

(6) Describe the triple point of water with suitable phase diagram.

(7) State and explain reduced phase rule.

(8) Explain the application of reduced phase rule to silver lead system.

(9) Give advantages of phase rule.

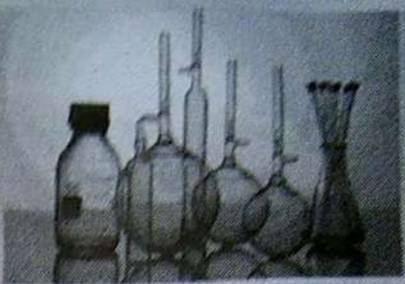
(10) Give limitations of phase rule.

(11) An alloy of tin and lead contains 66% tin. Find the mass of eutectic in kg of solid alloy; if the eutectic contains 55% of tin. **[Ans.** 755.56

(12) 650 kg of a sample of argentiferous lead containing 0.25% silver i melted and then allowed to cool. If eutectic contains 2.6% silver, wha amount of eutectic will be formed? How much amount of lead wil separate out? **[Ans.** 587.5 kg

* * *

CHAPTER 5



POLYMERS

5.1 Introduction

A quick look around would make us realize that we are surrounded by POLYMERS! From wood to plastic bags we use. Polymers are abundant in nature, found in all living systems. While natural polymers retain their intrinsic importance, today synthetic materials are mostly used, formed by chemical modification of natural materials. Totally synthetic polymer was developed in the twentieth century after the expansion of chemical industry. The important feedstock for synthetic polymer preparation is petrochemicals.

The word *polymer* is derived from two Greek words, *poly* means many and *mer* which means units. Basically, a polymer is a long-chain molecule covalently bonded to its identical neighbors and repeated along the length of molecule. These identical units are known as *monomers* i.e. single unit. Monomers must have two or more binding sites to produce a polymer. Polymers which have the same repeating unit along the molecule are known as *homopolymers* whereas polymers with more than one repeating units are called *copolymers*. The idea of repetitive units linked together to form a polymer has led to the concept of chain molecule, which has been very useful in modeling physical and mechanical properties. Simply stated, a polymer is a long-chain molecule that is composed of a large number of repeating units of identical structure. Those monomers can be simple just as an atom or two or three or they might be complicated ring-shaped structures containing a dozen or more atoms.

5.2 Classification of Polymers

Since polymers are numerous in number with different behaviors and can be naturally found or synthetically created, they can be classified in various ways. The following are some basic ways in which polymers can be classified.

(1) **Classification based on source :** The first classification of polymers is based on their source of origin.

  (i) **Natural polymers :** Natural polymers are polymers which occur in nature and are existing in natural sources like plants and animals. Some common examples are proteins (which are found in humans and animals alike), cellulose and starch (which are found in plants) or rubber (which is harvested from the latex of a tropical plant).

  (ii) **Synthetic polymers :** Synthetic polymers are polymers which are artificially created or synthesized in a laboratory by scientists. These are commercially produced by industries for human necessities. Some commonly produced polymers which we use daily are polyethylene (a mass-produced plastic which is used in packaging) or nylon fibers (commonly used in clothes, fishing nets).

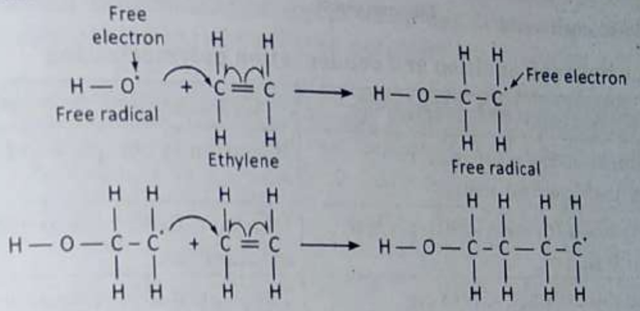
  (iii) **Semi-synthetic polymers :** Semi-synthetic polymers are polymers obtained by making modification to natural polymers artificially in a laboratory. These polymers formed by chemical reactions (in a controlled environment) are of commercial importance. Example : vulcanized rubber (sulphur is used in cross bonding the polymer chains found in natural rubber), cellulose acetate (rayon) etc.

(2) **Classification based on polymerization :** The chemical reaction in which high molecular mass molecules are formed from monomers is known as polymerization. There are two basic types of polymerization, addition polymerization undergoing chain-reaction and condensation polymerization undergoing step-reaction. Depending on polymerization there are two types of polymers, viz. addition and condensation. Their polymerization process is outlined below,

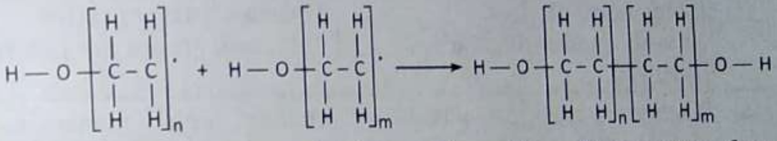
  (i) **Addition polymerization :** One of the most common types of polymer reactions is addition polymerization. This type of polymerization undergoes chain reaction mechanism which is a three step process. For addition polymerization to occur at least one carbon-carbon double bond is required. Example : polyethylene.

Step 1 - Initiation : Formation of free radicals from a radical initiator.

Step 2 - Propagation : Successive addition of monomer units to the chains.

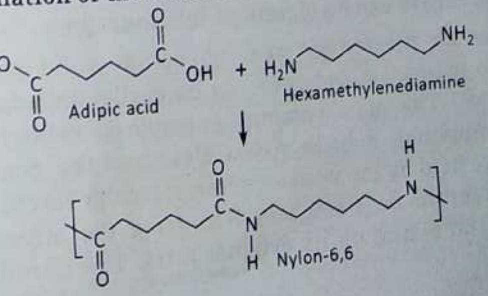


Step 3 - Termination : Through a combination of two chains.

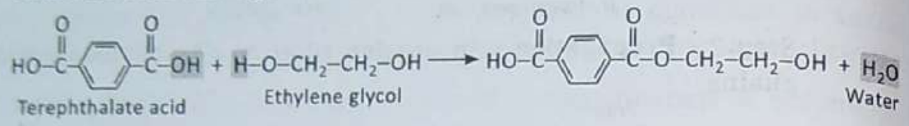


(ii) **Condensation polymerization :** Formation of polymers from polyfunctional monomers of organic molecules with elimination of small molecules like water, HCl, ammonia. Functional group of one monomer unit reacts with functional group of the other monomer. Some monomers have more than two reactive sites, allowing for branching between chains, as well as increasing the molecular mass of the polymer.

Example 1. Synthesis of Nylon-6,6 by the reaction between hexamethylenediamine and adipic acid to form amide linkage with the elimination of the water molecule.



Example 2. Formation of polyethylene terephthalate (PET) by the reaction between terephthalic acid and ethylene glycol to form PET that has ester linkage with the elimination of the water molecule.



Difference between addition and condensation polymerization

Sr. no.	Addition polymerization	Condensation polymerization
(1)	Reaction is faster under favorable conditions.	Reaction is comparatively slow.
(2)	Reaction follows chain growth mechanism.	Reaction follows step growth mechanism.
(3)	The reaction involves no by-products formation.	The reaction involves by-products formation.
(4)	Monomers with C=C (unsaturated carbon) are involved.	Monomers with reactive functional groups are involved.
(5)	Concentration of monomers decreases through the course of reaction.	Concentration of monomers decreases much faster in the early stage of the reaction.

(3) **Classification based on molecular forces :** Intramolecular forces are the forces that hold atoms together within a molecule. In polymers, strong covalent bonds connect atoms to each other in individual polymer molecules. Intermolecular forces (between the molecules) attract polymer molecules towards each other. Note that the properties exhibited by solid materials like polymers depend largely on the strength of the forces between these molecules.

Using this, polymers can be classified into four types,

(i) **Elastomers :** Elastomers are rubber-like solid polymers that are elastic in nature i.e. polymer can be easily stretched by applying a little force. The most common example is rubber bands (or hair bands). Applying a little stress elongates the band. The polymer chains are held by the weakest intermolecular forces, hence allowing the polymer to be stretched. Removing the stress results in the rubber band taking up its original form. The introduction of cross-links between the polymer chains helps it in retracting to its original position, and taking its original form. Other example is vulcanized rubber. The introduction of sulphur cross bonds the polymer chains of rubber.

(ii) **Thermoplastics :** Thermoplastic polymers are long-chain polymers in which intermolecules forces (van der Waals forces) hold the polymer chains together. These polymers when heated are softened (thick fluid like) and hardened when they are allowed to cool down, forming a hard mass. They do not contain any cross bond and can easily be shaped by heating and using moulds. A common example is polystyrene or PVC (which is used in making pipes).

(iii) **Thermosetting :** Thermosetting plastics are polymers which are semi-fluid in nature with low molecular masses. When heated, they start cross-linking between polymer chains, hence becoming hard and infusible. They form a three-dimensional structure on the application of heat. This reaction is irreversible in nature. The most common example of a thermosetting polymer is that of bakelite, which is used in making electrical insulation.

Difference between thermoplastic and thermosetting polymers

Sr. no.	Thermoplastic polymers	Thermosetting polymers
(1)	They soften on heating and harden on cooling.	They are fusible on initial heating, but turn into hard infusible mass on heating further.
(2)	They can be reshaped and recycled.	They cannot be reshaped and recycled.
(3)	They are formed by addition polymerization.	They are formed by condensation polymerization.
(4)	They are linear in structure.	They are three dimensional in structure.
(5)	They are soluble in some organic solvents.	Insoluble in organic solvents.
(6)	Moulded articles are taken out after cooling the mould to avoid deformation of the article.	Moulded articles are taken out from the mould even when they are hot.

(iv) **Fibres :** These are a class of polymers which are thread-like in nature, and can easily be woven. They have strong intermolecular forces between the chains giving them less elasticity and high tensile strength. The intermolecular forces may be hydrogen bonds or dipole-dipole interaction. Fibres have sharp and high melting points. A common example is that of Nylon-66, which is used in carpets and apparels.

(v) **Biopolymers :** Biopolymers are polymers which are obtained from living organisms. They can be naturally occurring for example, silk, cellulose, etc. or can be prepared synthetically like, polyglucoside. They are biodegradable and have a very well defined structure.

5.3 Properties of Polymers

(1) **Degree of polymerization :** The number of repetitive units along a polymer molecule is known as the degree of polymerization. The product of the degree of polymerization and the relative molar mass of the repeating unit defines the relative molar mass of the polymer molecule. Therefore, it is important to know the average relative molar mass of a polymer sample and the distribution of relative molar masses. Number of repeating units in the chain is called the degree of polymerization (n).

$$M = n\,M_o$$

where M is molecular weight of polymer

M_o is molecular weight of monomer

n stands for degree of polymerization

Strength of a polymer can be increased by increasing its degree of polymerization. Polymer with high degree of polymerization is hard and heat resistant. Polymer with low degree of polymerization is soft, gummy.

Example : Calculate the degree of polymerization for polyethene (PE) : $(C_2H_4)_n$, where n stands for degree of polymerization

If molecular weight of PE, $M = 28000$,

Molecular weight of repeat unit, $M_o = 28$,

$$M = n\,M_o$$

$$\text{Thus, } n = \frac{M}{M_o} = \frac{28000}{28} = 1000$$

$$\text{Degree of polymerization } (n) = 1000$$

(2) **Molecular weight of polymer :** Unlike simpler pure compounds, most polymers are not composed of identical molecules. Some of the polymer chains will be much larger and some will be much smaller. Hence, average molecular weights are considered about polymers. The average can be calculated in different ways as follows,

(i) **The number average molecular weight, M_n :** M_n the number average molecular weight, is calculated from the mole fraction distribution of different sized molecules in a sample. It is simpler to understand.

It is the total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample. The number average $\overline{M_n}$ molecular weight is given as,

$$\overline{M_n} = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{\sum_{i=1}^{N} W_i}{\sum_{i=1}^{N} (W_i/M_i)}$$

(ii) **The weight average molecular weight, M_W :** M_W the weight average molecular weight, is calculated from the weight fraction distribution of different sized molecules. The weight average is a little more complicated. It's based on the fact that a bigger molecule contains more of the total mass of the polymer sample than the smaller molecules do. The weight average molecular weight depends not only on the number of molecules present, but also on the weight of each molecule.

To calculate this, N_i is replaced with $N_i M_i$.

$$\overline{M_W} = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i} = \frac{\sum_{i=1}^{N} W_i M_i}{\sum_{i=1}^{N} W_i}$$

where W_i is the weight fraction of polymer with molecular weight M_i.

Solved Numericals

Example 1 : Find out number average molecular weight (M_n) and weighted average molecular weight (M_W) for an equimolar mixture of dodecane ($C_{12}H_{26}$) and octadecane ($C_{18}H_{38}$)?

Solution : Dodecane ($C_{12}H_{26}$) and octadecane ($C_{18}H_{38}$) have molecular weights of 170 and 254, respectively. For an equimolar mixture,

$$M_n = \frac{(1 \times 170) + (1 \times 254)}{1 + 1} = \frac{170 + 254}{2} = 212$$

The weight fractions are given by the proportion of mass,

$$\therefore M_W = \frac{1 \times (170)^2 + 1 \times (254)^2}{(1 \times 170) + (1 \times 254)} = 220.32$$

Example 2 : Consider a polymer sample comprising of 5 moles of polymer molecules having molecular weight of 40,000 g/mol and 15 moles of polymer molecules having molecular weight of 30,000 g/mol. Calculate the M_n and M_W of the polymer.

Solution : Total weight $= (5 \text{ mol} \times 40{,}000 \text{ g/mol}) + (15 \text{ mol} \times 30{,}000 \text{ g/mol})$

$$= 650{,}000 \text{ g}$$

Total number $= 5 \text{ mol} + 15 \text{ mol} = 20 \text{ mol}$

$$M_n = \frac{650{,}000 \text{ g}}{20 \text{ mol}} = 32{,}500 \text{ g/mol}$$

$$\therefore M_W = \frac{[5 \text{ mol} \times (40{,}000 \text{ g/mol})^2] + [15 \text{ mol} \times (30{,}000 \text{ g/mol})^2]}{[5 \text{ mol} \times 40{,}000 \text{ g/mol}] + [15 \text{ mol} \times 30{,}000 \text{ g/mol}]}$$

$$\therefore M_W = 33{,}076.9 \text{ g/mol}$$

Example 3 : Calculate M_W for a polymer sample comprising of 9 moles of polymer molecules having molecular weight of 30,000 g/mol and 5 moles of polymer molecules having molecular weight of 50,000 g/mol.

Solution : $$M_W = \frac{[9 \text{ mol} \times (30{,}000 \text{ g/mol})^2] + [5 \text{ mol} \times (50{,}000 \text{ g/mol})^2]}{[9 \text{ mol} \times 30{,}000 \text{ g/mol}] + [5 \text{ mol} \times 50{,}000 \text{ g/mol}]}$$

$$\therefore M_W = 39{,}615.38 \text{ g/mol}$$

Example 4 : In a polymer sample 30% molecules have a molecular mass 20,000, 40% have molecular mass 30,000 and the rest have 60,000. Calculate the weight average and number average molecular masses.

Solution : The polymer contains 30% molecules of mass 20,000, 40% molecules of molecular mass 30,000 and rest 30% of molecules of molecular mass 60,000.

Thus, $$\overline{M_n} = \frac{\sum_{i=1}^{N} N_i M_i}{\sum_{i=1}^{N} N_i} = \frac{(30 \times 20{,}000) + (40 \times 30{,}000) + (30 \times 60{,}000)}{30 + 40 + 30}$$

$$= 36{,}000$$

$$\overline{M_W} = \frac{\sum_{i=1}^{N} N_i M_i^2}{\sum_{i=1}^{N} N_i M_i} = \frac{30 \times (20{,}000)^2 + 40 \times (30{,}000)^2 + 30 \times (60{,}000)^2}{(30 \times 20{,}000) + (40 \times 30{,}000) + (30 \times 60{,}000)}$$

$$= 43{,}333.33$$

5.4 Conducting Polymers

Conducting or conductive polymers are organic polymers that can conduct electricity. Such compounds can show conductivity like metals or can be semiconductors. Conducting polymers are finding increased use due to their light weight, ease in processing and good mechanical properties. There are many applications of these materials in electronics, such as batteries, sensors, and microelectronics devices. Polyacetylene, polypyrrole, polyindole and polyaniline and their co-polymers are the main class of conductive polymers. The polypyrrole and polyaniline are currently used in protection of metals, as an anti-corrosive coating. In the medical field, the conductive polymers can be used in the production of artificial muscles, biosensors and drugs controlled-release agents.

Polymers are poor conductors of electricity, due to non-availability of large number of free electrons. However, polyconjugated polymers though insulators in pure state, can be converted into polymers with electrical conductivities comparable to metals.

In non-conjugated polymers like polyethylene (Fig. 5.1), the valence electrons are present in sp^3 hybridized covalent bonds. Such electrons involved in a σ-bond have low mobility and do not contribute to the electrical conductivity of the material.

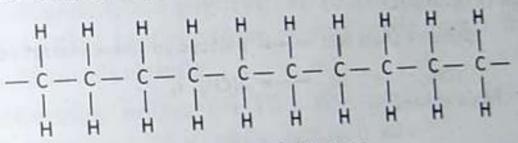


Fig. 5.1 : Polyethylene

However, in conjugated polymers like polyacetylene (Fig. 5.2), the condition is completely different. The valence electrons are present in sp^2 hybridized covalent bonds. One valence electron on each carbon atom resides in a p_z orbital, which is orthogonal to the other three σ-bonds. All the p_z orbitals combine with each other to a molecule wide set of delocalized electrons. The mobility of these delocalized electrons can be utilized to impart electrical conductivities to the conjugated polymers.

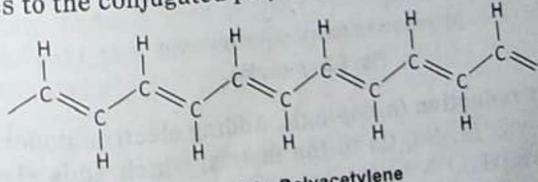


Fig. 5.2 : Polyacetylene

Such conjugated polymers are semiconductors or insulators. In such compounds, the energy gap between the conducting and valence bands can be > 2 eV, which is too high for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. However, higher electrical conductivity can be induced in conjugated polymers by either of the methods given below.

(1) **Excitation of π electrons in electric field :** In an electric field, the electrons get excited and are transported through the solid polymeric matrix. Overlapping orbitals of conjugated π electrons over the entire polymer forms valence and conduction bands. These are *intrinsically conducting polymers*.

(2) **Disturbance in conjugated polymer matrix :** Polymer matrix has to be disturbed by removing electrons (oxidation) by electron acceptors like AsF_5, iodine, etc. or inserting electrons (reduction) by electron donors like alkali-metal ion Li, Na, Ca. This process is referred to as doping and polymers are doped conducting polymers.

   (i) **Doping by oxidation (*p*-doping) :** Adding electron acceptors like AsF_5, iodine to the matrix, which removes some of the delocalized electrons. This creates a mobile positive charge on the polymer backbone (Fig. 5.3).

Polymer + Lewis acid ⟶ *p*-doped polymere (oxidative coupling)

$$\underset{\text{Polyacetylene}}{(CH)_x} + 3I_2 \longrightarrow 2(CH)_x^+ I_3^-$$

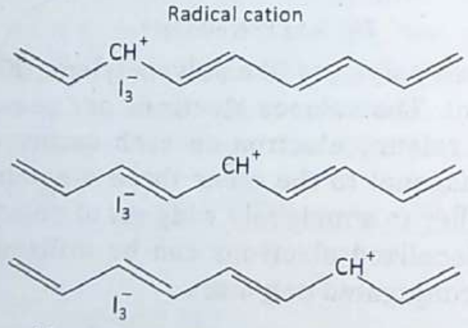


Fig. 5.3 : *p*-doping

   (ii) **Doping by reduction (*n*-doping) :** Adding electron donors like alkali-metal ion viz. Li, Na, Ca to the matrix, which adds electrons to an unfilled orbital.

This creates a mobile negative charge on polymer backbone (Fig. 5.4).

Polymer + Lewis base ⟶ *n*-doped polymer (reductive coupling)

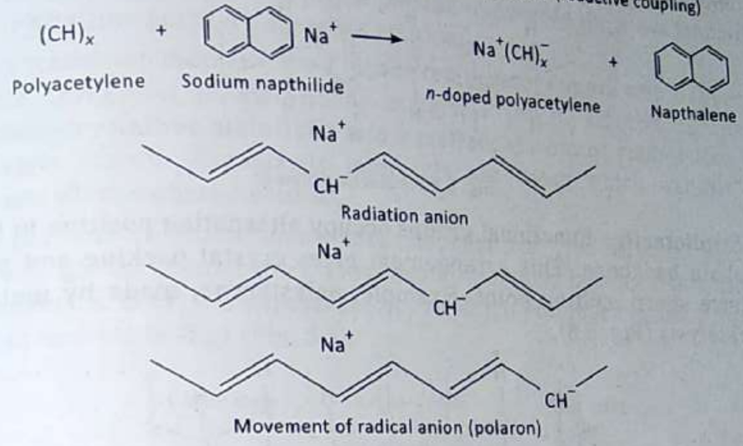


Fig. 5.4 : *n*-doping

The conductivity in polymers due to addition of external ingredients are called *extrinsically conducting polymers.*

(1) **Conducting element-filled polymer :** Here, polymer acts as a binder that binds the conducting elements like carbon black, metal oxides, metallic fibers that conduct electricity.

(2) **Blended conducting polymer :** This polymer is made by blending a conventional polymer with a conducting polymer.

A polymer whose repetitive units are coordination complexes are called coordination conducting polymers. A metal atom with a polydentate ligand, which is a charge transfer complex is bound to the polymer to make it conducting.

5.5 Tacticity

Orientation of side groups on the monomeric units in polymer takes place in orderly/disorderly fashion with respect to main chain. The difference in configuration affects the physical properties of the polymers and their respective applications.

Types of tacticity

(1) **Isotactic :** Functional groups are all on the same side of the main chain or the polymer backbone. Here the molecules pack best with other

molecules of the same shape. Isotactic polymers are usually sem crystalline and often form a helix configuration. Example, polypropyle formed by Ziegler Natta catalysis (Fig. 5.5).

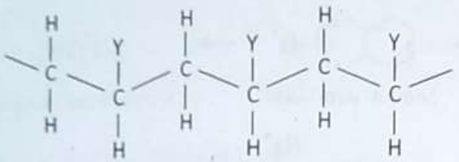


Fig. 5.5 : Isotactic polymer

(2) **Syndiotactic :** Functional groups occupy alternating position in the mai chain backbone. This arrangement gives crystal packing and polymer have sharp melting point. Example, polystyrene, made by metallocen catalysis (Fig. 5.6).

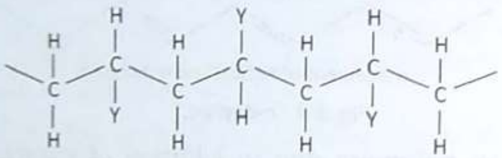


Fig. 5.6 : Syndiotactic polymer

(3) **Atactic :** Functional groups arranged in random manner. No regular array to make a nice crystal. Due to their random nature atactic polymers are usually amorphous. Example, polymers that are formed by free-radical mechanisms such as polyvinyl chloride are usually atactic (Fig. 5.7).

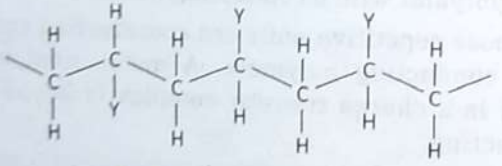


Fig. 5.7 : Atactic polymer

5.6 Melting and Glass Transition Temperatures

Melting is a transition which occurs in crystalline polymers. Melting happens when the polymer chains fall out of their crystal structures, and become a disordered liquid. The glass transition is a transition which happens to amorphous polymers, polymers whose chains are not arranged in ordered crystals, even though they are in the solid state.

The crystalline polymers will have some amorphous portion within it. This portion usually makes up 40-70% of the polymer sample. Hence the sample of a crystalline polymer can have both a glass transition temperature and a melting temperature. The amorphous portion undergoes the glass transition, and the crystalline portion undergoes melting.

The glass transition temperature T_g is the temperature above which there is a reversible transition in amorphous materials (or in amorphous regions within semi-crystalline materials) into a molten, viscous or rubber-like state (viscoelastic state). Viscoelastic materials are those which exhibit both viscous and elastic characteristics.

When a polymer is cooled below this temperature T_g, it becomes hard and brittle, like glass. Temperature above which polymer becomes soft, flexible and viscoelastic is (T_g). Temperature above which polymer becomes liquid or viscofluid in state is (T_m) (Fig. 5.8).

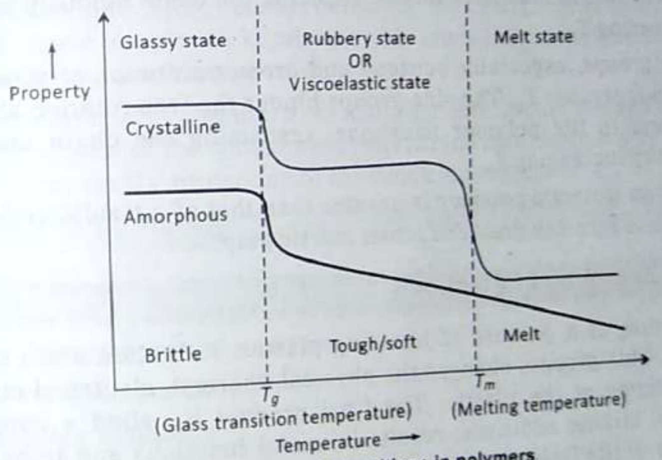


Fig. 5.8 : Thermal transitions in polymers

Hard plastics like polystyrene and polymethyl methacrylate are used well below their glass transition temperatures that is in their glassy state. Their T_g values are well above room temperature, both at around 100 °C (212 °F). Rubber elastomers like polyisoprene and polyisobutylene are used above their T_g, that is, in the rubbery state, where they are soft and flexible. Their T_g values are well below room temperature.

Significance of melting and glass transition temperature

- T_g value gives an indication of the temperature region at which a polymeric material transforms from a rigid solid to a soft viscous state.

- T_g and T_m are useful in choosing the right processing temperature i which materials are fabricated into finished products.
- T_g gives an indication of the flexibility of the polymer and its response t stress.

Factors affecting melting and glass transition temperatures

(1) T_g is directly proportional to the molecular weight of the polymer. T increases with increase in molecular weight upto 20,000; and beyond thi the effect is negligible.

(2) Greater the degree of cross-linking, higher the T_g. High branching/ cross linking brings the polymer chains closer, reducing the chain mobility and thereby increasing T_g.

(3) Polymers with strong intermolecular forces of attraction have greater T. Large number of polar groups in the polymer chain lead to strong intermolecular cohesive forces, reducing the chain mobility and thereby increasing T_g.

(4) Side groups, especially benzene and aromatic groups attached to main chain increases T_g. The side groups hinder the free rotation about the C-C bond in the polymer backbone, restricting the chain mobility and thereby increasing T_g.

(5) T_g of an isotactic polymer is greater than that of a syndiotactic polymer, which in turn has greater T_g than atactic polymer.

5.7 Compounding of Plastics

Compounding is a process of blending plastics in molten state with other additives. This process changes the physical, thermal, electrical or aesthetic characteristics of the plastic. The final product is called a *compound* or *composite*. Mixing additives, results in useful functions and imparts useful properties to the finished products. Main types of compounding ingredients are,

- **Binder** : Binders hold different constituents/additives together during manufacturing. Natural or synthetic resins are used in this case. If binders used have comparatively low molecular weight, then plastic article gets moulded easily and vice versa.
- **Plasticizers** : Low molecular weight organic liquids are added to polymer to improve its flexibility. Plasticizers are essentially used in thermosoftening plastics only and not in thermosetting polymers. Added quantity of plasticizers is 8-10% of total bulk of plastics (examples are oils, camphor, dioctyl phthalates)
- **Stabilizers** : Most polymers do not possess chemical stability. They change colors and decompose over a period. Stabilizers help improve stability of the plastic besides imparting rigidity. Organic, inorganic, organometallic compounds like CaO, BaO, organo-tin compounds are used as stabilizers.
- **Fillers/Extenders** : Fillers impart better tensile strength, enhance mechanical strength, hardness, finish, to the plastic material. Materials like asbestos powder, saw dust, cotton pulp, clay, etc. are used as fillers.
- **Lubricants** : They are useful during moulding operations. They give glossy finish to the product, prevents plastics from sticking to fabrication equipment. Oils, waxes, soaps etc. are used as lubricants.
- **Catalysts** : They are used to increase the rate of polymerization. Antioxidants like H_2O_2, benzoyl peroxide, ZnO, NH_3, Ag, Pb are added to the polymeric matrix to accelerate the cross-linking in thermosetting plastics during moulding process.
- **Coloring materials** : Organic dyes and pigments impart desired color for aesthetic appeal of the finished polymeric material. Some colors are also added to impart UV protection to the finished products.

5.8 Fabrication of Plastic

Plastic fabrication is the design, manufacture, or assembly of plastic products through one of a number of methods using various chemical process parameters like temperature and pressure.

Types of fabrication methods

(1) Compression moulding

This is most common method for moulding thermosetting materials which can withstand high temperature and pressure. Molten resin is moulded in the desired shape applying required temperature and pressure.

In this process, requisite quantity of resin powder is preheated to 1200 °C and the cavity of the heated mould is filled. Thereafter the two parts of mould are brought together under low pressure. Resultant mass is then compressed by hydraulic pressure of 2000 to 10000 psi. This pressure and temperature allows the resin to melt and flow, thereby filling the cavity between the two parts of mould. The material in the mould is kept for a specified time under optimum temperature and pressure for obtaining proper curve. The curing of moulded article is done by eith heating or cooling. After curing, the moulded articles are taken out b opening the mould apart (Fig. 5.9).

The electric switch boxes, radios and television cabinets ar manufactured by this method.

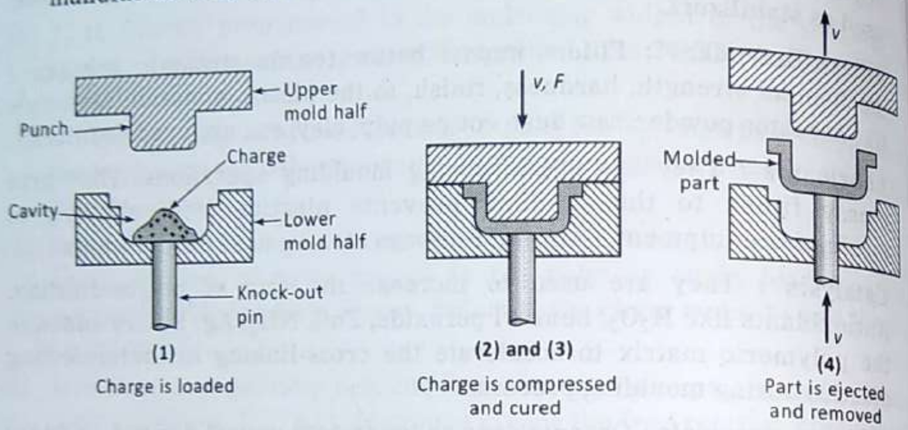


Fig. 5.9 : Compression moulding

Advantages of compression moulding

(i) Wastage of material is prevented.

(ii) Internal stress in the moulded article is minimized by the shorter and multidirectional flow of the material under pressure in the mould cavity.

(iii) Compression moulding is readily adaptable to automatic removal of moulded articles.

(iv) For high-impact, fluffy materials, compression moulding normally is recommended because of the difficulty in feeding the moulding compound from a hopper to the press or preformer.

(viii) Compression moulds usually are less expensive to build than transfer or injection types.

Disadvantages of compression moulding

(i) Articles which are intricately designed, containing undercuts, side draws and small holes, the compression method may not be practical, because of the need for complicated moulds and the possibility of distorting or breaking mould pins during the flow of the material under high pressure.

(ii) For heavy handle, compression moulding would be slower than transfer or injection because in transfer the plastic is thoroughly heated and is precompressed almost to its final density prior to entering the mould.

(2) Injection moulding

This method is applicable mainly to thermoplastic resins. An injection machine is made up of three primary components viz. the feed hopper, the screw and the heated barrel. A predetermined quantity of resin powder is fed into a heated cylinder by hopper. Material melts in the heated cylinder and is injected into the tightly locked mould at a controlled rate by means of a screw arrangement or by a piston plunger. A pressure of 1750 kg/cm^2 is used for injection. The mould is kept cold to allow the hot plastic to cure and become rigid. When material has been cured sufficiently, half of the mould is opened to allow the ejection of the finished articles without any deformation [Fig. 5.10(a) and (b)]. Heating is done by oil or electricity.

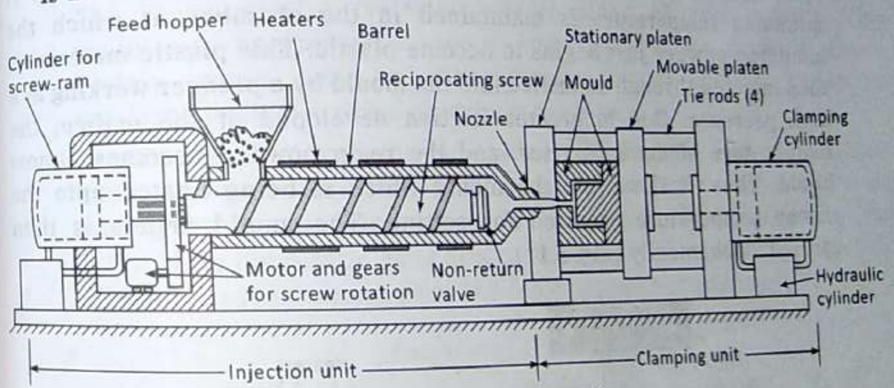


Fig. 5.10(a) : Injection moulding

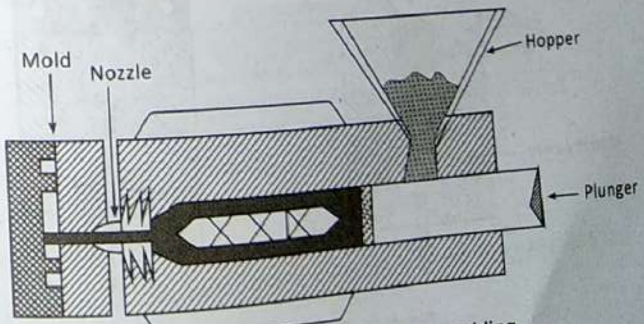


Fig. 5.10(b) : Simplified figure of injection moulding

Advantages

- (i) Fast production.
- (ii) Low labour costs.
- (iii) Design flexibility.
- (iv) High-output production.
- (v) Leaves little post-production scrap.
- (vi) Good product consistency.

Disadvantages

- (i) High initial tooling and machinery cost.
- (ii) Part design restrictions.
- (iii) Small runs of parts can be costly.

(3) Transfer moulding

This method uses the principle of injection moulding for thermosettin materials. The moulding powder is placed at a heated chamber. A minimum temperature is maintained in the chamber at which the moulding powder just begins to become plastic. This plastic material i then injected through an orifice into the mould by a plunger working at high pressure. Due to greater friction developed at the orifice, the temperature of material rises, and the resin powder becomes almos liquid. Thus, it flows into the mould which is being heated upto the curing temperature required for setting. The mould article is the ejected mechanically (Fig. 5.11).

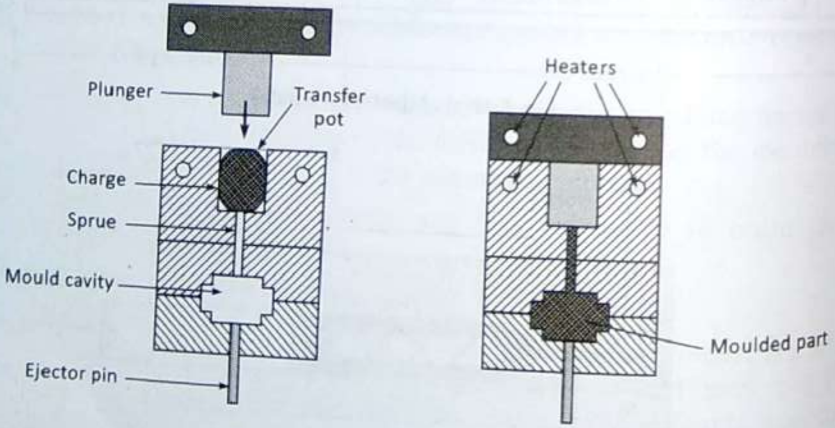


Fig. 5.11 : Transfer moulding

Advantages

- (i) Good surface quality.
- (ii) Large, complex shapes can be made.
- (iii) Low capital investment.
- (iv) Less material wastage and less labour.
- (v) Tooling flexibility.
- (vi) Low environmental impact.
- (vii) Zero air entrapment within the product.

Disadvantages

- (i) They are complex.
- (ii) Scrapes produced cannot be recycled since the polymers are thermosetting.
- (iii) Cleaning the tool is time consuming.

(4) Extrusion moulding method

The thermoplastic materials are moulded by this method. This manufacturing process is used to make pipes, hoses, drinking straws, curtain tracks, rods and fiber. Thermoplastics undergo continuous moulding to form articles of uniform cross-section.

In this method, the thermoplastic materials are heated to plastic conditions and then pushed by means of a screw conveyor into a die having the required outer shape of the article to be manufactured (Fig. 5.12). Here the plastic mass gets cooled due to the atmospheric exposure. A long conveyor carries away the cooled product continuously.

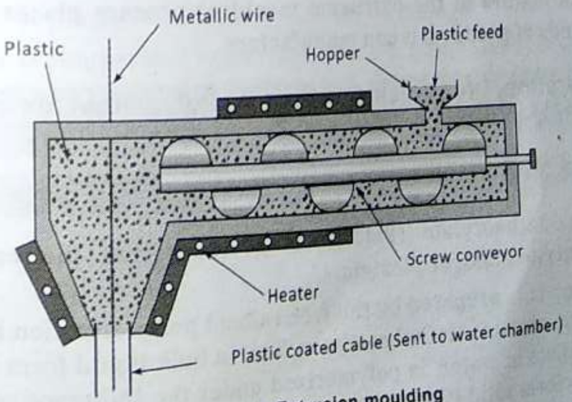


Fig. 5.12(a) : Extrusion moulding

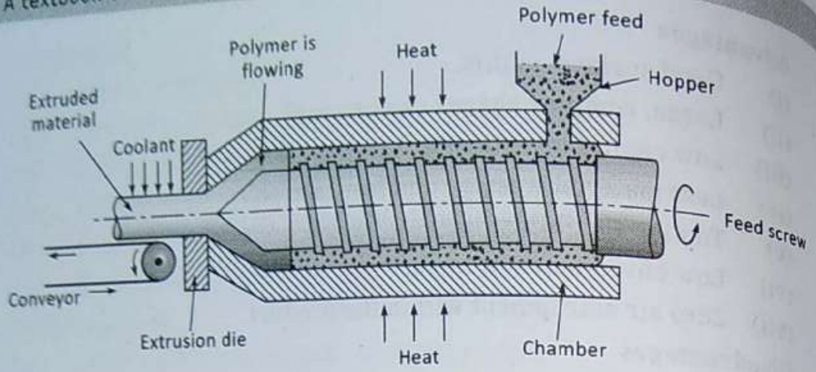


Fig. 5.12(b) : Extrusion moulding

Advantages

(i) Extrusion moulding has a low cost relative to other moulding processes. Most extrusion moulding uses thermoplastics, which can repeatedly undergo melting and hardening.

(ii) It provides considerable flexibility in manufacturing products with a consistent cross-section.

(iii) The plastic remains hot when it leaves the extruder, which allows for post-extrusion manipulation.

Disadvantages

(i) When the hot plastic exits the extruder, it frequently expands. Hence predicting the exact degree of expansion remains problematic as it arises from different factors in the process.

(ii) The nature of the extrusion moulding process places limits on the kinds of products it can manufacture.

5.9 Preparation, Properties and Uses of Polymethyl Methacrylate and Poly-paraphenylene Terephthalamide (Kevlar)

5.9.1 PMMA (Polymethyl methacrylate)

Polymethyl methacrylate (PMMA) is a transparent thermoplastic, also known as acrylic glass, or plexiglass.

Preparation : It is prepared by the free radical polymerization mechanism of methyl methacrylate. Methyl methacrylate, in bulk liquid form or suspended as fine droplets in water, is polymerized under the influence of free-radical initiators to form solid PMMA (Fig. 5.13).

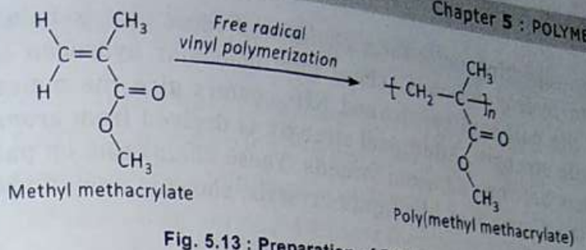


Fig. 5.13 : Preparation of PMMA

Properties

(1) Hard rigid material with high softening point.

(2) The glass transition temperature (T_g) of atactic PMMA is 105 °C (221 °F).

(3) High resistance to sunlight.

(4) High optical transparency.

(5) Low chemical resistance to hot acids and alkali.

(6) Low scratch resistance.

Uses

(1) Making lenses, jewellery, artificial eyes, dentures.

(2) Aircraft light fixtures, automotive appliances.

(3) Paints, adhesives, emulsions, T.V screens, guards.

(4) A casting resin, in inks and coatings.

(5) In sheet form as a lightweight or shatter-resistant alternative to glass.

5.9.2 Poly-paraphenylene terephthalamide (Kevlar)

Kevlar is a type of plastic with a very high tensile strength.

Preparation : It is synthesized in solution from the monomers 1, 4-phenylene-diamine (para-phenylenediamine) and terephthaloyl chloride by a condensation reaction yielding hydrochloric acid as a byproduct (Fig. 5.14).

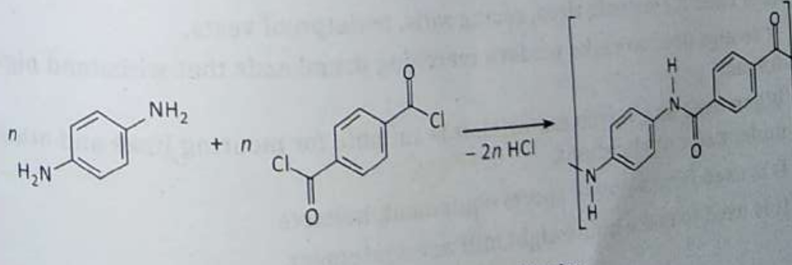


Fig. 5.14 : Preparation of kevlar

Here, the repeating units form chains and these chains have cross-linked interchain hydrogen bonds. These intermolecular hydrogen bonds formed between the carbonyl groups and NH- centers give the material its super high-tensile strength. Additional strength is derived from aromatic stacking interactions between adjacent strands. These chains line up parallel to each other on their own, just like liquid crystals, showing nematic behavior (Fig. 5.15).

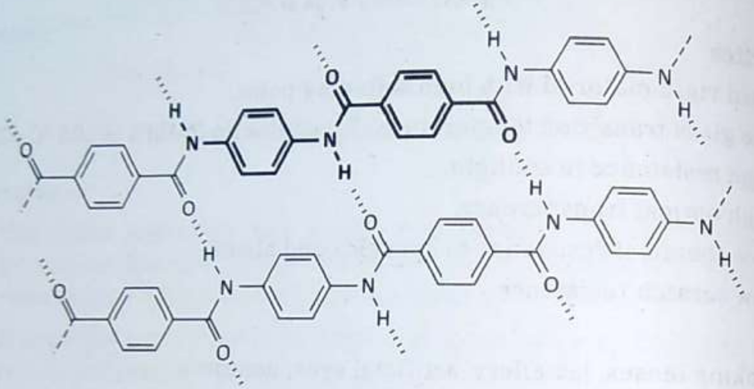


Fig. 5.15 : Repeating unit of kevlar

Properties

(1) It sustains cryogenic temperatures (–196 °C).

(2) It has high resistance to heat.

(3) It has high tensile strength of about 8 times more than that of a steel wire.

(4) It is light in weight for a strong material.

(5) It is highly resistant to abrasion.

Uses

(1) It is used for bicycle tires, racing sails, bulletproof vests.

(2) It is also used to make modern marching drumheads that withstand high impact.

(3) When used as a woven material, it is suitable for mooring lines and other underwater applications.

(4) It is used for making of sports equipment, helmets.

(5) It is used to make lightweight military equipment.

5.10 Review Questions

(1) Define terms: (i) Polymers (ii) Monomer (iii) Polymerization.

(2) Classify polymers based on the polymerization mechanism.

(3) Differentiate between addition and condensation polymerization.

(4) Differentiate between thermoplastic and thermoset polymers.

(5) Explain the concept of glass transition and melting transition in polymers.

(6) Give the significance of melting and glass transition temperatures

(7) List the factors affecting melting and glass transition temperatures.

(8) What are conducting polymers? Explain the different types of conducting polymers.

(9) Write a note on: Conduction in polymers by doping.

(10) What is molecular weight of polymer? How is it calculated by two different methods?

(11) Discuss the different additives that induce compounding of plastic.

(12) Give the structure, properties and applications of PMMA and Kevlar.

(13) How is the fabrication of plastic done? Discuss any one method.

(14) Describe the process with the advantages and disadvantages of the fabrication procedures:
   (i) Injection moulding
   (ii) Compression moulding
   (iii) Transfer moulding
   (iv) Extrusion moulding.

✻✻✻

CHAPTER 6

WATER

6.1 Introduction

Water is a universal solvent. It is one of the basic necessities of life and the most abundant commodity in nature. Natural water may be classified as surface water, underground water, rain water and sea water. Other than for drinking and household purposes, it is mainly required for agricultural and industrial purposes.

Hard and soft water

Sr. No.	Hard water	Soft water
(1)	It contains dissolved salts of higher valent metal ions mainly Ca^{2+} and Mg^{2+}.	It does not contain dissolved salts of hardness causing metal ions.
(2)	It does not give lathering with soap and produces scum (precipitate).	It gives lathering with soap.

6.2 Impurities in Water

Natural water is contaminated due to different types of impurities. The impurities present in water influence its characteristics such as colour, turbidity, taste, odour, acidity.

Disadvantages of using hard water

The disadvantages of hard water are listed below,

Domestic use

(1) **Washing :** No lather formation, wastage of soap.

(2) **Bathing :** The resulting scum sticks on body.

(3) **Cooking :** Due to dissolved salts, boiling point of water is elevated, causing unnecessarily wastage of time and fuel.

(4) **Drinking :** Bad effect on metabolic system. Calcium oxalate stones may develop in urinary tracts, if used regularly. Also it causes deposition of calcium in the bone joints.

Industrial use

(1) **Textiles :** Loss of soaps during washing of yarn and fabrics. Scum sticks on fabric and dyeing is not uniform. Also Fe, Mn etc. salts leave colored spots on fabrics.

(2) **Sugar :** Crystallization of sugar is affected.

(3) **Paper :** React with chemicals to provide smooth and glossy finishing to paper. Iron salts add unwarranted colour in paper.

(4) **Pharmaceuticals :** Undesirable products may be produced in medicines.

(5) Problems from boiler feed water are scales and sludge formation, corrosion, caustic embrittlement etc.

6.3 Hardness

Hardness of water is that characteristic which prevents the lathering of soap. The hardness is imparted due to the presence of certain salts of multivalent cations like Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Al^{3+} (heavy metals) dissolved in water.

Reaction

$$\underset{\substack{\text{Sodium stearate}\\ \text{(Sodium soap)}}}{2\,C_{17}H_{35}COONa} + CaCl_2 \longrightarrow \underset{\substack{\text{Calcium stearate}\\ \text{(Insoluble)}}}{(C_{17}H_{35}COO)_2Ca} + 2\,NaCl$$

The precipitate formed is called *scum*.

Hardness is classified as

(1) **Temporary hardness** (carbonate/alkaline hardness) is caused by the soluble bicarbonates of Ca and Mg. These soluble bicarbonates decompose to form insoluble precipitates when the water is heated. Hence, temporary hardness is removed by mere boiling and filtering off the precipitates formed.

$$Ca(HCO_3)_2 \xrightarrow{\Delta} CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \xrightarrow{\Delta} Mg(OH)_2\downarrow + 2CO_2\uparrow$$

(2) **Permanent hardness** (non-carbonate/non-alkaline hardness) is due to the more soluble chlorides, sulphates, nitrates of Ca, Mg, Fe and other heavy metals. Permanent hardness removal needs softening techniques.

Unit : mg/L or ppm (parts per million) of $CaCO_3$ equivalent

Hardness is the number of milligrams of $CaCO_3$ equivalent hardness of a constituent present in 1 L of water.

1 mg constituent/L water = 1 mg constituent/10^6 mg water

as 1 L water = 10^6 mg water, density of water being 1 g/cm^3

i.e. 1 part of constituent/10^6 parts of water or parts per million (10^6)

∴ mg/L = parts per million (ppm)

The $CaCO_3$ equivalent for a given quantity of constituent (mg/L), is expressed as,

$$\frac{\text{Weight of the constituent(mg/L)} \times \text{Chemical equivalent of } CaCO_3 \text{ (Equivalent weight of } CaCO_3)}{\text{Chemical equivalent of the constituent (Equivalent weight of constituent)}}$$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{n}$$

where n is either the positive or negative charge on the ions (present in the constituent)

Other units

1 ppm or 1 mg/L of $CaCO_3$ equivalent = 0.1° French (Fr).

It is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

1 ppm or 1 mg/L of $CaCO_3$ equivalent = 0.07° Clarke (Cl).

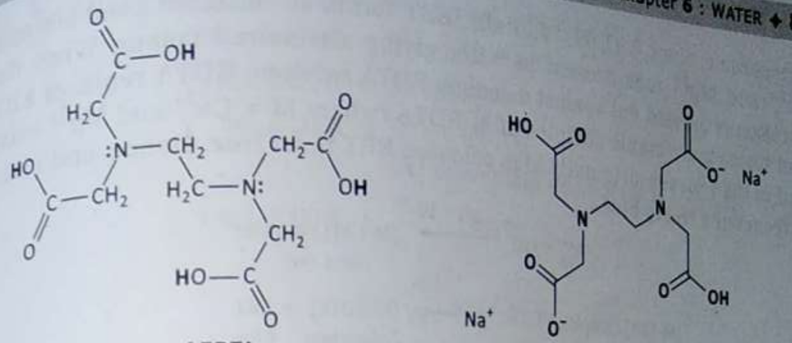
It is parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

6.4 Determination of Hardness by EDTA Method

EDTA (ethylenediaminetetraacetic acid) method is employed to determine hardness of water. It is a titrimetric, complexometric method.

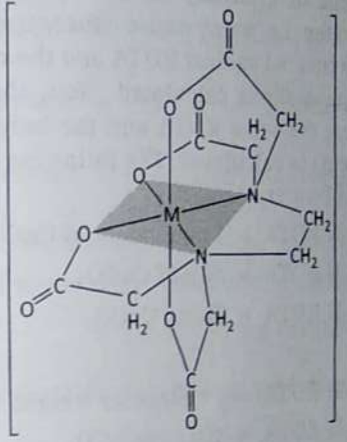
EDTA, written as H_4Y, is a common ligand in complexometric titrations. It has four carboxyl groups and two amine groups that can act as electron pair donors (Lewis bases). EDTA used as the disodium salt, Na_2H_2Y, yields an anion which forms complex with hardness causing divalent cations like Ca^{2+} and Mg^{2+} (Fig. 6.1).

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$



(a) Structure of EDTA

(b) Structure of disodium salt of EDTA



(c) Complex of disodium salt of EDTA with divalent metal ion

Fig. 6.1 : Chemistry of EDTA to form complex

The titration is carried out in a basic buffer solution where the H^+ ions are removed as they are formed. This moves the position of equilibrium to the right and favours formation of the complex (Le Châtelier's principle). Also, for EDTA, $pKa_4 = 10.26$.

Thus, if the solution is buffered to about pH 10.3, most of the EDTA will exist as Y^{4-} ions. The metal ions will not have to remove the hydrogen ions from H_2Y^{2-}. They can react directly according to the equation,

$$M^{2+} + Y^{4-} \longrightarrow MY^{2-}$$

Consequently, above pH 10.3, most metal ions react quantitatively with EDTA. Hence, during titration, pH of water is maintained at pH 10 using NH_4OH-NH_4Cl buffer and then indicator is added. The indicator used is

Eriochrome black-T (EBT). Initially, EBT forms an unstable complex with Ca^{2+} and Mg^{2+} ions present in water giving a wine-red colour. When the titration is carried out against disodium EDTA solution, EDTA replaces EBT and forms more stable complex of M-EDTA (where M = Ca^{2+} and Mg^{2+} ions) and in the process, originally blue coloured EBT is set free. Hence, end-point is from wine red to blue.

$$M^{2+} + EBT \xrightarrow{pH = 10} \underset{\text{Wine red}}{[M\text{-}EBT]\ \text{complex}}$$

$$\underset{\text{Wine red}}{[M\text{-}EBT]\ \text{complex}} + EDTA \longrightarrow \underset{\text{Colourless}}{[M\text{-}EDTA]} + \underset{\text{Blue}}{EBT}$$

In actual practice, while determining the hardness of unknown sample of water, standard hard water (i.e. water whose concentration in terms of $CaCO_3$ equivalent is known) is titrated against EDTA and the concentration of EDTA in terms of $CaCO_3$ equivalent is calculated. Now, the unknown sample of water is titrated against the same EDTA and the hardness of water sample (i.e. its $CaCO_3$ equivalent) is calculated. The following relations are useful to calculate the hardness of water.

$$1000 \text{ mL } 1 \text{ N EDTA} = 1 \text{ equivalent of } CaCO_3$$
$$1000 \text{ mL } 1 \text{ N EDTA} \equiv 50 \text{ g of } CaCO_3$$
$$1 \text{ mL of } 1 \text{ N EDTA} \equiv 50 \text{ mg } CaCO_3$$

OR

$$1000 \text{ mL } 1 \text{ M EDTA} = 1 \text{ molecular weight of } CaCO_3$$
$$1000 \text{ mL } 1 \text{ M EDTA} \equiv 100 \text{ g of } CaCO_3$$
$$1 \text{ mL of } 1 \text{ M EDTA} \equiv 100 \text{ mg } CaCO_3$$

With standard hard water sample, unknown water sample and EDTA, the steps and calculations given below are carried out for determining the hardness of unknown water sample.

Step 1 : EDTA solution is standardized with standard hard water (SHW).

Step 2 : Same EDTA used in step 1 is used to titrate unknown hard water sample (UHW).

Method : 50 mL of standard hard water (SHW) requires V_1 mL EDTA

(Given: Concentration of SHW = 1 mg/mL $CaCO_3$)

50 mL of sample hard water requires V_2 mL EDTA.

50 mL of sample hard water after boiling requires V_3 mL EDTA

(i) To determine $CaCO_3$ equivalent per mL EDTA,

$$50 \text{ mL SHW} \equiv V_1 \text{ mL EDTA}$$
$$V_1 \text{ mL EDTA} \equiv 50 \text{ mL SHW}$$
$$V_1 \text{ mL EDTA} \equiv 50 \text{ mg } CaCO_3$$

(As concentration of SHW = 1mg/mL $CaCO_3$)

$$\therefore\ 1 \text{ mL EDTA} = \frac{50}{V_1} \text{ ml SHW}$$
$$= \left(\frac{50}{V_1}\right) \text{ mg } CaCO_3$$

(ii) To find total hardness,

$$50 \text{ mL sample hard water} = V_2 \text{ mL EDTA} = \left(V_2 \times \frac{50}{V_1}\right) \text{ mg } CaCO_3$$
$$1000 \text{ mL sample hard water} = \left(V_2 \times \frac{50}{V_1} \times \frac{1000}{50}\right) \text{ mg } CaCO_3$$
$$\text{Total hardness} = \left(\frac{V_2}{V_1} \times 1000\right) \text{ mg/L or ppm}$$

(iii) To find permanent hardness,

$$50 \text{ mL sample hard water after boiling and filtration} = V_3 \text{ mL EDTA}$$
$$= \left(V_3 \times \frac{50}{V_1}\right) \text{ mg } CaCO_3$$

1000 mL sample hard water after boiling and filtration

$$= \left(V_3 \times \frac{50}{V_1} \times \frac{1000}{50}\right) \text{mg } CaCO_3$$
$$= \left(\frac{V_3}{V_1} \times 1000\right) \text{ mg } CaCO_3$$
$$\text{Permanent hardness} = \left(\frac{V_3}{V_1} \times 1000\right) \text{ mg/L or ppm}$$

(iv) To find temporary hardness,

$$\text{Total hardness} = \text{Temporary hardness} + \text{Permanent hardness}$$
$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$
$$= \left(\frac{V_2}{V_1} \times 1000\right) - \left(\frac{V_3}{V_1} \times 1000\right)$$
$$= \frac{1000}{V_1}\left(V_2 - V_3\right) \text{ mg/L or ppm}$$

6.5 Softening of Water

Softening of water means removal of hardness causing salts from water. Hardness is the undesired property of water which not only produces scum while washing but also causes nuisance in various industries. Hence, it needs to be softened initially before use. It involves external and internal treatment.

External : It involves removal of hardness causing salts from the water using methods such as lime-soda method, zeolite method and ion-exchange method.

Internal : It involves addition of certain chemicals to the water. In the process, an ion is not allowed to show its original property by complexing or converting it into other more soluble salt by adding a suitable reagent. The added chemicals either precipitate the scale forming impurities as a sludge (which can be removed by a blow-down operation) or the added chemical convert the scale forming impurities into compounds that stay in the dissolved form in the boiler thereby causing no harm. It includes methods like colloidal conditioning, phosphate conditioning, carbonate conditioning, calgon conditioning, treatment with sodium aluminate, electrical conditioning and complexometric methods.

6.5.1 Ion Exchange Process

Principle : A reversible exchange of ions occurs between the porous, stationary ion-exchange phase and the external liquid phase. The cation exchange resins are capable of exchanging rapidly cations like Ca^{2+} and Mg^{2+} from water by H^{1+} ions from cation exchange resin. The anion exchange resins are capable of exchanging rapidly anions like Cl^{1-}, SO_4^{2-} from water by OH^{1-} ions from anion exchange resin.

When ion exchange capacities are lost (resins are exhausted), the water will no longer be softened. The exhausted cation exchanger is regenerated by passing dilute HCl or H_2SO_4. The exhausted anion exchanger is regenerated by treating it with a dilute NaOH solution.

$$\begin{aligned} Ca^{2+} + RH_2 &\longrightarrow RCa + 2\,H^{1+} \\ 2\,Cl^{1-} + R'(OH)_2 &\longrightarrow R'Cl_2 + 2\,OH^{1-} \\ H^{1+} + OH^{1-} &\longrightarrow H_2O \\ RCa + 2\,HCl &\longrightarrow CaCl_2 + RH_2 \\ R'Cl_2 + 2\,NaOH &\longrightarrow R'(OH)_2 + 2\,NaCl \end{aligned}$$

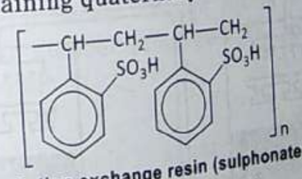
Total hardness of water ≡ Total volume of HCl (the acid) required for regeneration of cation exchanger in terms of mg $CaCO_3$ equivalent

Or Total hardness of water ≡ Total volume of NaOH (the alkali) required for regeneration of anion exchanger in terms of mg $CaCO_3$ equivalent.

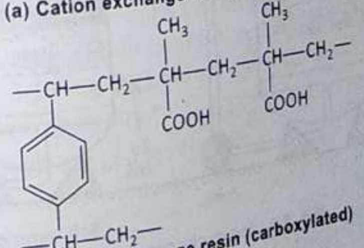
For the purpose of hardness removal, cations like Ca^{2+} and Mg^{2+} are exchanged for H^{1+} ions from the hydrogen cation exchanger along with other cations (non-hardness causing). Thus, the hardness factor of water is removed. Further to improve the quality of water, it is then passed through an anion exchanger where anions like Cl^{1-}, SO_4^{2-} are exchanged for OH^{1-} ions from the anion exchanger. The water thus obtained is free from all the dissolved salts and only $H^{1+} + OH^{1-}$ (H_2O) is obtained. Thus, demineralized water is obtained.

Ion exchange resins are water insoluble, cross-linked, long chain organic polymers with porous structure and the functional group attached to the chains undergo the ion-exchange property. Resins containing acidic functional groups (-COOH, $-SO_3H$) are capable of exchanging their H^{1+} ions with other cations. Resins containing basic functional groups [quaternary ammonium salt $(R_1R_2R_3)\text{-}N^{1+}OH^{1-}$] are capable of exchanging their OH^{1-} ions with other anions.

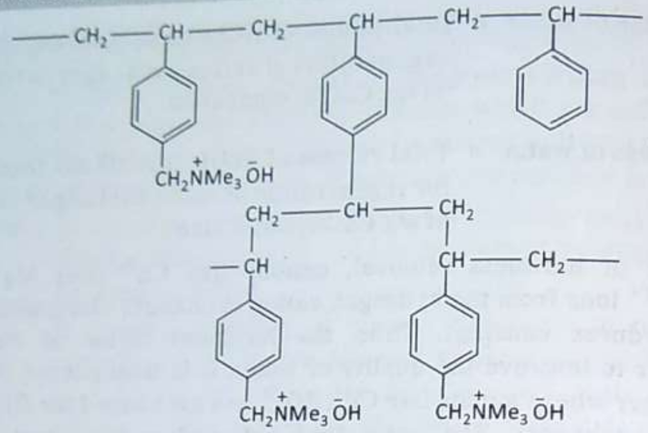
Ion exchangers have generally styrene-divinylbenzene as a basic unit. The cation exchange ion resins are sulphonated or carboxylated styrene-divinyl benzene copolymers and the anion exchange ion resins are styrene-divinyl benzene copolymers containing quaternary ammonium groups (Fig. 6.2).



(a) Cation exchange resin (sulphonated)



(b) Cation exchange resin (carboxylated)



(c) Anion exchange resin

Fig. 6.2 : Ion exchange resins

Process : A known volume of water is first passed over a cation exchange column at a specific rate, which removes cations from the water and equivalent amount of H^{1+} ions are released from column to water. After the cation exchange, the same batch of water is passed through anion exchange column at a specific rate, which removes anions from the water and equivalent amount of OH^{1-} ions are released from column to water. H^{1+} and OH^{1-} ions released from the cation and anion exchange respectively get combined to form water molecule (Fig. 6.3). Thus, the treated water is free from cations as well as anions. Hence, it is called as deionized or demineralised water. This exchange of ions continues till the exchange capacity of the ion exchangers ceases.

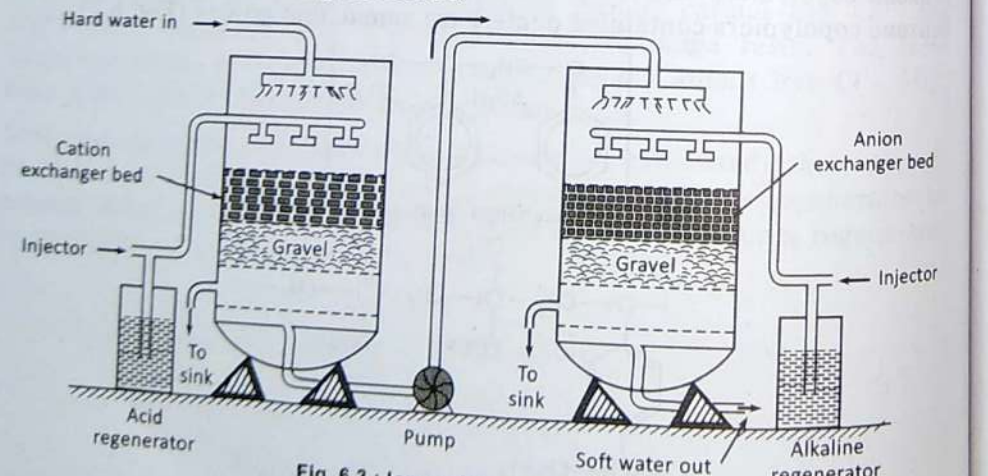


Fig. 6.3 : Ion exchange process

Regeneration : The supply of hard water is stopped and the exhausted ion exchangers are regenerated. The cation exchanger is regenerated by passing a solution of dilute HCl or H_2SO_4. The anion exchanger is regenerated by passing a solution of dilute NaOH. The columns are then washed with deionized water.

Advantages

(1) The ion exchange apparatus, once set up, is easy to operate and control.

(2) The ion exchange resins can be regenerated and reused.

(3) The residual hardness after the treatment is 0 ppm.

(4) The water can be used in high pressure boilers as it is free from alkalinity.

(5) The process is suitable to soften highly acidic or alkaline water.

Limitations

(1) The equipment is costly and the ion exchangers are expensive.

(2) Turbid water reduces the process output. Hence, the turbidity must be removed initially by sedimentation, coagulation or filtration.

6.6 Dissolved Oxygen, Biological Oxygen Demand and Chemical Oxygen Demand

The chemical characteristics that describe the waste water are dissolved oxygen, biological oxygen demand and chemical oxygen demand.

6.6.1 Dissolved Oxygen (DO)

The dissolved oxygen (DO) is the oxygen dissolved in water. Dissolved oxygen is expressed as the number of oxygen (O_2) molecules in milligrams dissolved in 1000 mL of water.

Unit : mg/L or ppm

Dissolved oxygen is freely available to aquatic life. It is vital to aquatic flora and fauna. It is also useful to prevent the odours. One of the best indicators that tell the health of a water body is dissolved oxygen parameter. Dissolved oxygen can range from 0-18 mg O_2/L. Most natural water systems require 5-6 mg O_2/L to support a diverse population.

Factors affecting dissolved oxygen levels are,

(i) Water temperature

(ii) Aquatic plant population

(iii) Stream flow

(iv) Atmospheric pressure

(v) Human activities

(v) Water discharge

(vi) Organic waste

Dissolved oxygen can be determined by Winkler's method (iodometric titration), by titrating a known volume of water sample against standard sodium thiosulphate ($Na_2S_2O_3$).

Dissolved oxygen (DO) can be calculated as follows,

$$N_aV_a = N_bV_b$$

N_a = Normality of sample (DO) solution

V_a = Volume of sample (DO) solution

N_b = Normality of $Na_2S_2O_3$

V_b = Volume of $Na_2S_2O_3$

Weight of dissolved oxygen per litre (DO) is,

$$\frac{V_b \times N_b \times 8 \times 1000}{V_a} \text{ mg of } O_2$$

6.6.2 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is defined as the amount in milligrams of oxygen required to oxidize the oxidizable material present in 1000 mL of water using a strong oxidizing agent such as acidified potassium dichromate ($K_2Cr_2O_7$).

Unit : mg/L or ppm

Chemical oxygen demand is calculated by refluxing a known volume of the water sample (V mL) with a known excess of $K_2Cr_2O_7$ (Y mL) and dilute H_2SO_4 in presence of Ag_2SO_4 catalyst for about two hours. The oxidizable material gets completely oxidized to produce CO_2 and H_2O.

Initially, known excess of $K_2Cr_2O_7$ (Y mL) is titrated against standard Mohr's salt solution (*x* N FAS i.e. ferrous ammonium sulphate) using ferroin indicator (blank titration reading). The unreacted $K_2Cr_2O_7$ - left over after oxidation is titrated against the same *x* N FAS using ferroin indicator (back titration reading). The $K_2Cr_2O_7$ consumed for oxidation is equivalent to the blank minus back FAS titration readings (V_1 mL).

The $K_2Cr_2O_7$ consumed for oxidation is equivalent to the oxygen required for the oxidation of oxidizable material.

$$COD = \frac{\text{Volume of oxidizing agent consumed } (V_1) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken (V)}}$$

$$COD = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken}}$$

Blank = Volume of burette solution (FAS) required to consume the total (i.e. known excess) $K_2Cr_2O_7$ added.

Back = Volume of burette solution (FAS) required to consume the excess $K_2Cr_2O_7$ left over after oxidizing the oxidizable matter in water.

6.6.3 Biological Oxygen Demand (BOD)

Biological oxygen demand (BOD) is defined as the amount in milligrams of oxygen required by microorganisms to oxidize the organic matter present in 1000 mL of water over a period of 5 days under aerobic conditions at 20 °C.

Unit : mg/L or ppm

Biological oxygen demand can be determined by diluting a known volume (V mL) of water sample to a known volume (V_1 mL) with distilled water. Equal quantities (V_2 mL) of the diluted water are taken in two biological oxygen demand bottles.

In the first bottle $(DO)_1$ is determined immediately by iodometric titration against standard sodium thiosulphate (*x* N $Na_2S_2O_3$). The titre value obtained (*a* mL) is the blank value and it is used to calculate the dissolved oxygen available at the start of the experiment. The water in the second bottle is incubated under aerobic conditions for 5 days and then $(DO)_2$ is determined by iodometric titration against standard sodium thiosulphate (*x* N $Na_2S_2O_3$). The titre value obtained (*b* mL) is the back value and it is used to calculate the dissolved oxygen remaining or left over after 5 days of aerobic oxidation.

$(DO)_1$ implies the dissolved oxygen present in water at the beginning of the experiment. This dissolved oxygen will be consumed by microbes under aerobic conditions. Therefore, the DO on the fifth day of the experiment will be decreased over day one. Hence, the difference in $(DO)_1$ and $(DO)_2$ implies the dissolved oxygen consumed by the microbes present in V_2 mL sample.

$(DO)_1$ = Dissolved oxygen of diluted water sample (V_2) immediately after its preparation.

$(DO)_2$ = Dissolved oxygen of diluted water sample (V_2) after incubation for 5 days at 20 °C.

$$\therefore \text{BOD} = \frac{(a-b) \times x\,\text{N} \times 8 \times \text{V}_1}{\text{V}_2} \times \frac{1000}{\text{V}}$$

$$\text{BOD} = \frac{(\text{Blank} - \text{Back}) \times \begin{pmatrix}\text{Normality}\\ \text{of Na}_2\text{S}_2\text{O}_3\end{pmatrix} \times 8 \times \begin{pmatrix}\text{Volume of}\\ \text{sample}\\ \text{water after}\\ \text{dilution}\end{pmatrix}}{\begin{pmatrix}\text{Volume of diluted sample water}\\ \text{taken for titration}\end{pmatrix}} \times \frac{1000}{\begin{pmatrix}\text{Volume of}\\ \text{initial sample}\\ \text{water taken}\end{pmatrix}}$$

The same formula can be represented as below,

$$\therefore \text{BOD} = \frac{a \times x\,\text{N} \times 8 \times 1000}{\text{V}_2} - \frac{b \times x\,\text{N} \times 8 \times 1000}{\text{V}_2} \times \frac{\text{V}_1}{\text{V}}$$

$$\therefore \text{BOD} = [(\text{DO})_1 - (\text{DO})_2] \times \frac{\text{Volume of sample after dilution (V}_1)}{\text{Volume of initial sample water taken (V)}}$$

COD is the total amount of oxygen required to oxidize all oxidizable impurities in a sample of sewage waste. COD is always greater than BOD since COD measurement involves both biodegradable and non-biodegradable oxidizable impurities. The difference in COD and BOD is equivalent to the quantity of biologically resistant oxidizable impurities.

Significance : COD and BOD serve as a yardstick to measure the effect an effluent (effect of oxidizable matter in water) will have on the receiving water body. However, COD is less specific, since it measures everything that can be chemically oxidized, rather than just levels of biodegradable organic matter.

Many governments impose strict regulations regarding the maximum COD allowed in wastewater before they can be returned to the environment.

BOD can be used as a gauge to check the effectiveness of wastewater treatment plants.

6.7 Water Purification - Membrane Technology

Membrane processes cover a group of separation processes in which the characteristics of a membrane (porosity, selectivity, electric charge) are used to separate the components of a solution or a suspension. In these processes, the feed stream is separated into two: the fraction that permeates through the membrane, called the permeate and the fraction containing the components that have not been transported through the membrane, usually called the *retentate*. The size of the components to be separated and the nature and magnitude of the driving force provide criteria for a classification of the membrane separation processes, as shown in the table.

Classification of membrane separation processes [Bowen (1991)]

Name of Process	Driving Force	Separation Size Range
Microfiltration	Pressure gradient	10 - 0.1 μm
Ultrafiltration	Pressure gradient	< 0.1 μm - 5 nm
Reverse osmosis (hyperfiltration)	Pressure gradient	< 5 nm
Electrodialysis	Electric field gradient	< 5 nm
Dialysis	Concentration gradient	< 5 nm

6.7.1 Electrodialysis

Principle : In this process, ions are driven through semi-permeable membrane under the influence of electric current, where the ions get separated. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes.

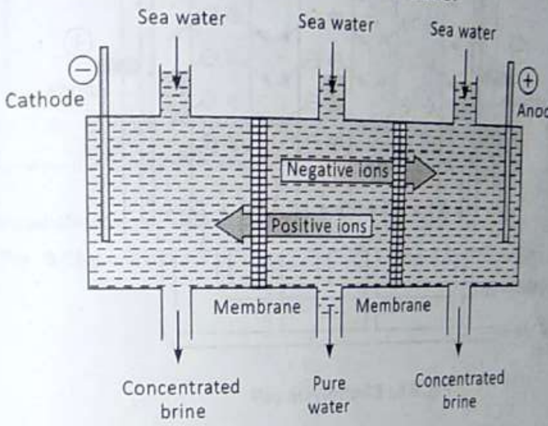


Fig. 6.4 : Electrolysis - line diagram

In an electrodialysis stack, the dilute feed stream and brine or concentrate stream are allowed to flow through the appropriate cell compartments formed by the ion exchange membranes. When direct current is passed through saline water, the positively charged ions (generally sodium ions) move towards cathode and the negatively charged ions (generally chloride ions) move towards anode. The overall result of the electrodialysis process is an ion concentration increase in the concentrate stream with a depletion of ions in the dilute solution feed stream (Fig. 6.4). The efficiency of the process is achieved by using ion-selective membranes.

Process : In actual practice, an electrodialysis cell consists of a large number of paired sets of rigid plastic membranes (Fig. 6.5). Saline water is passed under a pressure (of about 5 to 6 kg/m^2) between membrane pairs. An electric potential is applied perpendicular to the direction of water flow. The cation exchange membrane allows only cations to pass through it, leaving behind anions. Similarly, an anion exchange membrane allows only anions to pass through it, leaving behind cations. Due to this, water in one compartment of the cell is deprived of the salt and thus the salt concentration in the adjacent compartments to that compartment is increased. Hence, we get alternate streams of pure water and concentrated brine.

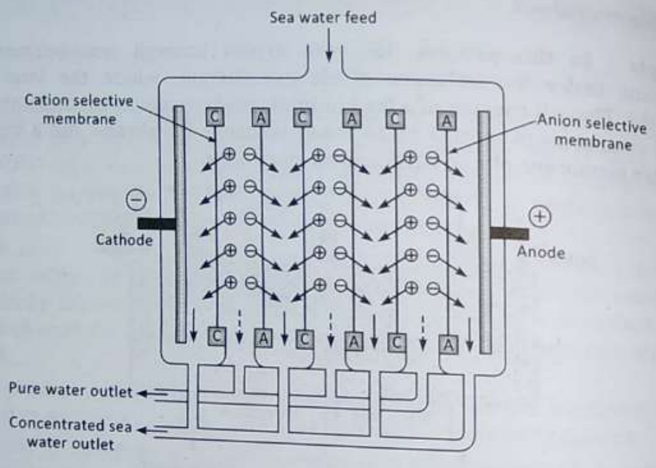


Fig. 6.5 : Electrolysis cell

It can be operated as continuous production or batch production processes. In a continuous process, feed is passed through a sufficient number of stacks placed in series to produce the final desired product quality. In batch processes, the diluate and/or concentrate streams are re-circulated through the electrodialysis systems until the final product or concentrate quality is achieved.

Applications : Electrodialysis is usually applied to deionization of aqueous solutions. However, desalting of sparingly conductive aqueous organic and organic solutions is also possible.

Advantages

(1) The unit is compact.

(2) The cost of installation of the plant as well as its operation is economical.

(3) If availability of electricity is easy, it is a suitable process.

6.7.2 Reverse Osmosis

Principle : Osmosis is a process in which when two aqueous solutions of different concentrations are separated by a semi-permeable membrane, water passes through the membrane from lower to higher concentration due to osmotic pressure. Reverse osmosis is process in which solvent moves through the membrane from higher to lower concentration when subjected to a hydrostatic pressure greater than the osmotic pressure (Fig. 6.6).

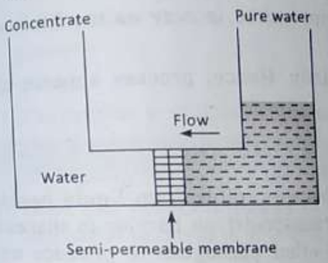


Fig. 6.6(a) : Osmosis

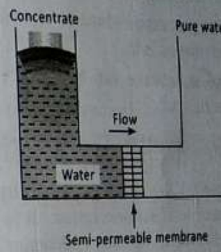


Fig. 6.6(b) : Reverse osmosis

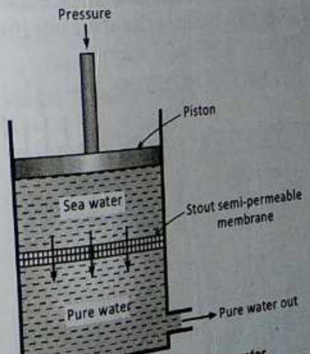


Fig. 6.7 : Process of osmosis for purification of sea water

Process : In the process, the pressure (of about 15 to 40 kg/cm^2) is applied to the water (solvent) to be purified, where pure water is forced to pass through the semi-permeable membrane and the dissolved impurities are retained. Thus, the pure water is removed from contaminants unlike other methods, which involve removal of impurities from the water to purify it.

Application : The process is useful to purify sea water for domestic use (Fig. 6.7).

Advantages

(1) It removes ionic, non-ionic, colloidal and high molecular weight organic matter.

(2) Colloidal silica, which is not removed by any process, can be removed by reverse osmosis.

(3) The process is economical and maintenance is easy as the lifespan of membrane is high.

(4) The membrane can be replaced easily. Hence, process appears to be continuous.

6.7.3 Ultrafiltration

Principle : Ultrafiltration physically separates solids from liquid based on the principle of size-exclusion. It is a pressure-driven barrier to suspended solids, bacteria, viruses, endotoxins and other pathogens to produce water with very high purity and low silt density. It is a membrane filtration process which uses hydrostatic pressure to force water through a semi-permeable membrane (Fig. 6.8). The pore size of the ultrafiltration membrane is usually 103 - 106 Daltons or 0.005 to 0.1 micron.

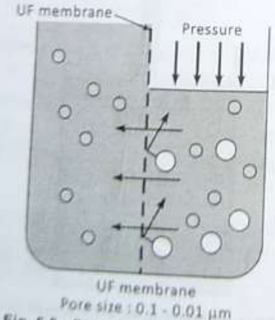


Fig. 6.8 : Process of ultrafiltration

Process : During the process, when pressure (about 200 to 700 kPa) is applied on the solvent (water), suspended solids and solutes of high molecular weight are retained, while water and low molecular weight solutes are passed through the membrane.

Applications

(1) The process is used in blood dialysis.

(2) It is used to remove particulates and macromolecules from raw water to produce potable water.

(3) It is used extensively in the dairy industry; particularly in the processing of cheese whey to obtain whey protein concentrate (WPC) and lactose-rich permeate.

(4) It is useful in the filtration of effluent from paper pulp mill.

(5) Radiocarbon dating of bone collagen is carried out by ultrafiltration process.

Advantages

(1) The process is simple to automate and plant is compact.

(2) There is no need for chemicals (coagulants, flocculates, disinfectants, pH adjustment) during the process. Thus, it is environmentally friendly.

(3) Good and constant quality of the treated water in terms of particle and microbial removal is obtained.

6.8 Solved Numericals

Example 1 : Calculate the temporary, permanent and total hardness for a water sample in ppm containing following salts : $Mg(HCO_3)_2$ = 18.25 ppm, $Al(NO_3)_3$ = 12 ppm, $CaCO_3$ = 15 ppm.

Solution : Refer the given table.

Constituent (Salt/Chemical/Ion)	Quantity (ppm)	Conversion factor = Quantity × (Eq.wt of $CaCO_3$/ Eq.wt of constituent)	$CaCO_3$ equivalent (ppm)	Type of Hardness
$Mg(HCO_3)_2$	18.25	18.25 × 50/73	12.5	Temporary
$Al(NO_3)_3$	12	12 × 50/71	8.45	Permanent
$CaCO_3$	15	15 × 50/50	15	Temporary

Temporary hardness = 12.5 +15 = 27.5 ppm

Permanent hardness = 8.45 = 8.45 ppm

Total hardness = 35.95 ppm

Example 2 : Two samples of water A and B were analysed for their salt content.

(i) Sample A was found to contain 42 mg/L of $MgCO_3$.

(ii) Sample B was found to contain 41mg/L of $Ca(NO_3)_2$ and 1 mg/L of SiO_2.

Calculate hardness of each sample and state which is harder.

Solution : Refer the table given below,

Constituent (Salt/Chemical/Ion)	Quantity (ppm)	Conversion factor = Quantity × (Eq.wt of $CaCO_3$/ Eq.wt of constituent)	$CaCO_3$ equivalent (ppm)	Type of Hardness
$MgCO_3$	42	42 × 50/42	50	Temporary
$Ca(NO_3)_2$	41	41 × 50/82	25	Permanent
SiO_2	1	Does not contribute to hardness		

Sample A is harder than B.

Example 3 : How much of $CaSO_4$ should be dissolved per litre to give 210 ppm hardness.

Solution :

The $CaCO_3$ equivalent hardness caused by $CaSO_4$ is 210 ppm

$$\text{Equivalent of } CaCO_3 \text{ for } CaSO_4 \equiv \frac{\left[\begin{array}{c}\text{Weight of the } CaSO_4(\text{mg/L}) \times \text{Chemical} \\ \text{equivalent of } CaCO_3 \text{ (Eq.wt of } CaCO_3)\end{array}\right]}{\left[\begin{array}{c}\text{Chemical equivalent of the } CaSO_4 \\ \text{(Eq.wt of } CaSO_4)\end{array}\right]}$$

$$\therefore 210 = \frac{\text{Weight of the } CaSO_4 \text{ (mg/L)} \times 50}{68}$$

$\therefore$ Weight of the $CaSO_4$ (mg/L) = 285.60

$\therefore$ 285.60 mg $CaSO_4$ should be dissolved per litre.

Example 4 : 50 mL of standard hard water (1 g $CaCO_3$/L) requires 20 mL of EDTA solution. 50 mL of water sample consumes 16 mL EDTA. 50 mL of boiled and filtered water sample consumes 10 mL of EDTA. Calculate the hardness of sample.

Solution : Strength of SHW,

Standard hard water contains 1 g $CaCO_3$ per 1000 mL

$$= 1000 \text{ mg } CaCO_3 \text{ per } 1000 \text{ mL}$$

$$1 \text{ mL SHW} = 1 \text{ mg } CaCO_3$$

(i) Standardization of EDTA,

$$\begin{aligned} 20 \text{ mL of EDTA solution} &\equiv 50 \text{ mL SHW} \\ &= (50 \times 1) \text{ mg } CaCO_3 \text{ equivalent} \\ 1 \text{ mL EDTA} &= 50 \times \frac{1}{20} = 2.5 \text{ mg } CaCO_3 \text{ equivalent} \end{aligned}$$

(ii) To calculate total hardness of water,

$$\begin{aligned} 50 \text{ mL sample water} &\equiv 16 \text{ mL EDTA} \\ &= (16 \times 2.5) \text{ mg } CaCO_3 \text{ equivalent} \\ 1000 \text{ mL water} &\equiv (16 \times 2.5 \times 1000/50) \\ &= 800 \text{ mg } CaCO_3 \text{ equivalent} \\ \text{Total hardness} &= 800 \text{ ppm} \end{aligned}$$

(iii) To calculate permanent hardness of water,

$$\begin{aligned} 50 \text{ mL of boiled and filtered sample water} &\equiv 10 \text{ mL EDTA} \\ &= (10 \times 2.5) \text{ mg } CaCO_3 \text{ equivalent} \\ 1000 \text{ mL boiled water} &\equiv (10 \times 2.5 \times 1000/50) \\ &= 500 \text{ mg } CaCO_3 \text{ equivalent} \\ \text{Permanent hardness} &= 500 \text{ ppm} \end{aligned}$$

(iv) To calculate temporary hardness of water,

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ \text{Temporary hardness} &= 800 - 500 = 300 \text{ ppm} \end{aligned}$$

Example 5 : 100 mL of standard hard water (1.2 g $CaCO_3$/L) requires 38 mL of EDTA solution. 120 mL of water sample consumes 18 mL EDTA. 150 mL of boiled and filtered water sample consumes 12 mL of EDTA. Calculate the hardness of sample.

Solution : Strength of SHW,

Standard hard water contains 1.2 g $CaCO_3$ per 1000 mL

= 1200 mg $CaCO_3$ per 1000 mL

$\therefore$ 1 mL SHW = 1.2 mg $CaCO_3$

(i) Standardization of EDTA,

38 mL of EDTA solution $\equiv$ 100 mL SHW

= (100×1.2) mg $CaCO_3$ equivalent

1 mL EDTA = $(100 \times 1.2/38)$

= 3.158 mg $CaCO_3$ equivalent

(ii) To calculate total hardness of water,

120 mL sample water $\equiv$ 18 mL EDTA

= (18×3.158) mg $CaCO_3$ equivalent

1000 mL water $\equiv$ $(18 \times 3.158 \times 1000/120)$

= 473.70 mg $CaCO_3$ equivalent

Total hardness = 473.70 ppm

(iii) To calculate permanent hardness of water,

150 mL of boiled and filtered sample water $\equiv$ 12 mL EDTA

= (12×3.158) mg $CaCO_3$ equivalent

1000 mL boiled water $\equiv$ $(12 \times 3.158 \times 1000/150)$

= 252.64 mg $CaCO_3$ equivalent

Permanent hardness = 252.64 ppm

(iv) To calculate temporary hardness of water,

Temporary hardness = Total hardness – Permanent hardness

Temporary hardness = 473.70 – 252.64 = 221.06 ppm

Example 6 : 50 mL sample hard water required 6 mL of N/10 disodium EDTA for titration. After boiling and filtration, the same volume required 4.2 mL of EDTA. Calculate the temporary hardness.

Solution : As 1000 mL 1 N EDTA $\equiv$ 50 gm of $CaCO_3$

1 mL 1 N EDTA $\equiv$ 50 mg of $CaCO_3$

(i) To calculate total hardness of water,

50 mL water sample $\equiv$ 6 mL of 0.1 N EDTA

1000 mL water sample = $(1000/50 \times 6)$ mL of 0.1 N EDTA

= 120 mL of 0.1 N EDTA

As 1 mL of 1 N EDTA $\equiv$ 50 mg of $CaCO_3$

120 mL of 0.1 N EDTA = $(120 \times 0.1 \times 50)$ mg of $CaCO_3$

= 600 mg of $CaCO_3$

1000 mL water sample = 600 mg of $CaCO_3$

Total hardness of water = 600 ppm

(ii) To calculate permanent hardness of water,

50 mL of boiled water = 4.2 mL of 0.1 N EDTA

1000 mL of boiled water = $(1000/50 \times 4.2)$ mL of 0.1 N EDTA

= 84 mL of 0.1 N EDTA

As 1 mL of 1N EDTA $\equiv$ 50 mg of $CaCO_3$

84 mL of 0.1N EDTA = $(84 \times 0.1 \times 50)$ mg of $CaCO_3$

= 420 mg of $CaCO_3$

1000 mL of boiled water = 420 mg of $CaCO_3$

Permanent hardness = 420 ppm

(iii) To calculate temporary hardness of water,

Temporary hardness = Total hardness – Permanent hardness

Temporary hardness = 600 – 420 = 180 ppm

Example 7 : 40 mL of sample water consumed 10 mL 0.04 M EDTA before boiling and 8 mL of same EDTA after boiling. Calculate the total, permanent and temporary hardness.

Solution : As 1000 mL 1 M EDTA $\equiv$ 100 g of $CaCO_3$

1 mL 1 M EDTA $\equiv$ 100 mg of $CaCO_3$

(i) To calculate total hardness of water,

40 mL sample water = 10 mL of 0.04 M EDTA

1000 mL water sample = $(1000/40 \times 10)$ mL of 0.04 M EDTA

= 250 mL of 0.04 M EDTA

As 1 mL of 1 M EDTA $\equiv$ 100 mg $CaCO_3$

250 mL of 0.04 M EDTA = $(250 \times 0.04 \times 100)$ mg $CaCO_3$

= 1000 mg $CaCO_3$

1000 mL water sample = 1000 mg $CaCO_3$

Total hardness = 1000 mg/L

(ii) To calculate permanent hardness of water,

40 mL of boiled water $\equiv$ 8 mL of 0.04 M EDTA

1000 mL of boiled water = $(1000/40 \times 8)$ mL of 0.04 M EDTA

$= 200$ mL of 0.04 M EDTA

As 1 mL of 1 M EDTA $\equiv 100$ mg $CaCO_3$

200 mL of 0.04 M EDTA $= (200 \times 0.04 \times 100)$ mg $CaCO_3$

$= 800$ mg $CaCO_3$

1000 mL of boiled water $= 800$ mg $CaCO_3$

Permanent hardness $= 800$ mg/L

(iii) To calculate temporary hardness of water,

Temporary hardness = Total hardness – Permanent hardness

Temporary hardness $= 1000 - 800 = 200$ mg/L

Example 8 : After treating 50000 L of water by ion exchanger, the cationic resin required 350 L of 0.5 N HCl and anionic resin required 350 L of 0.5 N NaOH solutions for regeneration. Find the hardness of the above sample of water.

Solution :

Total hardness of water $\equiv$ Total volume of HCl or NaOH required for regeneration of ion exchange resin in terms of mg $CaCO_3$ equivalent

Total hardness of 50000 L water = 350 L of 0.5 N HCl

= 350 L of 0.5 N $CaCO_3$ equivalent

= (350×0.5) L of 1 N $CaCO_3$ equivalent

= 175 L of 1 N $CaCO_3$ equivalent

= (175×50) g of $CaCO_3$ equivalent

= 8750 g of $CaCO_3$ equivalent

$\therefore$ Hardness in 1 L water = 8750/50000 = 0.175 g of $CaCO_3$ equivalent

Hardness (mg $CaCO_3$ equivalent) in 1 L water = 175 mg of $CaCO_3$ equivalent

$\therefore$ Hardness of water = 175 mg/L

Alternate method

Total hardness of water $\equiv$ Total volume of HCl or NaOH required for regeneration of ion exchange resin in terms of mg $CaCO_3$ equivalent

Total hardness of water = Quantity of water softened (L) × Hardness (mg/L)

Given, total volume of HCl required for regeneration = 350 L of 0.5 N HCl

As 1000 mL (1 L) 1 N HCl $\equiv 50$ g $CaCO_3$

350 L of 0.5 N HCl $= (350 \times 0.5 \times 50)$ g $CaCO_3$

$= 8750$ g $CaCO_3$

$= 8750000$ mg $CaCO_3$

$\therefore$ Total volume of HCl required for regeneration = 8750000 mg $CaCO_3$

$\therefore$ Total hardness of water = 8750000 mg $CaCO_3$

Quantity of water softened (L) × Hardness (mg/L) = 8750000 mg $CaCO_3$

Given, Quantity of water softened = 50000 L

$50000 \times$ Hardness $= 8750000$

$\therefore$ Hardness = 175 mg/L

Example 9 : A water sample having hardness of 50 ppm was softened by ion exchange process. The exhausted cation exchanger required 400 L of 0.25 N HCl whereas anionic resin required 400 L of 0.25 N NaOH solutions for regeneration. Calculate the quantity of water softened using the ion exchange softner.

Solution :

Total hardness of water $\equiv$ Total volume of HCl or NaOH required for regeneration of ion exchange resin in terms of mg $CaCO_3$ equivalent

Total hardness of water = Quantity of water softened (L) × Hardness (mg/L)

Given, Total volume of HClrequired for regeneration = 400 L of 0.25 N HCl

As 1000 mL (1 L) 1 N HCl $\equiv 50$ g $CaCO_3$

400 L of 0.25 N HCl $= (400 \times 0.25 \times 50)$ g $CaCO_3$

$= 5000$ g $CaCO_3$

$= 5000000$ mg $CaCO_3$

$\therefore$ Total volume of HCl required for regeneration = 5000000 mg $CaCO_3$

$\therefore$ Total hardness of water = 5000000 mg $CaCO_3$

$\therefore$ Quantity of water softened (L) × Hardness (mg/L) = 5000000 mg $CaCO_3$

Given, Hardness = 50 L

$\therefore$ Quantity of water softened × Hardness = 5000000

$\therefore$ Quantity of water softened = 100000 L

Example 10 : 30 ml of waste water is mixed with 35 mL of acidified potassium dichromate and refluxed. The unreacted potassium dichromate required 12.5 mL of 0.25 N ferrous ammonium sulphate. The blank titration reading was 26.4 mL. Calculate COD of water sample.

Solution : Volume of water taken = 30 mL

Blank reading = 26.4 mL

Back reading = 12.5 mL

Normality of ferrous ammonium sulphate (FAS) = 0.1 N

$$\text{COD} = \frac{\text{Volume of oxidising agent consumed } (V_1) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken (V)}}$$

$$\text{COD} = \frac{(\text{Blank} - \text{Back}) \times \text{Normality of FAS} \times 8 \times 1000}{\text{Volume of water taken}}$$

$$\text{COD} = \frac{(26.4 - 12.5) \times 0.25 \times 8 \times 1000}{30}$$

$$\text{COD} = 926.67 \text{ mg/L}$$

$$\therefore \text{COD of water sample} = 926.67 \text{ mg/L}$$

Example 11 : 60 mL of water sample was diluted to 100 mL. Equal volumes of it are taken for dissolved oxygen estimation. The dissolved oxygen on day-1 was 770 ppm and dissolved oxygen after incubation for 5 days was 340 ppm. Calculate the biological oxygen demand (BOD) of the sample.

Solution : Volume of sample before dilution = 60 mL

Volume of sample after dilution = 100 mL

$(\text{DO})_1 = 770$ ppm

$(\text{DO})_2 = 340$ ppm

$$\text{BOD} = [(\text{DO})_1 - (\text{DO})_2] \times \frac{\text{Volume of sample after dilution}}{\text{Volume of initial sample water taken}}$$

$$= (770 - 340) \times \frac{100}{60}$$

$$= 716.67 \text{ ppm}$$

$$\therefore \text{BOD of water sample} = 716.67 \text{ ppm}$$

Example 12 : 10 mL of wastewater is diluted to 250 mL and equal volumes are filled in two biological oxygen demand bottles. In the blank titration, 100 mL of diluted wastewater when titrated immediately required 5.8 mL of 0.02 N $Na_2S_2O_3$. 100 mL of the incubated sample after 5 days required 2.5 mL of same $Na_2S_2O_3$. Calculate biological oxygen demand of the waste water.

Solution :

Volume of initial sample water taken = V mL = 10 mL

Volume of sample water after dilution = V_1 mL = 250 mL

Volume of diluted water sample taken for titration = V_2 mL = 100 mL

Volume of $Na_2S_2O_3$ required for blank

i.e. to determine $(\text{DO})_1$ = a mL = 5.8 mL

Volume of $Na_2S_2O_3$ required after 5 days

i.e. to determine $(\text{DO})_2$ = b mL = 2.5 mL

Normality of $Na_2S_2O_3$ = x N = 0.02 N

$$\text{BOD} = [(\text{DO})_1 - (\text{DO})_2] \times \frac{\text{Volume of sample after dilution}}{\text{Volume of initial sample water taken}}$$

$(\text{DO})_1$ can be calculated as follows:

$$\text{Normality of sample solution} = \frac{\text{Normality of } Na_2S_2O_3 \times \text{Volume of } Na_2S_2O_3}{\text{Volume of oxygen solution}}$$

$$\therefore \text{Normality of sample solution} = \frac{0.02 \times 5.8}{100} = 1.16 \times 10^{-3} \text{ N}$$

Weight of dissolved oxygen per litre present initially

$$\text{i.e. } (\text{DO})_1 = 1.16 \times 10^{-3} \times 8 \times 1000$$

$$\therefore (\text{DO})_1 = 9.28 \text{ mg/L}$$

$(\text{DO})_2$ can be calculated as follows:

$$\text{Normality of sample solution} = \frac{\text{Normality of } Na_2S_2O_3 \times \text{Volume of } Na_2S_2O_3}{\text{Volume of oxygen solution}}$$

$$\therefore \text{Normality of sample solution} = \frac{0.02 \times 2.5}{100} = 0.50 \times 10^{-3} \text{ N}$$

Weight of dissolved oxygen per litre after 5 days

$$\text{i.e. } (\text{DO})_2 = 0.50 \times 10^{-3} \times 8 \times 1000$$

$$(\text{DO})_2 = 4.0 \text{ mg/L}$$

Substituting the values of $(\text{DO})_1$ and $(\text{DO})_2$ in the formula,

$$\text{BOD} = [(\text{DO})_1 - (\text{DO})_2] \times \frac{\text{Volume of sample after dilution } (V_1)}{\text{Volume of sample before dilution (V)}}$$

$$\text{BOD} = (9.28 - 4.0) \times \frac{250}{10}$$

$$\therefore \text{BOD} = 132 \text{ mg/L}$$

Alternate Method

$$\therefore \text{BOD} = \frac{(a-b)\times x\,\text{N}\times 8\times \text{V}_1}{\text{V}_2}\times\frac{1000}{\text{V}}$$

$$\therefore \text{BOD} = \frac{(5.8-2.5)\times 0.02\times 8\times 250}{100}\times\frac{1000}{10} = 132\ \text{mg/L}$$

$\therefore$ BOD of the waste water = 132 mg/L

6.9 Review Questions

(1) What is hardness of water and what are its types? List its disadvantages.

(2) What is softening of water and discuss the various types?

(3) Discuss the process details of ion-exchange method of water softening.

(4) List the advantages and limitations of ion-exchange method of water softening.

(5) Explain the term Chemical Oxygen Demand (COD) and give its significance.

(6) Explain the term Biological Oxygen Demand (BOD) and give its significance.

(7) Write a note on,
   - (i) Electrodialysis
   - (ii) Reverse Osmosis
   - (iii) Ultrafiltration

(8) Calculate the temporary, permanent and total hardness for a water sample in ppm containing following salts: $Mg(NO_3)_2$ = 3.7 ppm, $Ca(HCO_3)_2$ = 8.1 ppm, $MgCl_2$ = 4.75 ppm, $MgSO_4$ = 9 ppm, SiO_2 = 8 ppm.

[**Ans.** Temporary hardness = 5 ppm, Permanent hardness = 15 ppm, Total hardness = 20 ppm]

(9) Two samples of water A and B were analysed for their salt content.
   - (i) Sample A was found to contain 37 mg/L of $Mg(NO_3)_2$
   - (ii) Sample B was found to contain 20.5 mg/L of $Ca(NO_3)_2$ and 1 mg/L of SiO_2.

Calculate hardness of each sample and state which is harder.

[**Ans.** Hardness of sample A = 25 ppm, Hardness of sample B = 12.5 ppm, sample A is harder]

(10) 100 mL of standard hard water (1.4 g $CaCO_3$/L) requires 40 mL of EDTA solution. 120 mL of water sample consumes 20 mL EDTA. 200 mL of boiled and filtered water sample consumes 15 mL of EDTA. Calculate the hardness of sample.

[**Ans.** Total hardness = 583.33 ppm, Temporary hardness = 262.50 ppm, Permanent hardness = 320.83 ppm]

(11) 100 mL sample hard water required 12 mL of N/10 (0.1 N) disodium EDTA for titration. After boiling and filtration, 200 mL of the same sample required 8.8 mL of 0.1 N EDTA. Calculate the temporary hardness.

[**Ans.** Total hardness = 600 ppm, Permanent hardness = 220 ppm, Temporary hardness = 380 ppm]

(12) 40 mL of sample water consumed 12 mL 0.03 M EDTA before boiling and 10 mL of same EDTA after boiling. Calculate the total, permanent and temporary hardness.

[**Ans.** Total hardness = 900 ppm, Permanent hardness = 750 ppm, Temporary hardness = 150 ppm]

(13) After treating 60000 L of water by ion exchanger, the cationic resin required 400 L of 0.55 N HCl and anionic resin required 400 L of 0.55 N NaOH solution for regeneration. Find the hardness of the above sample of water. [**Ans.** 183.333 mg/L]

(14) 75 mL of water sample was diluted to 200 mL and incubated for 5 days. The initial DO was 820 ppm and after 5 days it became 445 ppm. Calculate the BOD of the sample. [**Ans.** 1000 ppm]

(15) 20 mL of wastewater was diluted to 200 mL and equal volumes were filled in two BOD bottles. In the blank titration, 50 mL of diluted waste water when titrated immediately required 4.7 mL of 0.05 N $Na_2S_2O_3$. 50 mL of the incubated sample after 5 days required 2.2 mL of same $Na_2S_2O_3$. Calculate BOD of the wastewater. [**Ans.** 200 ppm]

(16) 25 mL of wastewater is mixed with 60 mL of acidified potassium dichromate and refluxed. The unreacted potassium dichromate required 22.6 mL of 0.3 N ferrous ammonium sulphate. The blank titration reading was 32.2 mL. Calculate COD of water sample.

[**Ans.** 921.6 mg/L]

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