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RAS 102/202 : ENGINEERING CHEMISTRY

UNIT-I : MOLECULAR ORBITAL THEORY

(4 H—51 H)

Molecular orbital theory and its applications to homo-nuclear diatomic molecules. Band theory of solids. Liquid crystals and its applications. Point defects in Solids. Structure and applications of Graphite and Fullerenes. Concepts of nano-materials and its applications.

UNIT-II : POLYMERS AND ORGANOMETALLICS

(52 H—82 H)

Polymers: Basic concepts of polymer- blends and composites. Conducting and biodegradable polymers. Preparations and applications of some industrially important polymers (Buna N, Buna S, Neoprene, Nylon 6, Nylon 6,6, Terylene). General methods of synthesis of organometallic compound (Grignard Reagent) and their applications in polymerization.

UNIT-III : ELECTROCHEMISTRY

(83 H—128 H)

Electrochemistry: Galvanic cell, electrode potential; Lead storage battery. Corrosion, causes and its prevention. Setting and hardening of cement, applications of cement. Plaster of paris. Lubricants- Classification, mechanism and applications.

UNIT-IV : WATER TREATMENT

(129 H—171 H)

Hardness of water. Disadvantage of hard water. Boiler troubles, Techniques for water softening; Lime-soda, Zeolite, Ion exchange resin, Reverse osmosis. Phase Rule and its application to water system.

UNIT-V : FUELS AND SPECTRAL TECHNIQUES

(172 H—212 H)

Fuels: Classification of fuels. Analysis of Coal. Determination of Calorific values (bomb calorimeter & Dulong's method). Biogas. Elementary ideas and simple applications of UV, Visible, IR and ¹H NMR spectral Techniques.

VERY SHORT ANSWER TYPE QUESTIONS

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UNIT 1

1 UNIT

Molecular Orbital Theory

Part-1 (5H - 22H)

• *Molecular Orbital Theory and its Application to Homo-Nuclear Diatomic Molecules*

A. Concept Outline : Part-1 5H
B. Long and Medium Answer Type Questions 5H

Part-2 (22H - 37H)

• *Band Theory of Solids*
• *Liquid Crystal and its Applications*
• *Point Defects in Solids*
• *Structure and Applications of Graphite and Fullerenes*

A. Concept Outline : Part-2 22H
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Part-3 (37H - 51H)

• *Concepts of Nano-Materials and its Applications*

A. Concept Outline : Part-3 37H
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4 (Sem-1 & 2) H

PART-1

Molecular Orbital Theory and its Applications to Homo-Nuclear Diatomic Molecules.

CONCEPT OUTLINE : PART-1

- **Introduction :** A molecule will only be formed if it is more stable, and has lower energy than the individual atoms.
- **Bond :** The bond is an attractive force resulting from the electrical interaction between the electrons and nuclei of the atoms.
- **Ionic bond :** The ionic bond is a result of the transference of electrons from one atom to another.
- **Covalent bond :** The covalent bond is formed by the sharing of electrons between the two atoms.
- **Sigma bond :** A covalent bond which is formed between two atoms by the overlap of orbitals along their axis (end to end, head to head) is called a sigma bond.
- **π -bond :** A covalent bond which is formed between the two atoms by the overlap of orbitals along a line perpendicular to axis, side to side or lateral overlapping.
- **Theories of chemical bonding :**
 - a. Valence shell electron pair repulsion theory
 - b. Valence bond theory
 - c. Molecular orbital theory
- **Types of molecular orbitals :**
 - a. Homo-molecular orbitals : C_{2v} , B_{2v} , F_{2g} etc.
 - b. Hetero-molecular orbitals : CO, NO etc.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.1. Explain molecular orbital theory. Also, discuss filling of electrons in molecular orbitals.

Answer

1. According to valence bond theory, a covalent bond is formed by the overlapping of atomic orbitals and the bonded atoms in the molecule are held together by one or more pair of electrons.
2. According to this theory, the atoms retain their identity even after bond formation.

3. On the other hand in the molecular orbital method, the valency electrons are considered to be associated with all the nuclei in the molecule i.e., electrons move in the field of more than one nucleus.
 4. The molecular orbital theory given by R.S. Mulliken and F. Hund incorporates the following points :
 - a. When nuclei of two atoms come close to each other, their atomic orbitals interact, to form molecular orbitals in which the identity of both the atomic orbitals is lost.
 - b. The number of molecular orbitals is equal to the number of atomic orbitals involved in their formation.
 - c. Just as atomic orbitals in an atom are quantized, similarly molecular orbitals are also believed to be quantized.
 - d. The electrons in the atomic orbital are influenced by one nucleus, the electrons in the molecular orbitals are influenced by all the nuclei.
 - e. Electrons are filled in the molecular orbitals in the same way as they are filled in atomic orbitals, following Aufbau principle, Hund's rule of maximum multiplicity.
 - f. The molecular orbitals are represented by σ , σ^* , π , π^* etc.
- For simple homoatomic molecules, the filling of electrons is carried out in a similar fashion as in atomic orbitals. Following rules are followed :
1. **Aufbau principle** : The orbital with lowest energy is to be filled first of all i.e., electrons enter various molecular orbitals in the order of their increasing energies.
 2. **Pauli's exclusion principle** : The maximum number of electrons in a molecular orbital cannot exceed two and these should have opposite spins.
 3. **Hund's rule** : Pairing of electrons takes place only when each molecular orbital of the same energy has at least one electron each.
 4. A bond between two atoms is said to be formed when the total number of electrons in bonding orbitals is greater than the numbers in antibonding orbitals.
 5. **Bond order** : Bond order is defined as half of the difference between the number of electrons present in the bonding and the antibonding orbitals i.e.,

$$\text{Bond order} = \frac{1}{2} (\text{No. of bonding orbitals} - \text{No. of antibonding orbitals})$$

A negative or zero bond order corresponds to an unstable molecule whereas positive bond order indicates a stable molecule.

Que 1.2. Discuss hydrogen molecule with the help of diagram and calculates its bond order.

Answer

1. **Hydrogen molecule-ion (H_2^+)** : This is the simplest molecular specie containing one electron only. Its existence has been detected spectroscopically when electric discharge is passed through hydrogen gas under reduced pressure. The only electron present in H_2^+ ion enters the σ_{1s} molecular orbital. Thus, electronic configuration of H_2^+ is written as σ_{1s}^1 and bond order $= \frac{1}{2} (1 - 0) = \frac{1}{2}$.

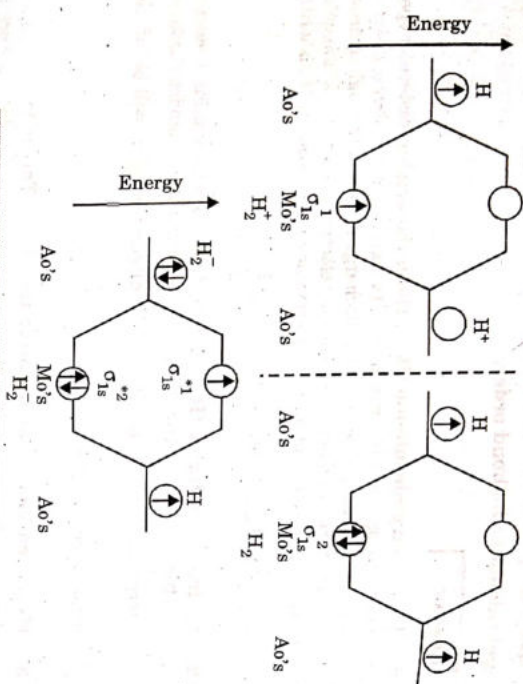
2. **Hydrogen molecule (H_2)** : Each hydrogen atom contains 1 electron and hence, there are two electrons in the molecule, occupying the lowest energy level. Thus, the electronic configuration of H_2 will be σ_{1s}^2 and bond order $= \frac{1}{2} (2 - 0) = 1$.

3. **Hydrogen molecular negative ion (H_2^-)** : This is formed by the combination of one hydrogen atom having one electron in its orbital with a hydrogen ion having 2 electrons. Thus, H_2^- ion has 3 electrons. The electronic configuration will thus be $\sigma_{1s}^2 \sigma_{1s}^1$ and bond order

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

Table 1.2.1 : Characteristics of H_2^+ , H_2 , H_2^-

Specie	Electronic configuration	Bond order	Magnetic character
H_2^+	σ_{1s}^1	$\frac{1}{2}$	Paramagnetic
H_2	σ_{1s}^2	1	Diamagnetic
H_2^-	$\sigma_{1s}^2 \sigma_{1s}^1$	$\frac{1}{2}$	Paramagnetic

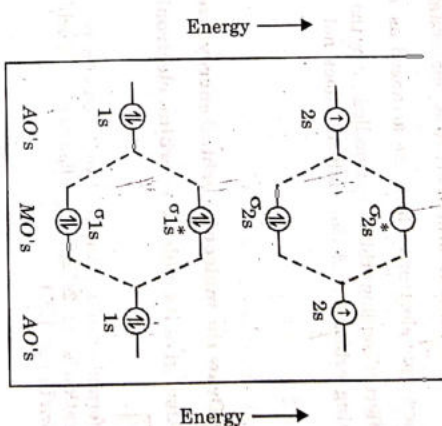
Fig. 1.2.1. Energy level diagrams for H_2^+ , H_2 , and H_2^- .

Que 1.3. Show molecular orbitals of Li_2 molecule with the help of diagram and calculate its bond order.

Answer

1. Lithium molecule is formed by the overlap between two lithium atoms each having the electronic configuration of $1s^2 2s^1$.
2. Molecular orbital electronic configuration of Li_2 molecule
 $= \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 = KK \sigma 2s^2$
3. Since, the inner shell of filled $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals do not contribute to the bonding.
4. Bond order (Li_2)
 $= \frac{1}{2} (N_b - N_a)$
 $= \frac{1}{2} (4 - 2) \text{ or } \frac{1}{2} (2 - 0)$
 $= 1$
5. Positive bond order for Li_2 suggests that it is stable molecule and it should exist.

6. Magnetic behaviour of Li_2 is diamagnetic as there is no unpaired electron.

Fig. 1.3.1. Molecular orbital energy level diagram for Li_2 molecule.

Que 1.4. With the help of molecular orbital diagram, explain helium molecule.

Answer

Helium molecule ion (He_2^+): This may be considered to be formed from He atom and a He^+ ion. In the molecular ion, there are three electrons which are arranged in the molecular orbitals as $\sigma_{1s}^2 \sigma_{1s}^*$. Thus, helium molecular ion can exist, but it is not very stable. Bond order $\frac{1}{2} (2 - 1) = \frac{1}{2}$.

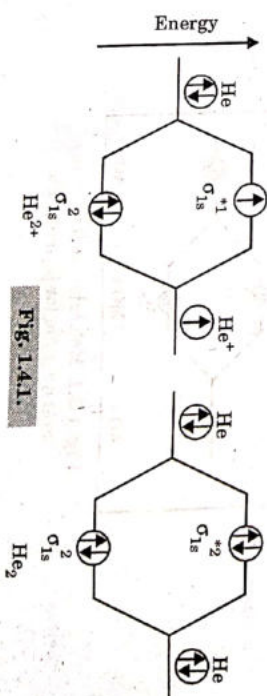


Fig. 1.4.1.

Helium molecule (He_2): The electronic configuration of the atom is $1s^2$. He molecule can be considered to form from two atomic orbitals. In the molecular He_2 , there are four electrons which are arranged as $\sigma_{1s}^2, \sigma_{1s}^{*2}$. Thus, the stabilizing effect of bonding orbitals is cancelled out by the destabilizing effect of antibonding orbitals and the molecule does not exist. Bond order

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

Que 1.5. Draw the molecular orbital energy level diagram for B_2 molecule. Also, give its molecular electronic configuration.

Answer

1. For the formation of B_2 molecule, two B atoms are required. Its electronic configuration is: $1s^2 2s^2 2p^1$. The filled molecular orbitals in B_2 molecule are shown in Fig. 1.5.1.

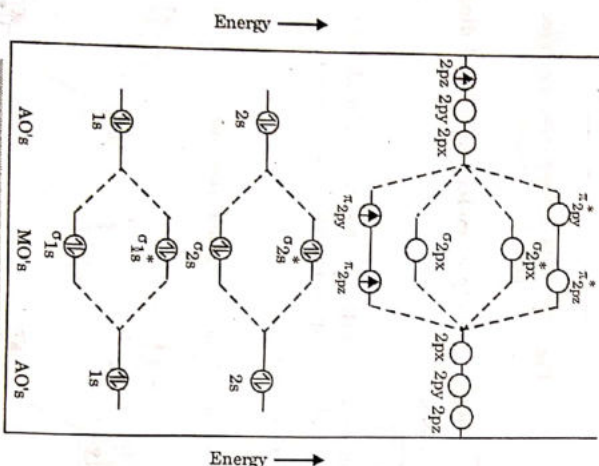


Fig. 1.5.1. Molecular orbital energy level diagram for B_2 molecule.

- It is to be noted that since the molecular orbitals π_{2py} and π_{2pz} have identical energies, these orbitals are degenerate.
- Stabilization occurs by the filling of two electrons in these orbitals.
- Hence, molecular orbital electronic configuration of B_2 molecule is,

$$KK \sigma 2s^2 \sigma^* 2s^2 (\pi 2p_x^1 \pi 2p_y^1)$$

$$\text{Bond order} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} (4 - 2) = 1$$

- As the bond order is one, hence B_2 molecule exists and there is single bond between two boron atoms.

Que 1.6. Calculate the bond order of N_2 , N_2^+ , N_2^- and N_2^{2-} molecules and explain them.

Answer

- Nitrogen molecule (N_2):** Nitrogen atom has seven electrons. In the formation of N_2 molecule, a total of 14 electrons are arranged in molecular orbitals as:

$$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \left\{ \begin{matrix} \pi_{2py}^2 \\ \pi_{2pz}^2 \end{matrix} \right\} \sigma_{2px}^2, \text{ Bond order} = \frac{1}{2} (10 - 4) = 3$$

Thus, nitrogen molecule contains a triple bond and is highly stable, therefore, nitrogen exist as N_2 molecule. Moreover, all the electrons are paired, therefore, it is diamagnetic.

- N_2^+ ion: N_2^+ ion has one electron less than N_2 molecule. This electron will be lost from σ_{2px} orbital. Hence, the molecular electronic configuration will be:

$$N_2^+ = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 = \pi_{2py}^2 \sigma_{2px}^1$$

$$\text{Bond order} = \frac{1}{2} (7 - 2) = 2 \frac{1}{2}$$

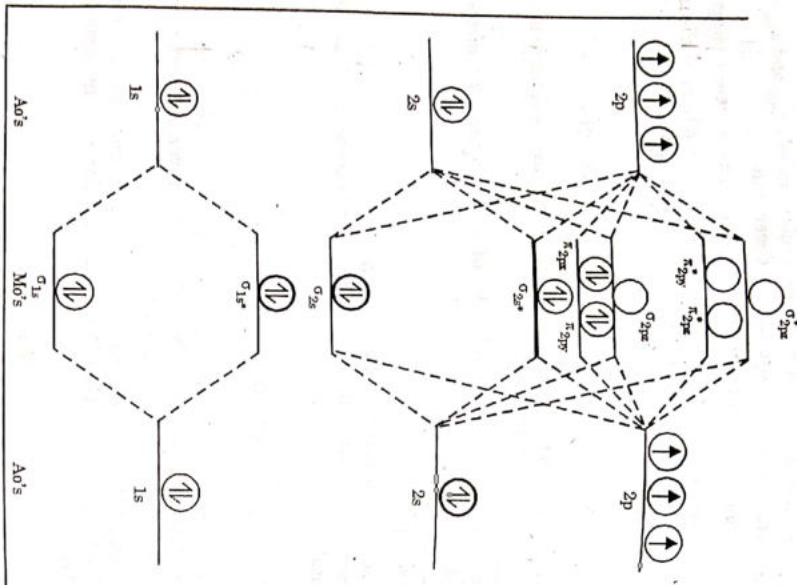
The ion is paramagnetic due to the presence of unpaired electron.

- N_2^- ion: N_2^- ion has one more electron than the nitrogen molecule. This extra electron is added in $\pi_{2px}^* \pi_{2py}^*$ orbital, thus molecular ion electronic configuration will be:

$$N_2^- = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 = \pi_{2py}^2 \sigma_{2px}^2 \pi_{2px}^{*1}$$

$$\text{Bond order} = \frac{1}{2} (8 - 3) = 2 \frac{1}{2}$$

Moreover, as it contains one unpaired electron, the ion is paramagnetic.

Fig. 1.6.1. Energy level diagram for N_2^-

4. N_2^- ion : N_2^- ion has two more electrons than nitrogen molecule. These two extra electrons are added one each in π_{2px}^* and π_{2py}^* orbitals. Electronic configuration of N_2^- ion can be written as :

$$N_2^- = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \left\{ \begin{matrix} \pi_{2px}^2 \\ \pi_{2py}^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi_{2px}^{*1} \\ \pi_{2py}^{*1} \end{matrix} \right\}$$

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

Further, it contains two unpaired electrons, therefore, it is paramagnetic.

Table 1.6.2 : Comparison of N_2 , N_2^+ , N_2^- and N_2^{2-}

Molecular specie	Electronic configuration	Bond order	Magnetic character
N_2	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2$	3	Diamagnetic
N_2^+	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^1$	$2 \frac{1}{2}$	Paramagnetic
N_2^-	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2 \pi_{2px}^{*1} \pi_{2py}^{*1}$	$2 \frac{1}{2}$	Paramagnetic
N_2^{2-}	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 \pi_{2py}^2 \sigma_{2pz}^2 \pi_{2px}^{*1} \pi_{2py}^{*1}$	2	Paramagnetic

Stability of these species is in the order :

$$N_2 > N_2^+ = N_2^- > N_2^{2-}$$

Que 1.7. Explain molecular orbitals of oxygen molecule.

Answer

Oxygen molecule (O_2) : Each oxygen atom has 6 valence electrons. Assuming that inner orbitals do not participate in bonding, altogether 12 electrons have to be accommodated in molecular orbitals. The molecular electronic configuration will be :

$$O_2 = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left\{ \begin{matrix} \pi_{2px}^2 \\ \pi_{2py}^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi_{2px}^{*1} \\ \pi_{2py}^{*1} \end{matrix} \right\}$$

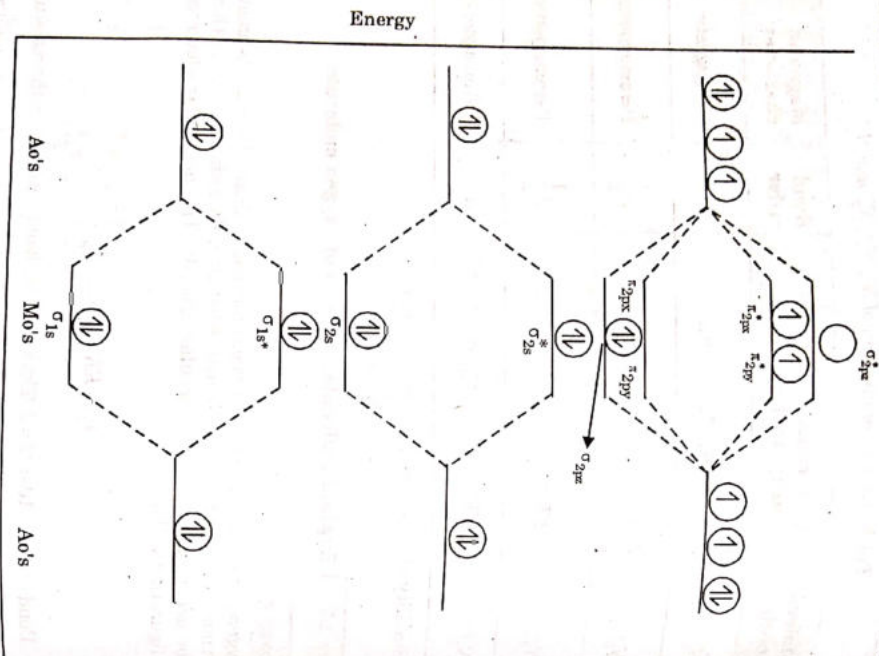
Bond order = $(10 - 6)/2 = 2$. Thus, a double bond is present in the molecule.

O_2^- ion : These superoxide ion O_2^- has 17 electrons i.e., one electron more than O_2 and hence, this extra electron enters the π_{2px}^* or π_{2py}^* orbital. The molecular orbital configuration becomes :

$$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left\{ \begin{matrix} \pi_{2px}^2 \\ \pi_{2py}^2 \end{matrix} \right\} \left\{ \begin{matrix} \pi_{2px}^{*1} \\ \pi_{2py}^{*1} \end{matrix} \right\}$$

$$\text{Bond order} = (10 - 7)/2 = 1 \frac{1}{2}$$

The superoxide ion is paramagnetic.

Fig. 1.7.1. Energy level diagram for O_2 molecule.

O_2^- ion : The peroxide ion O_2^- has 18 electrons and has molecular orbital configuration as :

$$= KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left\{ \pi_{2py}^2 \pi_{2py}^{*2} \right\} \left\{ \pi_{2px}^2 \pi_{2px}^{*2} \right\}$$

$$\text{Bond order} = \frac{(10 - 8)}{2} = 1.$$

O_2^- ion : This ion has 15 electrons. The molecular orbital configuration can be written as :

$$= KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left\{ \pi_{2py}^2 \pi_{2py}^{*1} \right\} \left\{ \pi_{2px}^2 \pi_{2px}^{*1} \right\}$$

$$\text{Bond order} = \frac{1}{2} (8 - 3) = 2 \frac{1}{2}$$

Higher bond orders are associated with shorter bond lengths and higher bond strengths. Therefore, we can conclude that bond strength of the above species in decreasing order can be arranged as :

$$O_2^+ > O_2 > O_2^- > O_2^{2-}$$

Table 1.7.1 : Comparison of O_2^+ , O_2 , O_2^- and O_2^{2-}

Molecular Species	Electronic Configuration	Bond Order	Magnetic Character
O_2^+	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*1}$	$2 \frac{1}{2}$	Paramagnetic
O_2	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*1} \pi_{2py}^{*1}$	2	Paramagnetic
O_2^-	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*1} \pi_{2py}^{*1} \pi_{2px}^{*1} \pi_{2py}^{*1}$	$1 \frac{1}{2}$	Paramagnetic
O_2^{2-}	$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \pi_{2px}^2 \pi_{2py}^2 \pi_{2px}^{*2} \pi_{2py}^{*2}$	1	Diamagnetic

Que 1.8. Draw the molecular orbital diagram of F_2 and N_2 . State their magnetic behaviour.

Answer

Flourine molecule (F_2) : Flourine atom has 7 electrons in the outermost shell and hence 14 electrons are arranged in the molecular orbital as-

$$KK \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2pz}^2 \left\{ \pi_{2py}^2 \pi_{2py}^{*2} \right\} \left\{ \pi_{2px}^2 \pi_{2px}^{*2} \right\}$$

$$\text{Bond order} = \frac{(8 - 6)}{2} = 1$$

The F-F bond is rather weak. Since, there are no unpaired electrons, the molecule is diamagnetic.

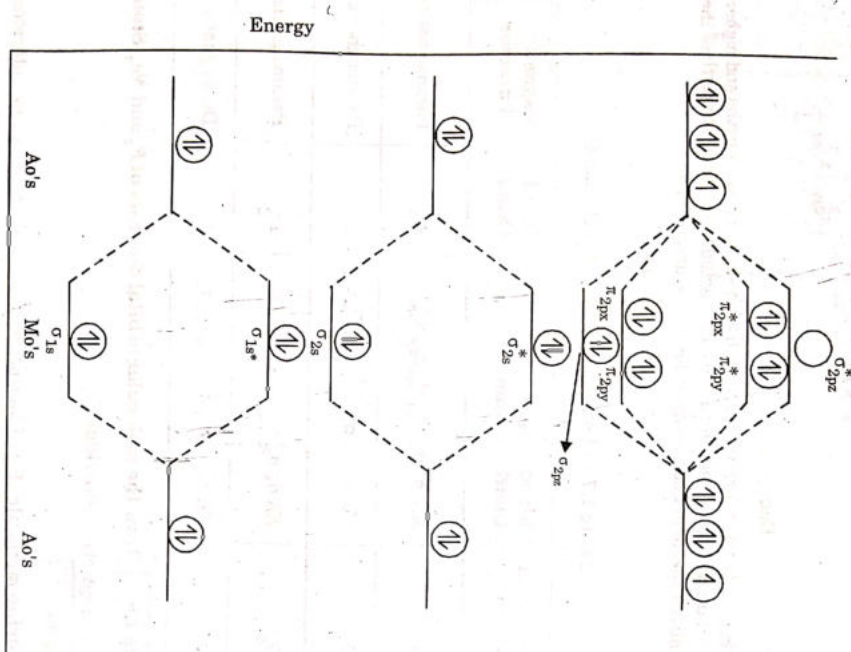
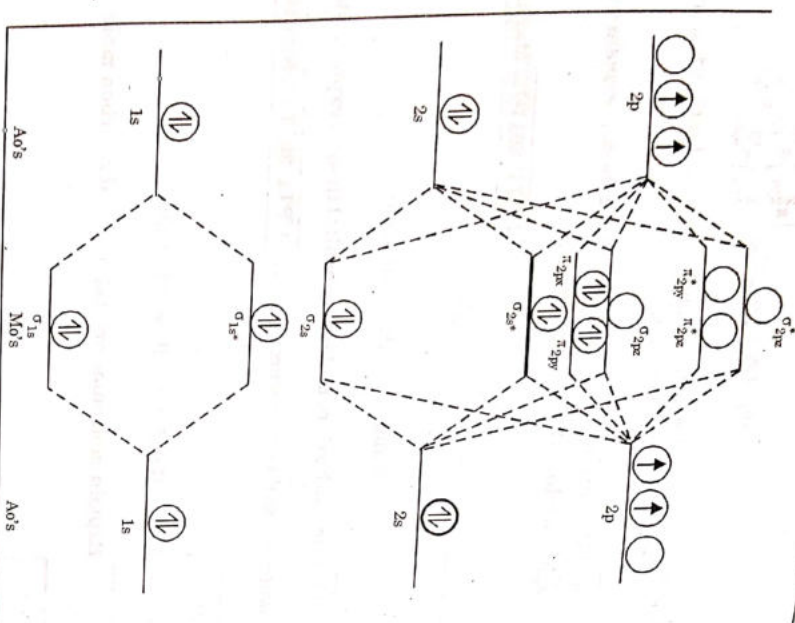


Fig. 1.8.1. Energy level diagram of fluorine molecule.

Neon molecule (Ne_2): Neon atom has 8 electrons in its valence shell. In the formation of Neon molecule, if possible, 16 electrons have to be accommodated in molecular orbitals. The molecular electronic configuration of Neon molecule would be :

Fig. 1.11.1. Energy level diagram for C_2 .**Que 1.12.**

Write the basic principles of Valence bond theory.

OR

What do you mean by Valence bond theory ? Distinguish between Valence bond theory and Molecular orbital theory.

Answer**Valence bond theory :** In the valence bond (electron pair) theory :

1. A molecule is considered to be made up of atoms.
2. Electrons in atoms occupy atomic orbitals.
3. Orbitals may or may not be hybridized.

Principle of valence bond theory :

1. Two combining atoms must come closer to each other for overlapping. The extent of overlapping depends upon :
 - a. Nature of involved orbitals
 - b. Types of overlapping
2. The overlapping orbitals must have unpaired and opposite spin electrons.
3. A new localized orbital is formed where probability of finding electrons is maximum.
4. Electrostatic attraction between nuclei and attraction between spins of antispin electrons is responsible for the formation of covalent bond.
5. More the extent of overlapping, greater will be attraction, bond energy and stability, and lesser bond strength.
6. Sigma bond is formed by the overlapping of orbitals along their axis while pi bond is formed by the sideways overlapping of two half-filled orbitals.

Difference between Valence bond theory and Molecular orbital theory :

S.No	Valence bond method	Molecular orbital method
1.	In valence bond method, a molecule is composed of atoms which retain their individual identity even after bond formation.	In molecular orbital method, the combining atoms lose their individual identity.
2.	An electron moves in the field of one nucleus only, i.e., atomic orbitals are monocentric.	An electron moves in the field of more than one nucleus i.e., molecular orbitals are polycentric.
3.	Valence bond method does not explain the paramagnetism of O_2 successfully.	Molecular orbital theory explains the paramagnetism of oxygen successfully.
4.	It does not involve the formation of bonding and antibonding orbitals.	It involves the formation of bonding and antibonding orbitals.
5.	Atomic orbitals in valence bond method are represented by s, p, d and f.	Molecular orbitals in molecular method are represented by $\sigma\sigma^*$, $\pi\pi^*$ etc.

Que 1.13.

What is metallic bond ? Explain it on the basis of molecular orbital theory ?

UPTU 2013-14, Marks 05

Answer**Metallic bond theory :**

1. The atomic orbitals of the atoms, with same symmetry and same energy, overlap each other and resulting in the almost continuous energy band of extremely large number of energy level of molecular orbitals.
2. In the formation of metallic crystals, approximate 10^5 molecular orbitals combined.

Explanation :

1. In the formation of Li crystal, n atoms of lithium are allowed to overlap each other to form a Li_n solid,

$$n Li \rightarrow Li_n \text{ (solid)}$$

2. The lithium atom consists 1s atomic orbital which is completely filled, 2s atomic orbital which is half filled and 2p atomic orbital which is empty.
3. The combination of n times 1s atomic orbital, 2s orbital and 2p orbital can explain with the help of band theory in the following manner :
 - a. **1s band :** This band is formed by the combination of n times 1s atomic orbitals of n Li atoms and contain n energy level all of which are completely filled. The 1s band is non-conduction band because it is narrow and there is no possibility to come out of the electrons from this band.
 - b. **2s band :** This band is formed by the combination of n times 2s atomic orbital of Li atom. The 2s band is half filled, the electron can easily move in this band, even at room temperature therefore, this is also known as conduction band.
 - c. **2p band :** The 2p band is formed by the combining of 2p atomic orbitals of Li atom. The energy of 2p and 2s band is nearer, therefore, they overlap each other and formed overlap zone.

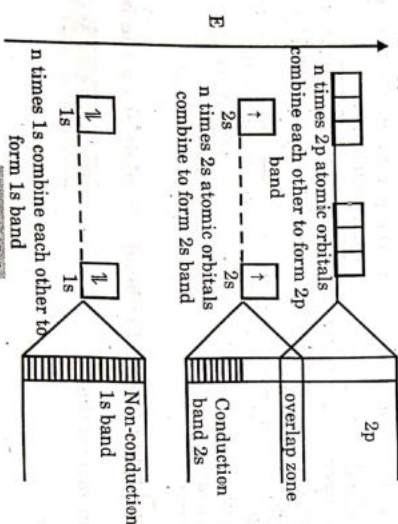


Fig. 1.13.1.

Que 1.14. How valence bond theory account for the following :

$[Ni(CN)_4]^{2-}$ is diamagnetic and square planar, $[NiCl_4]^{2-}$ is paramagnetic and tetrahedral, $[Ni(CO)_4]$ is diamagnetic and tetrahedral.

UPTU 2012-13, Marks 04

Answer

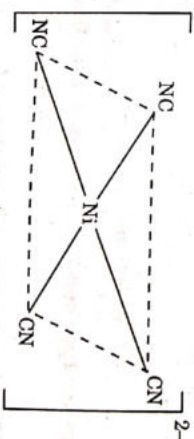
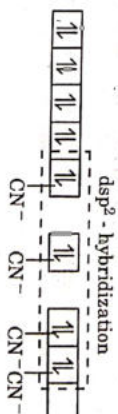
1. The period 4 metals that form square planar complexes use one d -orbital + one s -orbital + two p -orbitals to form a valence bond hybrid called dsp^2 .

Example :

2. $[Ni(CN)_4]^{2-}$: The period 4 metals that form tetrahedral complexes use the hybridization sp^3 , a combination of one s -orbital and three p -orbitals. Examples : $Ni(CO)_4$, $[NiCl]^{2-}$. In dsp^2 hybridization, one d -orbital (which is $d(x^2 - y^2)$) is involved in hybridization with one s and two p -orbitals. This leads to the square planar geometry.

4. $[Ni(CN)_4]^{2-}$ and $Ni(CO)_4$ are diamagnetic having paired electrons, while $[NiCl_4]^{2-}$ is paramagnetic.

5. Few compounds undergoing this hybridization are $[Ni(CN)_4]^{2-}$.

a. Ni**b. Ni^{2+}** **c. $[Ni(CN)_4]^{2-}$** 

- e. No motion of electrons occurs in the conduction band, because it is empty.
- f. Moreover, these bands are separated by a large band gap.
- g. Therefore, a large amount of input energy is required to promote an electron from the filled lower energy (valence) band to the unfilled higher energy (conduction) band.

3. Semiconductors :

- a. Semiconductor are of two types : intrinsic and extrinsic semiconductors.
- b. Intrinsic semiconductors (like Si or Ge) are having small energy gap between the filled valence band (VB) and empty conduction band (CB) as shown in Fig. 1.15.1, sufficient to promote an electron from VB to CB.
- c. The hole left in the VB and the promoted electron in the CB both contributes towards conductivity.
- d. It is obvious that number of electrons promoted to CB increase with rise in temperature, thus conductivity of semiconductors increase with temperature.
- e. The conductance of semiconductors can also be improved by doping.
- f. Doping means treatment of Si and Ge (typically semiconductors) with impurity atoms of Group (III) and Group (V) giving respectively *p*-type and *n*-type extrinsic semiconductors.

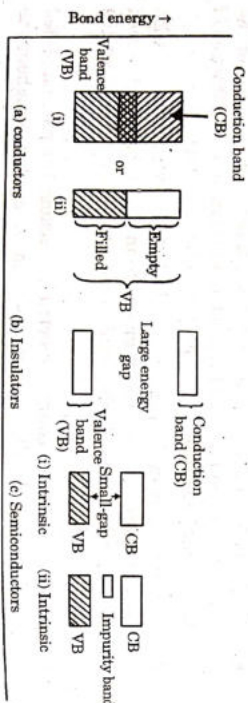


Fig. 1.15.1. Energy band in (A) Conductors (B) Insulators and (C) Semi-conductor.

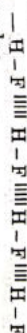
Que 1.16. What is hydrogen bonding? Differentiate between intra and intermolecular hydrogen bonding with suitable example.

UPTU 2011-12, Marks 05

UPTU 2012-13, Marks 08

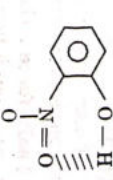
Answer

Hydrogen bonding : The attractive force which binds hydrogen atom of one molecule with electronegative atom (F, O or N) of another molecule is known as hydrogen bonding



Type of hydrogen bonds :

- (a) Intermolecular H-bond
- (b) Intramolecular H-bond

S.No.	Intermolecular H bonding	Intramolecular H bonding
1.	The hydrogen bonding occurring between two or more similar or different molecules is called intermolecular H bonding. $\text{H}-\text{F} \cdots \text{H}-\text{F} \cdots \text{H}-\text{F}$	The hydrogen bonding occurring within a single molecule is called intra-molecular hydrogen bonding. 
2.	In this type of hydrogen bonding, association of molecules takes place.	No association of molecules takes place.
3.	This type of hydrogen bonding is external.	This type of hydrogen bonding is internal.
4.	Ring formation does not take place.	Chelation takes place.

Que 1.17. Describe the properties of hydrogen bond and consequence of hydrogen bonding.

UPTU 2012-13, Marks 04

Answer

Consequences of hydrogen bonding :

- Boiling points : Boiling point of liquids increases because H-bonding leads to increase in intermolecular attractions which leads to increase in heat of vapourization.
- The solubility of organic compounds in water is attributed to hydrogen bond formation.
- Intermolecular H-bonding increases attractions between the molecules in the different layers of the H-bonded liquids.
- With the help of H-bonding, we can compare the density of ice and water. Hydrogen bonding explains why ice is less dense than water.

Properties of hydrogen bond :

- High electronegativity :** The electronegativity of the atoms to which hydrogen atom is linked should be high. More is the electronegativity of the element to which hydrogen is linked, greater is the polar character and hence stronger is the hydrogen bond.
- Small size of the atom attached to hydrogen :** The smaller the size, greater will be the polarity of the covalent bond and hence greater will be electrostatic attraction between the two molecules.

Que 1.18. Mention briefly the type of Vander Waal's forces.

UPTU 2012-13, Marks 04

Answer

The force of attraction or repulsion which acts between atoms, ions or molecules is termed as intermolecular force.

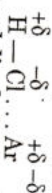
Vander Waal's force : The weak force of attraction between two non-bonded atoms or ions is termed as Vander Waal's force.

It is of three types :

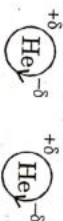
- Dipole-Dipole :** Due to electronegativity difference between atoms in a polar covalent molecules like HCl, a force of attraction between adjacent molecules termed as dipole-dipole attraction.

**Dipole-Dipole**

- Dipole-induced dipole forces :** A small dipole moment is induced on the Argon atom by the distortion of electron around it by polar HCl which creates dipole-induced dipole force between HCl and Argon.



- Induced dipole-induced dipole forces :** This is the force of attraction between pair of atoms, that is, developed by the constant fluctuations in electron density.



Que 1.19. What is liquid crystal ? Distinguish between nematic and smectic liquid crystal and give its applications.

OR

UPTU 2013-14, Marks 10

What are liquid crystal ? Distinguish between nematic and smectic liquid crystals.

UPTU 2011-12, Marks 03

UPTU 2013-14, Marks 10

OR

Discuss the principle, working and applications of liquid crystals in LCDs :

- Nematic phase
- Chiral nematic phase
- Smectic phase

UPTU 2014-15, Marks 10

OR

What is liquid crystalline state ? Describe the various types of liquid crystals. Give the application of liquid crystals.

UPTU 2014-15, Marks 10

Answer**Liquid crystals :**

- Liquid crystals are the substances that exhibit a phase of matter that has properties between those of a conventional liquid, and those of a solid crystal.
- There are certain solids which undergo two sharp phase transformation one after other. They first fuse sharply yielding turbid liquids and then again equally sharply at high temperature giving clear liquids.
- They may flow like liquid but have anisotropy in it. They show double refraction and interference in all directions termed as liquid crystals or crystalline liquids or anisotropic liquids or mesomorphic state.
- For example, Cholesteryl Benzoate ($\text{C}_{18}\text{H}_{33}\text{COOC}_6\text{H}_5$) has two melting point :

**Principle of liquid crystal :****Principle of display :**

- The molecules in fluidic liquid crystal phase are mobile and their movement, alignment in thin film can be controlled by application of small electric field. Due to this nature, the aligned molecules in different directions have different optical properties.

- A liquid crystal display consists of an array of tiny segments called as pixels that can be manipulated to present the information. Each one of the pixels effectively a separate red, blue or green light that can be switched on or off very rapidly electronically using liquid crystals to rotate polarized light to make the moving colour picture.

Working of liquid crystals :

1. Liquid crystals have rod like molecules and can rotate the direction of polarized light based upon alignment.
2. The alignment of molecules can be controlled by application of electric field. A twisted nematic LC display cell consists of two glass plates with conductive transparent indium tin oxide coating and nematic LC material sealed light passing through one polarizer between them. There is a spacer to control cell gap.
3. Light passing through polarizer has its polarization rotated with the alignment direction of LC. As the light reaches to analyzer, it can be passed or blocked, depending upon extent of rotation. Electric field is controlled with the transparent conductors and the direction of LC molecules.
4. The liquid crystal cell acts as a light switch. When a voltage is applied, the LC molecules tend to align with the resulting electric field and the optical property of cell gets lost i.e., cell is dark. When the electric field is turned off, the molecules relax back to their twisted state and the cell becomes transparent again.

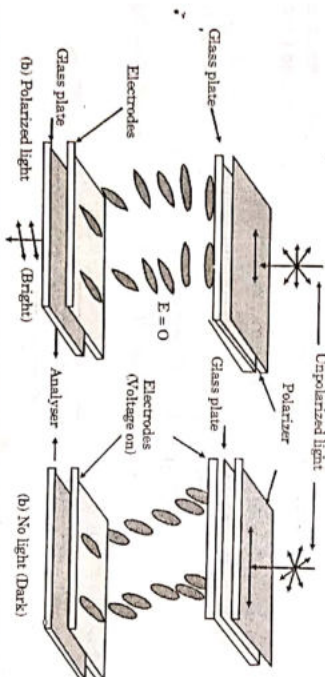


Fig. 1.19.1. Geometry of a working LCD cell. The polarizer and analyzer (which are arranged parallel to the director orientation at their adjacent glass plates) are oriented a 90 degrees to each other.

Classification of liquid crystals :

Liquid crystals can be divided into thermotropic and lyotropic LCs :

1. The transitions between the liquid crystals are given by the change in temperature and hence these are called thermotropic.
2. The phase transitions may also depend on concentration of the mesogen in the solvent, and these liquid crystals are called lyotropic. Thermotropic are mostly used for technical applications while lyotropic are important for biological systems, for example, membranes

Thermotropic liquid crystals are classified as :

1. Nematic phase :
 - a. In Greek, nematic means thread. They are thread like turbid and less anisotropic than smectic.
 - b. The molecules flow like liquid and their center of mass positions are randomly distributed as in a liquid.
 - c. Nematics have fluid like structure as isotropic liquids but can easily aligned by an external magnetic or electric field which has optical properties of uniaxial crystal & makes them extremely useful in LCDs.

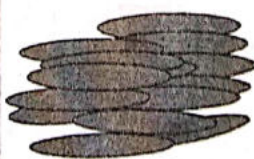


Fig. 1.19.2. Schematic of mesogen ordering in a nematic phase.

2.

Smectic phase :

- a. It is found at lower temperature than nematic phase form well defined layers that can slide over one another like soap.
- b. In smectic phase A, the molecules are oriented along the layer normal, while in phase C they are tilted away from the layer normal.
- c. This phase has mobility within the layer only and is not affected by magnetic field.
- d. Smectic liquid crystals are different from nematics in that they have one more degree of orientation order than do the nematics.

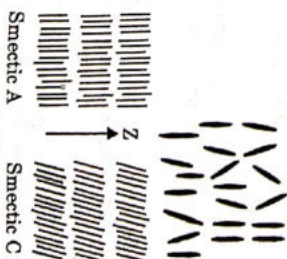


Fig. 1.19.3.

3. Chiral nematic/Cholesteric phase :

- Another common phase is cholesteric, also known as chiral nematic.
- In this phase, the molecules twist slightly from one layer to the next, resulting in a spiral formation.
- This phase shows nematic ordering but the preferred direction rotates throughout the samples. An example of this is shown in Fig. 1.19.4.

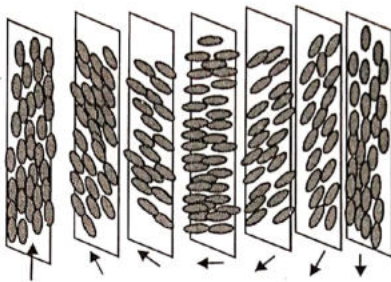


Fig. 1.19.4. Schematic diagram of a chiral nematic liquid.

There are several applications of liquid crystals :

The most successful applications are liquid crystal displays well-known from wrist watches, pocket calculators or flat screens of laptop computer which take advantage of electro-optical effects.

1. Liquid crystal displays :

- The most common application of liquid crystal technology is liquid crystal displays (LCD).
- Liquid crystals rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field.
- A liquid crystal display (LCD) is a thin, flat display device made up of any number of colour or monochrome pixels arrayed in front of a light source or reflector.
- It is often utilized in battery-powered electronic devices because it uses very small amounts of electric power.
- LCD (liquid crystal display) is the technology used for displays in notebook and other smaller computers.

2. Liquid crystal thermometers :

- Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch.
- Because the pitch is dependent upon temperature, the color reflected is also dependent upon temperature.
- Liquid crystal makes it possible to accurately gauge temperature just by looking at the colour of the thermometer.

3. Optical imaging :

- Application of liquid crystals is now being explored in optical imaging and recording.
- In this technology, a liquid crystal cell is placed between two layers of photoconductor.
- Light is applied to the photoconductor, which increases the material's conductivity.
- This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light.

4. Other liquid crystal applications :

- Liquid crystals have a multitude of other uses. They are used for nondestructive mechanical testing of materials under stress.
- This technique is also used for the visualization of RF (radio frequency) waves in waveguides.
- They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured.
- Low molar mass (LMMD) liquid crystal have application including erasable optical disks, full colour "electronic slides" for computer-aided drawing (CAD), and light modulators for colour electronic imaging.

Que 1.20. What are crystal imperfections ? Explain the one and two dimensional imperfections in solid.

UPTU 2013-14, Marks 10

Answer

Crystal imperfections :

An ionic crystal which has the same unit cell containing the same lattice points throughout the whole crystal is known as ideal crystal. Any deviation from completely ordered arrangement in a crystal is called disorder or a defect. There are two common types of imperfections :

- Electronic imperfections :** These correspond to defects in ionic crystals due to the electrons. The bonds from which electrons have been removed become electron deficient and are referred as holes. Free electrons and holes in crystals are considered to be electronic imperfections.

2. Point defects or atomic imperfections : The defects which arise due to the irregularity or deviations from ideal arrangement of atoms around a point or an atom in a crystalline substance are called point defects or atomic imperfections.

Types of point defects :

1. Schottky defects :

- When one positive ion and one negative ion are missing from any site in crystal lattice, then a pair of vacancies or holes is created.
- The paired vacancies at different sites in a crystal arise due to missing of pairs of cation-anion, is known as Schottky defect.

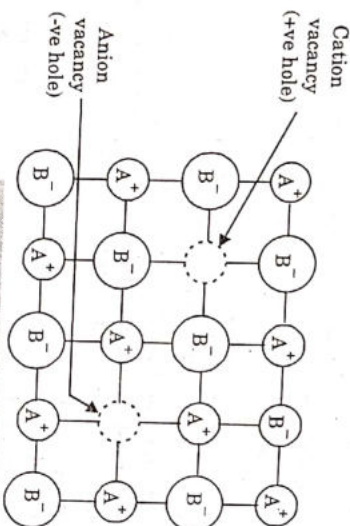


Fig. 1.20.1. Schottky defects.

- The Schottky defect is generated in ionic crystals when
 - Co-ordination number of an ion is high,
 - When the size of anions and cations are almost equal.
 - Schottky defect is found in crystals of NaCl, KBr, etc., show Schottky defect. Crystallographic studies on NaCl, shows that over 10 lakh paired vacancies are present in each gm-mole of NaCl.
- 2. Frenkel defect:**
- When an ion (generally cation) shifts from its position to interstitial position in the crystal lattice, then a vacancy or hole is created. The defect is known as Frenkel defect.
 - Generally, cations are smaller than anions and a cation may occupy the void (empty space) between the anions i.e., a cation occupies the interstitial position between the anions.
 - This defect can occur in ionic crystals when :
 - The anion is much larger than the size of cation.
 - The ion has low co-ordination number.

- In such cases, the energy required to shift a small cation to interstitial site is small. The Frenkel defect is observed in LiCl, ZnS, AgBr, AgCl, CaF₂ etc.

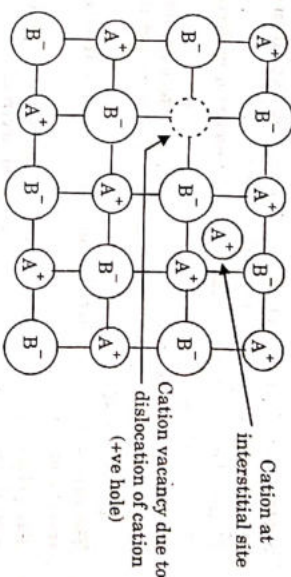


Fig. 1.20.1. Frenkel defects.

Que 1.21. What are stoichiometric and non-stoichiometric defects ? Explain Frenkel and Schottky defects found in solids.

UPTU 2014-15, Marks 05

Answer

Stoichiometric defect : The compounds in which the number of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects do not disturb the stoichiometry (the ratio of positive and negative ions) are called stoichiometric defects. These are of following types :

- Interstitial defects :** This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystals.
- Schottky defect :** Refer Q. 1.20, Page 31H, Unit-1.
- Frenkel defect :** Refer Q. 1.20, Page 31H, Unit-1.

Non-stoichiometric defects : The defects which disturb the stoichiometry of the compounds are called non-stoichiometry defects. These defects are either due to the presence of excess metal ions or deficiency of metal ions.

1. Metal excess defects due to anion vacancies :

- A compound may have excess metal anion if a negative ion is absent from its lattice site, leaving a 'hole', which is occupied by electron to maintain electrical neutrality.
- This type of defects is found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali metal halides are reduced by heating the alkali metal halides crystals in an atmosphere of alkali metal vapours.

c. The 'holes' occupied by electrons are called F-centres (or colour centres).

2. Metal excess defects due to interstitial cations :

- Another way in which metal excess defects may occur if an extra positive ion is present in an interstitial site.
- Electrical neutrality is maintained by the presence of an electron in the interstitial site.
- This type of defects are exhibit by the crystals which are likely to exhibit Frenkel defects, for example, when ZnO is heated, it loses oxygen reversibly.
- The excess is accommodated in interstitial sites, with electrons trapped in the neighbourhood.
- The yellow colour and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.

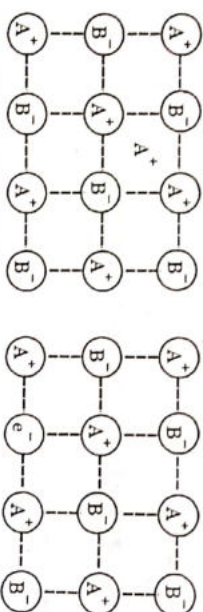


Fig. 1.21.1. Metal excess defect due to extra cation.

Fig. 1.21.2. Metal excess defect due to anion vacancy.

Que 1.22. With the help of neat diagram, describe the structure of graphite. Also, give at least five applications of graphite.

UPTU 2013-14, Marks 05

OR

UPTU 2014-15, Marks 05

Explain the structure of graphite.

Answer

Graphite :

- Graphite has a planar two dimensional sheet like structure. It consists of number of flat-plates made up of network of hexagons.
- In it, each carbon atom is directly and covalently bonded to three other carbon atoms by making use of three sp^2 hybrid orbitals.
- A singly occupied p -orbitals remains on each carbon atom which lies at right angles to the plane of the molecule.

- Such p -orbitals undergo overlapping leading to their merger and formation of a new, giant, π -orbital whose one part lies above the hexagonal plane and the other part lies below it.
 - Thus, in graphite, each carbon atom uses only three valence electrons for bonding.
 - The fourth valence electron over each carbon atom is free to move under the influence of applied potential difference.
 - As a result, graphite is a good conductor of electricity. Moreover, graphite is a good thermal conductor due to the π -electrons.
 - In graphite, adjacent sheet are $3.4 \text{ \AA}$ apart and are held together by weak Vander Wall's forces. Due to this structural feature :
 - Density of graphite (2.25 g/cm^3) becomes lesser than that of diamond (3.5 g/cm^3).
 - Coefficient of friction of graphite is low so that even a small force is sufficient to slide the layers parallel to each other. As a result, graphite is soapy to touch and it can be used as lubricant.
 - When we write on a paper with a lead pencil (which contains clay and graphite), thin layers rub off onto the paper, and the resultant impressions helps us to read whatever is written.
- It is to be noted that carbon atoms of each graphite layer are firmly held together by covalent bond. As a result, melting point of graphite is high.

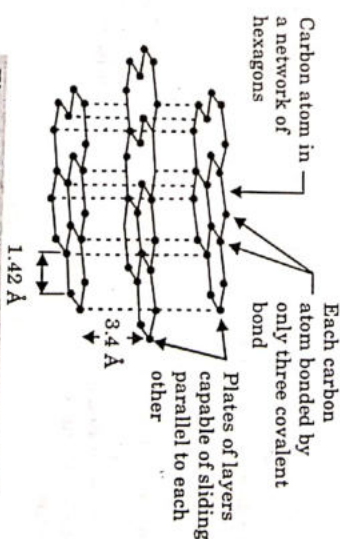


Fig. 1.22.1. Layered structure of graphite.

- Properties of graphite :**
- Density = 2.22 gm/cc .
 - Very soft because of easy sliding of weakly bonded planes of carbon atoms.
 - It is very good conductor of electricity due to π -electron bonds on both sides of planes of carbon atoms.
 - It has higher chemical reactivity than diamond because it contains $C = C$.
 - Graphite sheet-molecules on folding form carbon nano tubes.

- Graphite forms conducting intercalation compounds i.e., compounds formed by insertion of ions, molecules or atoms between graphite layers. The alkali metals, halides, etc., form graphite intercalation compounds.
- Graphite has very good adsorption ability because of C-atoms on surface have unsatisfied valences.

Applications of graphite :

- Being soft, it is used as lubricant either in solid powder form or mixture of graphite with oil.
- Lead-pencils.
- As an adsorbent.
- For electrodes.
- As conductor of electricity.
- For making carbon fibers required for reinforcement.
- Support for catalysts like Pt, Pd, Ph, etc., in electricity, reactions.

Que 1.23.

Discuss the structure, preparation, properties and application of fullerene.

OR

Discuss the structure and applications of fullerenes.

UPTU 2014-15, Marks 05

Answer

- Fullerene is an allotrope of carbon (C_{60}) which is popularly known as Buckminster fullerene in the honor of an architect Buckminster Fuller who designed dome structures based on hexagon and pentagons which resemble with C_{60} .
- Some other discrete molecules with clusters of C atoms like C_{50} , C_{70} , C_{82} have been formed and collectively known as fullerenes.
- Preparation :** Fullerenes are prepared by vaporizing a graphite rod in helium atmosphere. Mixture of fullerenes like C_{60} , C_{70} , etc., are formed which are separated by solvent extraction. Pure C_{60} is isolated from this mixture by column chromatography.

Structure :

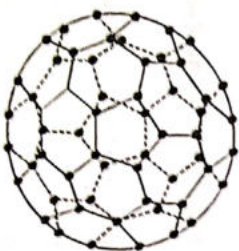


Fig. 1.23.1. Structure of a buckyball.

- The molecule is ionised from having 32 faces in which 12 are pentagons and 20 are hexagons.
- The valences of each C-atom are satisfied by two single bond and one double bond.
- It is a spherical cluster of C atoms arranged in a series of five and six member rings to form soccer ball.

Synthesis of fullerene : It can be prepared :

- by vaporizing the graphite rod in a helium atmosphere,
- evaporation of C using resistive heat,
- when an electric spark is struck between graphite rods.

Properties of fullerene :

- It is black powdery material.
- It forms deep magenta solution when dissolved in benzene.
- It is very tough and thermally stable.
- Some fullerenes like K_3C_{60} exhibits super conductivity.
- It exists as a discrete molecule.
- A magnetic fullerene has been formed by mixing with an organic compound.
- It can be compressed to lose 30% of its volume without destroying its carbon cage structure.

Application of fullerene :

- It is used in making superconductors.
- It is used in making soft ferromagnets.
- It is used in electronic devices.
- It is used in microelectronic and non-linear optical devices.
- It is used as a lubricant.

PART-3

Concepts of Nano-Materials and its Applications.

CONCEPT OUTLINE : PART-3

- Nano-materials :** The materials having at least one dimension in the nano scale are called nano-materials.
- Nano-technology :** It can be defined as the manipulation of atoms and molecules at nano scale (1–100 nm).
- Nano-chemistry :** It involves the study of synthesis and characterization of nano-materials.

• **General method of synthesis :**

1. Bottom-up approach
2. Top-down approach

• **Materials self-assembly :** It is defined as the reversible and spontaneous organization of molecule into ordered structures. It takes place by non-covalent interactions and there is no external work required.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.24. Explain nanotechnology.

UPTU 2012-13, Marks 04

Answer

1. Nanotechnology (sometimes shortened to "nanotech") is the manipulation of matter on an atomic and molecular scale.
2. The earliest widespread description of nanotechnology referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macro scale products, also referred to as molecular nanotechnology.
3. Nanotechnology as defined by size is naturally very broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, micro fabrication, etc.
4. All materials are composed of grains, which in turn comprise of many atoms. Depending on the size, these grains may be visible or invisible to the naked eye.
5. Conventional materials have grains of size varying from hundreds of microns to centimeters. The size of any bulk material can be expressed in three dimensions.
6. The area of any planar material can be expressed in two dimensions and the length of any linear material can be expressed in one dimension.
7. Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.
8. Materials that are nanoscale in one dimension (and are extended in the other two dimensions) are layers, such as thin films or surface coatings.
9. Materials that are nanoscale in two dimensions (and are extended in one dimension) include nanowires and nanotubes.

10. Materials that are nanoscale in three dimensions are particles, for example, precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials which are made up of nanometre-sized grains also fall in this category.

11. Nanoscience can be defined as the study of phenomenon and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.
12. Nanotechnology can be defined as the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometre scale.

Applications of nanomaterials :

1. Nanoparticles are "the small particles with a big future". Because of their extremely small particle size, they have extremely large specific surface area. Hence, they are chemically very active.
2. They are stronger and more ductile. They have electronic states quite different from those of bulk.
3. In dispersed state, nanoparticles are used as fillers, paints, magnetic recording media, ferro fluids, drugs, phosphors, rocket propellants, fuel additives, etc.
4. In consolidate state, nanoparticles are used as catalysts, fuel cells, sensors, adsorbents, synthetic bone, self cleaning glass etc.
5. In ordered assembly form, nanoparticles are used as quantum electronic devices, photonic crystals, DNA chips, biosensors etc.
6. In very dense phase, nanoparticles are used in synthesis of flexible / dense ceramics and insulators, harder metals etc.

Que 1.25. What are nano-materials ? Give its properties.

Answer

Nano-materials : The materials having at least one dimension in the nano scale are called nano-materials.

Properties of nano-materials :

1. **Size-dependent properties :**
 - a. **Particle-size v/s surface area :**
 - i. If a macroscopic object is divided into smaller parts, the ratio of surface atoms to interior atoms becomes a significant number of the total fraction of atoms.

- ii. For example, a cube of iron with side 10 cm long, the percentage of surface atoms is only $10^{-5}\%$.
- iii. When the same cube is cut into smaller cubes with side length 10 nm, the percentage of surface atoms increases to 10%.
- iv. When the cube is further cut into cube with side length 1 nm, every atom comes on the surface. This inverse relation between the particle size and surface area is responsible for the remarkable changes in the physical and chemical properties of nano-materials.

b. Surface chemistry of materials :

- i. Due to increased surface area, nano-materials possess greater surface energy and are thermodynamically less stable.
- ii. The atoms or molecules that exist on the surface or the interface are somewhat different from atoms/molecules in the bulk/interior of the material.
- iii. These have enhanced reactivity and greater tendency to agglomerate. These have higher surface energy and are relatively unstable. As a system, the nano-materials thus strive to attain the lower energy state.

2. Electronic properties :

- a. Various physical properties such as thermal, optical and magnetic properties are dependent on the electronic state of the material.
- b. To understand the electronic properties of nano-materials, let us first understand the electronic properties of solids.
- c. In solids, these are determined by the energy levels, types of bonds between atoms, energy bands, energy gaps and Fermi levels.
- d. Some characteristics of electronic structure of solids are :
 - i. In an isolated solid, the electrons move in quantified energy levels. When the distance between atoms is less, electron orbitals interact with each other, which lead to broadening of energy levels to form energy bands.
 - ii. The inner-shell electrons form narrow bands called internal band and electrons in external shell form valence bands. The electrons in excited state form conduction band.
 - iii. The difference of energy between valence band and conduction bands is called energy gap. In metals, (or conductors) this energy gap is zero; it is small in case of semiconductors and large in case of insulators.

- iv. The maximum energy for electrons at absolute zero (0 K) is called Fermi level energy. The physical properties of materials are mainly governed by electrons that have energy larger than Fermi energy.

3. Mechanical properties :

- a. Nanocrystalline materials have an average crystallite size in the range 1 to 100 nm and are characterized by numerous grain boundaries due to the small size of the grain.
- b. The mechanical properties of nanocrystalline materials are determined by their small grain size and the grain boundary.
- c. These properties are enhanced by reducing the grain size, as grains of nano size have no defects inside, unlike micro-grains of relatively larger size.
- d. For example, nanocrystalline copper is found to be three times more resistant to applied stress than normal copper crystals and deformed homogeneously.
- e. The crystallinity of the grain structure is maintained right up to the grain boundary. The fraction of atoms out of the total volume present at the grain boundaries is large for small size grains and decreases with increase in their size.
- f. In bulk materials constituted by nanoparticles, large number of grain boundaries allow extended grain boundary sliding leading to high plasticity.
- g. In nanometer range, it is generally accepted that grain boundaries act both as sources and sinks for dislocations. So, intrinsic plastic deformations arise from the interplay between dislocation and grain boundaries.
- h. In nanostructured materials, the intrinsic elastic modulus is the same as conventional grain size materials.
- i. However, when the grain size falls below 5 nm, the number of atoms presents at the grain boundary increases and elastic modulus decreases. This decrease is related to increase in the Poisson's ratio.
- j. The nanocrystalline materials exhibit no significant change in ductility as compared to conventional micro-materials.
- k. The reduced ductility of hard nano-materials results in their low toughness and low fracture toughness, thus limiting their use.

Que 1.26. What are the general methods of synthesis for nano-materials ?

Answer:

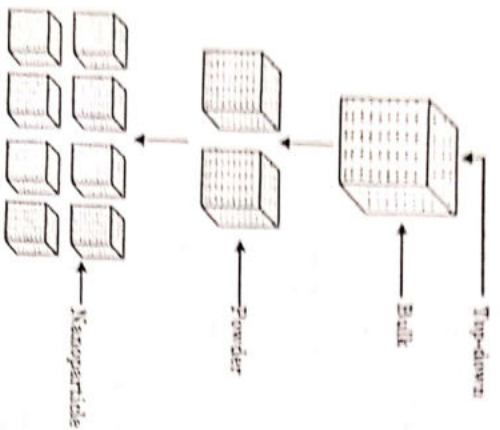


Fig. 1.28.1. Schematic representation of the building up of nanostructures.

Bottom-up approach:

1. Wet chemical synthesis of nanomaterials (sol-gel process):

- i. The sol-gel process is a wet chemical technique (also known as chemical solution deposition) widely used recently in the fields of material sciences and ceramic engineering.
- ii. Such methods are used primarily for the fabrication of materials (typically a metal oxide) starting from a chemical solution (sol).

Engineering Chemistry

about for solution) which acts as the precursor for an integrated network (or gel) of either discrete particles or network polymers.

iii. The reactions involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides $M(OR)_4$ can be described as follows:



2. Liquid solid reactions (precipitation):

- i. In this method, ultrafine particles of the desired material are produced by precipitation.
- ii. The presence of desired nuclei in the solution is a necessary condition to initiate the process.
- iii. For examples, TiO_2 powder with particle sizes in the range 70-300 nm have been prepared from titanium tetraisopropoxide by this method.
- iv. Similarly, ZnS powder may be produced by reaction of aqueous zinc salt solutions with thiocetamide.

3. Gas condensation processing (GPC):

- i. Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys.
- ii. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as electron beam evaporation devices in an inert gas atmosphere.
- iii. Clusters of nanoparticles form in the vicinity of the source by homogeneous nucleation in the gas phase and grow by coalescence and incorporation of atoms form the gas phase.
- iv. The cluster of particle size depends critically on:
 - a. The time spent by the particles in the growth phase,
 - b. Gas pressure,
 - c. The kind of inert gas used, and
 - d. The evaporation rate/vapour pressure of the evaporating material.
- v. The size of nanoparticles increases with increase in gas pressure, vapour pressure and mass of the inert gas.

4. Chemical vapour condensation (CVC):

- i. This technique involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere.
- ii. Nanoparticles of ZrO_2 , Y_2O_3 and many others have been produced by this method. The evaporative source used in GPC is replaced by a hot wall reactor in the CVC process.
- iii. Nanosized particles of metals and ceramics can be obtained in good amounts by adjusting the residence time of the precursor molecules.

changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber and the temperature of the reactor.

- iv. The production capabilities in CVC process are much larger than in GPC processing, however, the microstructure of nanoparticles as well as the properties of materials obtained by CVC are identical to those obtained by GPC prepared powders.

5. Laser ablation :

- i. This method is extensively used for the preparation of nanoparticles and particulate films.
- ii. In this process, a laser beam is used as the primary excitation source for vapourization of metal precursor from the surface and generating clusters directly from a solid sample.
- iii. A high energy pulsed laser beam hitting the target material generates temperatures (greater than 10^4 K) which vapourizes the substance quickly.
- iv. The hot metal vapours are directed in a pulsed flow of inert carrier gas (helium) and expanded through a nozzle into a vacuum.
- v. The cool, high-density helium flowing over the target serves as a buffer gas in which clusters of the target material are formed.

6. Hydrothermal synthesis :

- i. This technique is emerging as an important tool for advanced materials processing. It is based on the ability of water and aqueous solution to dilute the substances at high temperatures and pressures, which are practically insoluble under normal conditions. These include oxides, silicates and sulphides. Autoclaves are used for this purpose because they can withstand high temperature and pressure conditions for a longer period of time.

- iii. A gradient of temperature is maintained at the opposite end so that the hotter end dissolves the nutrient and the cooler end causes the seed to take growth.

- iv. The possible advantages of the process over the other processes are the ability to create crystalline phases that are not stable at the melting point.

7. Thermolysis :

- i. This method involves solvent-less pyrolysis of a suitable precursor material. One of the oldest nano-materials, activated charcoal, is prepared using this method.
- ii. Precursor materials such as wood or coal are pyrolyzed at temperatures 600–900°C in the absence of air to obtain charcoal of specific surface (porous) area up to $2,000 \text{ m}^2 \text{ g}^{-1}$.

- iii. In the process, the materials are carbonized in oxidizing atmosphere of CO_2 , O_2 or steam at 600–1200°C and activation is carried using chemical such as KOH, NaOH, ZnCl_2 or phosphoric acid.

8. **Solvothrmal synthesis :** This is a versatile method for synthesizing nano-materials at temperatures generally below 200°C. This technique enables synthesis of crystalline products at low temperatures and also helps control the size morphology of the resultant products.

9. Electrodeposition :

- i. This technique involves creation of solid materials from electrochemical reactions in liquids. A conducting substrate is placed in liquid containing electrolytes.
- ii. When a potential is applied, redox reaction takes place and the material is deposited as thin film at the cathode.
- iii. Electroless deposition can also be obtained by using complex chemical solutions wherein deposition occurs spontaneously (without applied electric potential) and sometimes auto-catalytically on surfaces.
- iv. Nanorods and nanoparticles can be fabricated by both the methods using templates.
- v. For example, semiconductor ZnO nanotube arrays are synthesized by direct electrochemical deposition from aqueous solution into the pore channels of anodically-formed alumina.

Top-down approach :

1. High-energy ball milling is the milling process commonly used in ceramic processing and powder metallurgy, and involves particle size reduction, solid-state alloying, mixing or blending, and particle shape changes.
2. The process is used only for hard, brittle materials which fracture, deform and cold weld during the milling operation.
3. The technique has been extended to produce a variety of nanocrystalline, amorphous and quasicrystalline materials.
4. A variety of ball mills such as tumblers mills, attrition mills, shaker mills, vibratory mills, planetary mills, etc., are used.
5. In this process, powders with particle diameters of about 50 μm are placed together with a number of hardened steel or tungsten carbide coated balls in sealed container which is rigorously agitated.
6. The most effective ratio for the ball to powders masses is 5–10. High-energy milling forces can be obtained using high frequencies and small amplitudes of vibration.
7. The balls are made up of dense material to ensure sufficiently high kinetic energy, which is a function of mass and velocity.
8. The temperature rise during milling is modest and is estimated to be less than or equal to 100–200°C. The process offers the advantage of high production rates of nanopowders.

Que 1.27. Characterize the nano-materials on the basis of self-assembly.

Answer

1. Self-assembly process is generally considered a bottom-up technique but can combine top-down and bottom-up approaches when small structures are arranged on a template synthesized by top-down method.
2. Self-assembly can be defined as the reversible and spontaneous organization of molecules into order structures. It takes place by non-covalent interactions and there is no external work required as shown in Fig. 1.27.1.
3. They organize themselves in a state of maximum stability and minimum energy.

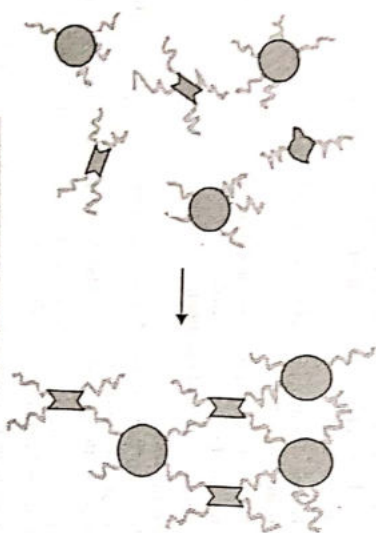


Fig. 1.27.1. Self-assembly.

4. The significance of self-assembly is due to the spontaneity and precision of the process which is also reversible.
 5. In nature, self-assembly is the process by which several complex structures are synthesized ranging from galaxies to assemblies at nanoscale. Self-assembled structures are ubiquitous in biological system and chemistry.
 6. There are several examples of self-assembly at nanoscale, for example, formation of lipid bilayer membrane, folded proteins, DNA helix, etc.
- Characteristics of self-assembly :**
1. Building units
 2. Thermodynamic stability
 3. Environment
 4. Spontaneity and reversibility

f. Mass transport
Classification of self-assembly : The self-assembly can be classified on the following basis :

a. Equilibrium state of the system :

- i. Based on this, the self-assembly can be static or dynamic.
- ii. Static self-assembly systems are stable, as the system approaches equilibrium on forming the ordered structure and therefore do not dissipate energy. The formation of molecular crystals, folded and globular proteins are some examples of static self-assembly.
- iii. In dynamic self-assembly, the interactions between the components can occur only when the system dissipates energy. Reaction-diffusion patterns in oscillating chemical reactions, bacterial colonies are some examples of dynamic self-assembly.

b. Size or nature of building units :

- i. Self-assembly can also be classified based on the size or nature of the building units : atomic, molecular and colloidal.

c. System :

Self-assembly can also be classified based on the system : biological or interfacial.

Types of self-assembly :

1. Directed self-assembly :

- a. Directed self-assembly is quite distinct from spontaneous self-assembly. Physical, chemical and geometrical cues can be added to a self-assembly process so that a desired structure may be obtained.
- b. Directing a self-assembly may involve lithographically patterning a substrate on which self-assembly occurs, so that self-assembly occurs only on specific regions.

c. Honeycomb structured patterns, grid structures, trenches and so on, have been formed by self-assembly directed by lithographic patterning.

2. Molecular self-assembly :

- a. Spontaneous assembly of molecules, without any external intervention is said to be molecular self-assembly. Molecular self-assembly is found in biology, chemistry and materials science.
- b. Formation of molecular crystals, phase separated polymers, colloids, lipid bilayers, protein folding, nucleic acid folding, self-assembled nanolayers (SAMs) all are examples of molecular and intramolecular self-assembly.
- c. There are two types of molecular self-assembly : intermolecular and intramolecular self-assembly.

3. Two-dimensional assemblies :

- Interfaces (region where there is a gradual change of physicochemical properties from one phase to the adjacent phase) can undergo direct self-assembly along certain directions by providing physical, geometrical and chemical spaces.
- This type of self-assembly is known as interfacial or surface self-assembly. Since, there is a restriction of at least one of the dimensions of self-assembly in the length scales of the components, it is also known as two-dimensional self-assembly.
- The average size of the assembly is 10 nm. It differs from one-dimensional assemblies as one dimensional assemblies form arrays while two-dimensional assemblies form lattice.

Que 1.28. Write a short note on mesoscale self-assembly.

Answer

- Mesoscale self-assembly (MESA) is the self-assembly of objects ranging in size from 10 nm to 10 μ m through non-covalent forces such as capillary, magnetic, electrostatic and light forces. This involves the extension of ideas emerging from molecular self-assembly to larger objects.
- Regular arrays of topologically complex, mesoscale objects can be prepared by self-assembly in fluids, with the structure of the arrays determined by shapes of the assembling objects, the wettability of their surfaces and the lateral capillary forces at the interfaces.
- Self-assembly results from minimization of the interfacial free energy of the liquid-liquid interface. The capillary interactions between objects can be viewed as a type of 'bond' that is analogous to chemical bonds that act between atoms and molecules.
- Some examples of MESA involve nanocrystals of CdSe assembled into 3D arrays by changing solvent polarity and the crystallization of polystyrene spheres assembled on a glass plate of Hg surface using capillary or electrostatic forces.

Que 1.29. What are nanoscale materials ? Give application of nanocrystals and clusters.

Answer

Nanoscale materials are nanostructures with size ranging from 1 - 100 nm. They can be constructed by bottom-up or top-down techniques. The various nanoscale materials are discussed as :

Nanocrystals and clusters

- The size of nanocrystals ranges between 1 nm and 100 nm. Nanoclusters are groups of atoms or molecules with an intermediate state of matter between molecules and solids.
- The diameter of nanoclusters ranges upto about 10 nm. Nanoclusters consist up to a few hundreds of atoms, while larger aggregates containing 10^3 or more atoms are often called nanoparticles.
- Nanoclusters have properties and structures which are very sensitive to their composition and size (to the count of every atom) which can lead to new and interesting properties not realised in the corresponding bulk material.
- Traditional materials in the micrometer size particles replaced by metal and semiconductor clusters seem to hold the promise to future leading to miniaturization of devices and eventually a big jump in the world of novel technologies.

Applications of nanocrystals and clusters :

- Many techniques are developed to produce clusters for use in different applications like thin film manufacture for advanced electronic or optical devices, production of nanoporous structures, and fabrication of thin membranes of nanoporous materials.
- Nanoclusters of technologically important inorganic bulk materials such as SiO_2 , ZnO , CdS , etc., were found to be photoinitiators while their corresponding bulk materials did not exhibit this property. ZnS clusters and its aggregates act as effective photocatalysts in reduction of organic compounds.
- The nanoclusters of cerium oxides (CeO_2) materials have been found to possess a significant concentration of Ce^{3+} and oxygen vacancies resulting in excellent poisoning resistance against H_2O and CO_2 and substantial reduction in the temperature of selective SO_2 reduction by CO .

Que 1.30. What are various types of nanocomposite materials ?

UPTU 2012-13, Marks 04

Answer

Different types of nanocomposite materials are :

1. Ceramic-matrix nanocomposites :

- In this group of composites, the main part of the volume is occupied by a ceramic, i.e., a chemical compound from the group of oxides, nitrides, borides, silicides etc.
- In most cases, ceramic-matrix nanocomposites encompass a metal as the second component.

3. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties.

ii. Metal-matrix nanocomposites :

1. Metal matrix nanocomposites can also define as reinforced metal matrix composites. This kind of composites can be classified as continuous and non-continuous reinforced materials.
2. One of the important nanocomposites is carbon nanotube metal matrix composites which is emerging new materials that are being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials.
3. Critical to the realization of CNT-MMC possessing optimal properties in these areas are the development of synthetic techniques that are :
 - a. Economically producible,
 - b. Provide for a homogeneous dispersion of nanotubes in the metallic matrix, and
 - c. Lead to strong interfacial adhesion.

iii. Polymer-matrix nanocomposites :

1. In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in, very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term nanofilled polymer composites).
2. This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix.

Que 1.31. Give general application of nano-materials.

Answer

General applications of nano-materials are :

a. In medicine :

1. **Diagnostics :** Magnetic nanoparticles, bound to a suitable antibody, are used to label molecules, structures of micro-organisms.
2. **Drug delivery :** Drug consumption and side-effects can be reduced considerably by depositing the active agent in the diseased regions and inappropriate dose.
3. **Tissue repair :** Nanotechnology can help to regenerate or to repair damaged tissues and the technique is called tissue engineering.

4. **Transdermal drug delivery :** It involves nanosized protrusions on the underside of patches that would be fixed to the skin like a plaster.

b. In electronics and communication :

1. Quantum well lasers for telecommunication.
2. High electron mobility transistors (HEMT) with low noise.
3. High gain microwave application and vertical cavity surface emitting lasers for data communication and sensor coding.
- c. The devices made from nano-materials are light in weight, easy to carry or move and have reduced power requirement. Some consumer products using nano-materials are :
 1. Computer hardware
 2. Display devices
 3. Mobile and communication products
 4. Audio products
 5. Cameras and films, etc.
- d. Nanomaterials are used to develop semiconductors with much advanced properties. These include :
 1. Transistors from carbon nanotubes with nanometer dimensions.
 2. Memory chips with density of one tetra-byte per square inch.
 3. Very high speed transistors from single atom thick graphene film.



UNIT 2

2

UNIT

Polymers and Organometallics

Part-1 (53H - 72H)

- Polymers
- Basic Concepts of Polymer-Blends and Composites
- Conducting and Biodegradable Polymers

A. Concept Outline : Part-1 53H
B. Long and Medium Answer Type Questions 53H

Part-2 (73H - 76H)

- Preparations and Applications of Some Industrially Important Polymers (Buna N, Buna S, Neoprene, Nylon 6, 6, Terylene)

A. Concept Outline : Part-2 73H
B. Long and Medium Answer Type Questions 73H

Part-3 (77H - 82H)

- General Methods of Synthesis of Organometallic Compound (Grignard Reagent) and Their Applications in Polymerization

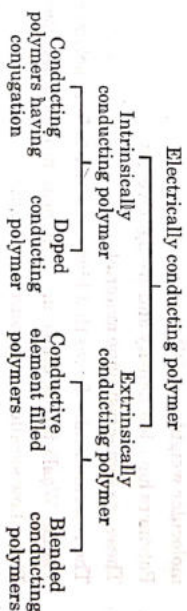
A. Concept Outline : Part-3 77H
B. Long and Medium Answer Type Questions 77H

PART-1

Polymers : Basic Concepts of Polymer-Blends and Composites, Conducting and Biodegradable Polymers.

CONCEPT OUTLINE : PART-1

- **Polymer** : A polymer is a long molecule formed by the joining of thousands of small molecular units by chemical bonds.
- **Polymerization** : The process by which the monomer molecules are linked to form a big polymer molecule is called polymerization.
- **Polymers are classified in a number of ways** :
 1. Based upon source of availability.
 2. Based upon structure.
 3. Based upon mode of polymerization.
 4. Based upon molecular forces.
 5. Based upon the type of mechanism involved during the growth of polymerization chain.
- **Conducting polymer** : A polymer which can conduct electricity is termed as conducting polymer.
- Electrically conducting polymers can be classified in following ways :



- **Biodegradable polymer** : The polymer which gets decomposed by biodegradation are called biodegradable polymers.

Types :
a. Natural
b. Synthetic

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 2.1. Define polymer. Give its characteristics.

Answer

1. The word 'polymer' is derived from the classical Greek words poly meaning 'many' and meros meaning 'part'.
2. Simply stated, a polymer is a molecular compound with high molecular mass, ranging into thousands and millions of grams.
3. It is composed of a large number of repeating units of identical structure called monomers.
4. For example, polythene is a polymer formed by linking together of a large number of ethene molecules.



5. Certain polymers, such as proteins, cellulose, and silk are found in nature and hence are called natural polymers, whereas, a number of polymers are produced by synthetic routes and are called synthetic polymers.
6. In some cases, naturally occurring polymers can also be prepared synthetically. For e.g., rubber, which is also known as polyisoprene.

Characteristics of polymers are :

1. Polymers are also known as macromolecules because their average molecular weights are 10^5 or more.
2. Polymers have low density and are light weight.
3. These are semi-crystalline materials.
4. The intermolecular forces that bind monomer to form polymers are Vander Waal's forces, dipole-dipole attractions or hydrogen bonding.
5. They show excellent resistance to corrosion.
6. Polymers are good thermal and electrical insulators.
7. They have low tensile strength and stiffness.
8. Polymers like rubbers possess good elastic properties.
9. They are tailor made materials that can be moulded easily in desired shape.

Que 2.2 What do you mean by degree of polymerization and functionality of polymers ?

Answer

Degree of polymerization : The number of repeating units in a chain formed in a polymer is known as the 'degree of polymerization'. Polymers with high degree of polymerization are termed as 'high polymers' and those with low degree of polymerization are called oligopolymers.

Functionality of polymers :

1. Functionality means the number of bonding sites in a monomer. The double bond in vinyl monomers ($\text{CH}_2 = \text{CHX}$) can be considered as a site for two free valences.
2. When the double bond is broken, two single bonds become available for combination.
3. For example,



4. Thus, vinyl monomers can be considered as bifunctional because they have two reactive (or bonding) sites. For a substance to act as a monomer, it must have at least two reactive (or bonding) sites.

Functionality and structures of polymers :

1. When the functionality of monomer is two, linear or straight-chain polymer molecule is formed.

Examples of Bifunctional monomers : all vinyl monomers, Hexamethylene diamine, Adipic acid, Terephthalic acid, Ethylene glycol, Amino-acid, etc.

2. When the functionality of monomer is three, three-dimensional network polymer is formed.

Examples of Trifunctional monomers : Phenol, Melamine, etc.

3. When a trifunctional monomer is mixed in small amounts with a bifunctional monomer, a branched chain polymer is formed.

4. When a bifunctional monomer is mixed in small amounts with a trifunctional monomer, a three-dimensional network polymer is formed.

Que 2.3. How are polymers classified ? Explain.

OR

What is meant by tacticity ? With suitable examples, explain Isotactic Syndiotactic and Atactic polymers.

UPTU 2014-15, Marks 05

OR

What are graft and block copolymers ? Give examples.

UPTU 2011-12, Marks 05

OR

How would you obtain syndiotactic and isotactic polymers from propylene ?

UPTU 2012-13, Marks 04

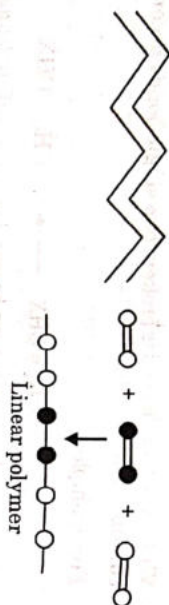
Answer

Polymers can be classified as :

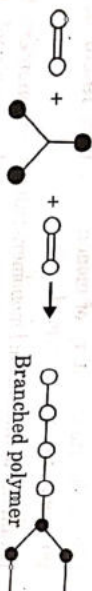
1. Based on polymeric structure : A polymer molecule may be of three types on this basis :

- a. **Linear** : In linear polymers, the monomer units are join together end to end in a single chain.

For example, High density polyethylene, Nylons etc.



- b. **Branched** : Branched polymers are the polymers in which the same side chains or branches are connected to the main chain. For example, low density polyethylene, starch etc.



- c. **Cross linked or Network** : Polymers in which monomers are cross linked together in all three dimensions to form three dimensional network structure are termed as network polymers. For example, Thermosets, Rubbers etc.



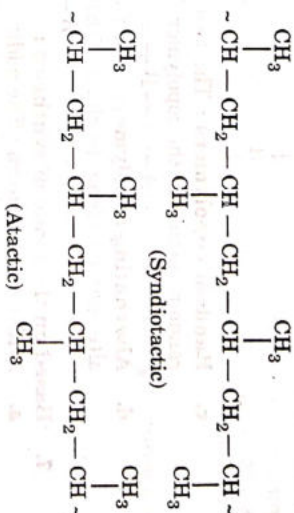
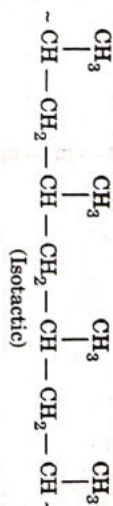
2. **Based on tacticity or stereochemistry** : The arrangement of monomers to form polymers are termed as tacticity. Depending upon the tacticity, polymers are of three types :

- a. **Isotactic polymer** : In isotactic polymers all the functional groups or alkyl groups lie on one side of the chain and the hydrogen atoms on the other side.

For example, Natural rubber.

- b. **Atactic polymer** : If the groups are arranged randomly above and below the chain, then polymers are known as atactic polymers. For example, Polypropylene.

- c. **Syndiotactic polymer** : If the alkyl groups and hydrogen atoms fall alternatively above and below the chain, then this orientation is referred to as syndiotactic.



3. **Based on physical state** : Polymers can be amorphous (Rubbers) or semicrystalline (example, Nylon, Polyesters).

4. **Based on its origin** : Polymers are of two types on the basis of its sources :

- a. **Natural polymer** : The polymers obtained from natural sources (such as plants & animals) are natural polymers. For example, starch.

- b. **Synthetic polymer** : Synthetic polymers are man-made materials and made from smaller molecules by chemical means. The raw materials for the preparation of synthetic polymers are obtained from petroleum and coal tar, for example, polyethylene, rubber (synthetic), terylene etc.

5. **Based on the chemical structure** :

- a. **Homopolymer** : The polymers in which the entire polymer chain is made up of one single repeating unit. For example, Polyethylene, polyvinyl chloride etc.

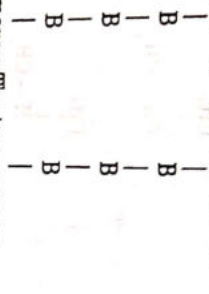
- b. **Copolymer** : The polymers in which the polymer is having more than one type of repeating unit in polymer backbone. For example, Nylon 6, 6, Terylene. This process is known as co-polymerization.

6. **Based on the types of monomers** :

- a. **Block copolymers** : A sequence of one monomer is followed by a sequence of the other monomer in the copolymer.

$\sim A - A - A - B - B - B - A - A - A - A -$
(A, B = different monomers)

- b. **Graft copolymers** : The polymers that contain main chain of exclusively one monomer with branches of the second monomer.



- c. **Random copolymers** : The two monomers are arranged in a random manner in the copolymer. Thus,



- d. **Alternating copolymers** : The two monomers are incorporated alternately along the chain of the copolymer. Thus,

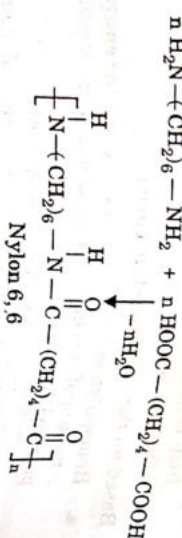


7. **Based on the mode of synthesis** :
- a. **Addition polymers** : The addition polymer is one in which the monomers with multiple bonds undergo true addition, to form the polymers.

For example, Polystyrene, polyvinyl chloride etc.



- b. **Condensation polymers** : In a condensation polymer, two organic molecules combine with the elimination of smaller molecules like water, alcohol or ammonia to give a polymer. For example, Nylon 6, 6.



8. **Based on the behaviour when heated** : These are of two types :
- a. **Thermoplastics** : The polymers which gets soften on heating and hardened on cooling without or with little change in their properties. For example, LDPE, HDPE, Nylon 6, 6, etc.
- b. **Thermosetting** : The polymers which once hardened can not be softened again. For example, Bakelite.
9. **On the basis of ultimate form** : Depending on their ultimate form and use, a polymer can be classified as :

- a. **Plastics** : All the synthetic polymers (other than elastomers) are usually referred to as plastics. The polymers which are shaped into hard and tough utility articles by the application of heat and pressure are called plastics. At some stage of manufacture, these are in plastic condition (Plasticity is the property by virtue of which a material undergoes permanent deformation under stress).

- b. **Elastomers** : The polymers which are capable of being stretched rapidly at least 150 percent of their original length without breaking and return to their original shape on release of stress are known as elastomers. Synthetic rubbers constitute important examples of this group.

Que 2.4. Give the statistical methods for average molecular weights of polymers.

OR

Why do polymers have an average molecular weight ?

Answer

The principal statistical methods for calculating average molecular weight of a polymer, are given below,

1. **Number average molecular weight ($\bar{M}_n$)** :

- a. Consider a small piece of a polymer, which contains total number of polymer molecules as 'n'.
- b. Out of the 'n' molecules, if n_1 molecules in the polymer have molecular weight M_1 .
- c. n_2 molecules in the polymer have molecular weight M_2 .
- d. n_3 molecules in the polymer have molecular weight M_3 .
- And so on.

- e. The total number of molecules = $n = n_1 + n_2 + n_3 \dots + n_i = \sum_{i=1}^{i=n} n_i$

- f. Molecular weight of n_1 molecules is $n_1 M_1$ and the molecular weight contribution by n_1 molecules will be, $\frac{n_1 M_1}{\sum n_i}$

- g. And similarly molecular weight contribution by $n_2, n_3, \dots, n_i$ molecules.

$$\text{Hence, the } \bar{M}_n = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + \dots + n_i M_i}{\sum n_i} = \frac{\sum n_i M_i}{\sum n_i}$$

- h. The $\bar{M}_n$ can be found experimentally by the study of colligative properties. The property of solution, which depends upon the number of particles in solution and independent of size of particles, is the colligative property.

2. Weight average molecular weight ($\bar{M}_w$) :

- Consider a piece of polymer having weight W ,
- Suppose w_1 is the weight of polymer molecules having M_1 molecular weight;
- w_2 is the weight of polymer molecules having M_2 molecular weight, and so on.
- The total weight of polymer is, $W = w_1 + w_2 + w_3 \dots = \sum w_i$
- Weight fraction of w_1 weight = $\frac{w_1}{W}$ and the molecular weight contribution by w_1 weight fraction = $\frac{w_1 M_1}{W}$
- Similarly, the contribution to molecular weight by other weight fractions can be considered.

The weight average molecular weight,

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 \dots}{\sum w_i} = \frac{\sum w_i M_i}{\sum w_i} \dots (2.4.1)$$

g. If weight w_1 contains n_1 molecules having M_1 molecular weight each, then

$$w_1 = n_1 M_1$$

$$\sum w_i = \sum n_i M_i$$

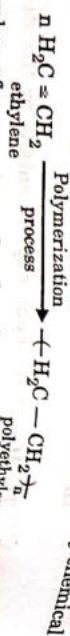
Hence, Replacing the w_i terms by $n_i M_i$, Equation (2.4.1) becomes

$$\bar{M}_w = \frac{\sum n_i M_i \cdot M_i}{\sum n_i M_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

- The weight average molecular weight is found experimentally, by light scattering or ultramicroscope technique, in which the polymer chain size makes the contribution to the measured results.
- The solution of a polymer is always colloidal and it possesses the property of light scattering.

Que 2.5. Define polymerization and monomer.**Answer****Polymerization :**

- The process of joining large number of simple molecules to form polymer molecules is known as polymerization.
- A large number of ethylene molecules (monomer) get joined by huge bonds to form polyethylene.



- The number of monomer molecules that get joined to form polymer molecules is generally greater than 100 and may be up to many thousands.

Monomers :

- Monomer is the simple chemical substance of low molecular weight which can be converted into a polymer and the molecule of monomer has at least two easily reacting positions.
- The monomer molecules act as the building blocks of polymer.
- A monomer molecule has the easily reacting positions in the form of either functional groups or in the form of $C \equiv C$.
- The functional groups in the monomer organic molecules can be like $-OH$, $-COOH$, $-NH_2$, $-C \equiv N$, $-COOR$, $-Cl$, cyclic amide (lactam) group, cyclic acid anhydride group, etc.
- A $C \equiv C$ contains a weak π -bond and it can easily be broken by the action of heat or a reagent.
- When the π -bond is broken, two positions become available for polymerization.

Que 2.6. State the difference between addition and condensation polymerization.**Answer**

S. No.	Addition polymerization	Condensation polymerization
1.	The polymerization reaction in which monomer form polymer without elimination of any atom or group, example, PE, PP, PVC.	The polymerization reaction in which monomer form polymer with elimination of small molecules like water, alcohol, example, Nylon 6, 6, Nylon 6, 10.
2.	Generally one type of monomers is involved.	Generally more than one type of monomers is involved.
3.	The polymer is the exact multiple of monomer.	The polymer is not the exact multiple of monomer.
4.	Generally alkenes and their derivatives used as monomers.	Generally, bifunctional monomers are used.
5.	Homopolymers are formed.	Copolymers are formed.
6.	Initiator is needed.	No initiator is needed.
7.	This is also known as chain reaction polymerization.	This is also known as step growth polymerization.

Que 2.7. Classify the polymers on the basis of polymerization reaction.**OR**

Define condensation polymerization.

Answer

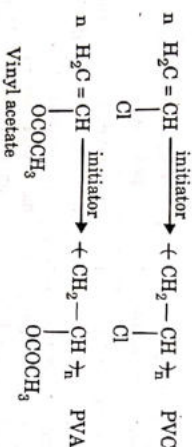
On the basis of type of polymerization reaction, polymers are classified as :

1. Addition or chain polymers :

- The polymers obtained by addition or chain polymerization of monomer having π bond, are the addition or chain polymers.
- During the addition reaction, π -bond in the monomer is utilized for polymerization and there is no byproduct formation.
- Addition or chain reaction forms the polymer having formula exact multiple of monomer formula.

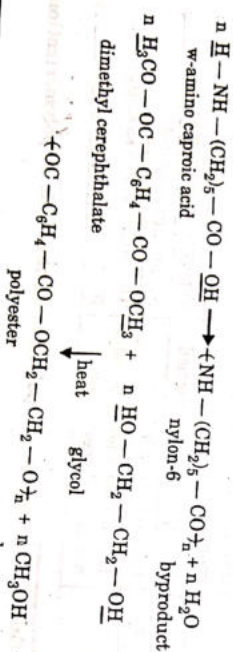


All vinylic monomers undergo the addition reaction during polymerization, in the presence of a catalyst or initiator. This type of reaction is fast and exothermic. For example, PE, PVC, PS, PMMA, ABS plastics, PTFE, PVA, etc.



2. Condensation or step polymers :

- The polymer formed by stepwise condensation reaction between functional groups of monomers along with a byproduct formation, is called as condensation polymer.
- For example, polyester, polyamide (nylon), urea-formaldehyde resins, epoxy polymers, etc.



Que 2.8. Write a short note on step growth and chain growth polymerization.

Answer

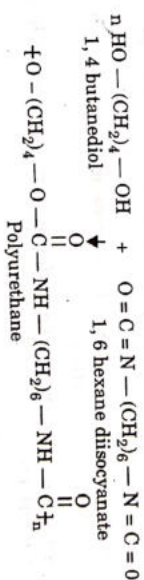
Another classification scheme based on polymerization kinetics has been adopted over the traditional addition and condensation categories. According to new scheme, all polymerization mechanisms are classified as either chain growth or step growth polymerizations.

1. Chain growth polymerization :

- During chain growth polymerization, high molecular weight polymer is formed early during polymerization and polymer yield gradually increases with time.
- Chain growth polymerizations require the presence of an initiating molecule that is used to activate the monomer molecule at the start of the polymerization.
- Most of the addition polymers are chain growth polymers and hence in most of the books the term chain growth and addition polymerization are used interchangeably.

2. Step growth polymerization :

- In step growth polymerization, high molecular weight polymer is formed only near the end of the polymerization.
- Most of the condensation polymers are step growth polymerization, but a number of important exceptions exist.
- In step growth polymerization, the reaction takes place in stepwise manner and polymer build-up is slow (unlike chain growth, where the polymer build-up is very rapid).
- Apart from condensation reactions discussed earlier, step growth polymerization includes some addition reactions also.
- Example, the non-condensation step growth polymerization of a polyurethane prepared by ionic addition of a diol (1, 4 butanediol) to a diisocyanate (1, 6 hexane diisocyanate)



Que 2.9. Giving suitable examples, distinguish between thermoplastic and thermosetting polymers.

UPTU 2013-14, Marks 05

Answer

S.No.	Thermoplastic	Thermosetting
1.	They soften on heating.	They do not soften on heating.
2.	They are long - chain linear molecules structure.	They have three dimensional cross linked network structure.
3.	They are formed by addition polymerization.	They are formed by condensation polymerization.
4.	They can be softened, reshaped and reused.	They cannot be reshaped and reused.
5.	They are weak, soft and less brittle.	They are strong, hard and more brittle.
6.	They can be reclaimed by waste.	They cannot be reclaimed by waste.
7.	They are soluble in organic solvent.	They are insoluble in organic solvent.
	Examples: Polythene, polypropylene, polyvinylchloride etc.	Examples: Bakelite, epoxy resin, melamine etc.

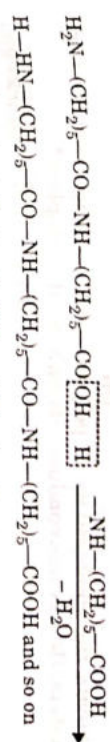
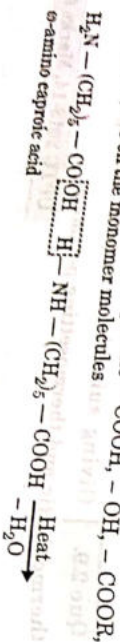
Que 2.10. What is the necessary condition for a monomer to undergo condensation polymerization ?

Answer

UPTU 2014-15, Marks 05

Condition : The monomer contains certain functional groups.

1. In this mechanism, the polymer molecule build-up proceeds through the stepwise reaction between the reactive functional groups on monomer molecules.
2. The reaction takes place slowly in stepwise manner to join monomer molecules one after another.
3. In most of the cases, there is formation of a simple byproduct like H_2O , $NaCl$, $R-OH$, etc.
4. Monomers contain functional groups like $-COOH$, $-OH$, $-COOR$, $-NH_2$ etc., are on the monomer molecules



The final product of nylon 6 will have following structure,



5. The byproduct of reaction here is water.
6. The two ends of the polymer have $-NH_2$ and $-COOH$ groups and hence the polymer molecule can grow further if more monomer made available.

Que 2.11. Giving suitable example distinguish between chain growth and step growth polymerization process.

UPTU 2013-14, Marks 05

Answer

S.No.	Chain or addition polymerization	Step or condensation polymerization
1.	Monomer molecule has $C=C$ bond.	Monomer molecule has functional group.
2.	Catalyst is essential.	Catalyst may or may not be required.
3.	Exothermic reaction.	Endothermic reaction.
4.	Once the reaction initiated, it goes very fast.	Reaction on growing chain takes place slowly and in stepwise manner.
5.	By product not formed.	Generally byproduct is obtained along with polymer.
6.	Polymer chain ends are dead.	Polymer chain ends are live.
7.	Molecular weight relatively lower.	Molecular weight varies low to very high depending upon time and temperature of reaction.
8.	Mechanism involves, initiation, propagation, termination steps.	Mechanism involves monomer molecules reacting one after another.

Que 2.12. Discuss the differences between thermoplastic and thermosetting polymers. Write a brief note on conducting polymers.

UPTU 2014-15, Marks 10

OR

Explain the conductivity of polymers with conjugated π -electron system. How is this conductivity enhanced by doping?

OR

What are the conditions which make the polymer conducting?

Answer

Conducting polymers :

A polymer which can conduct electricity is termed as conducting polymer.

Examples :

- Polyaniline is used to make rechargeable batteries in the shape as flat buttons or as laminated rolled films.
- Polypyrrole is used in 'smart' windows. These smart windows can change their colour in response to changes in temperature or amount of sunlight. The colour change is from a transparent yellow-green to blue-black.

Classification of conducting polymers :

Conducting polymer can be classified into following types :

- Intrinsically conducting polymers :** These polymers have extensive conjugation in the backbone which is responsible for conductance. These are further of two types :

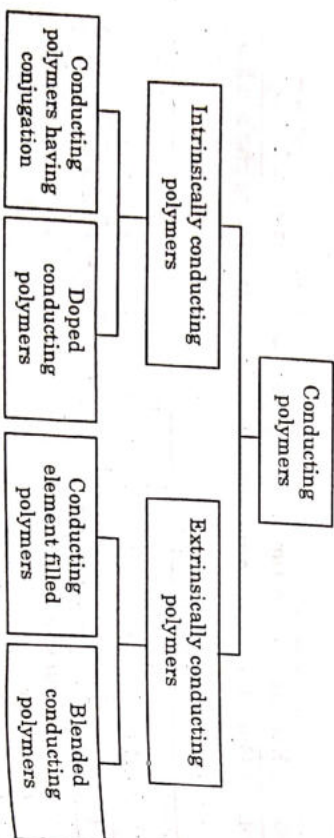
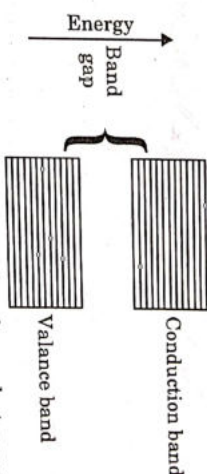


Fig. 2.12.1.

- Conjugated π -electrons conducting polymers :**

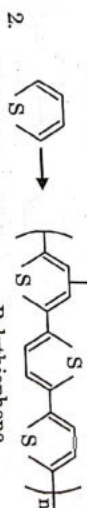
- A key property of a conductive polymer is the presence of conjugated double along the backbone of the polymer.
- The orbitals of conjugated π -electrons overlap over the entire backbone of the polymer, resulting into the formation of valence bands as well as conduction bands, extending over the entire polymer molecule.

- The energy spacing between the highest occupied and lowest unoccupied band is called the band gap. The highest occupied band is called the valence band and the lowest unoccupied band is the conduction band.
- If the band gap is narrow, the electrons from the valence band are excited to conduction band giving rise to conductivity. If the band gap is too wide, the substance is an insulator.
- In an electric field, conjugated π -electrons get excited and electrons have sufficient energy to jump the gap and reach conduction band.



- In other words, electrons thereby can be transported through the solid polymeric material and hence polymer becomes conducting.

Examples :



- Doped conducting polymers :**

- It was shown that electrical conductivity of polyacetylene could be increased by a factor of 10^2 S cm^{-1} when it was doped with an electron donor, such as alkali metal ion or an electron acceptor, such as arsenic pentafluoride (AsF_5) or iodine.

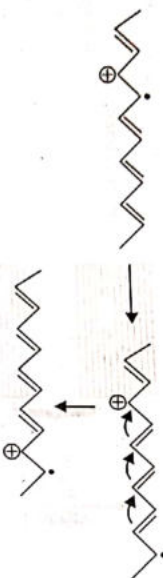
- The process of doping can be carried out by two methods :

1. Oxidation :

- In this process, doping typically removes some electrons from π bond of the conjugated double bonds as they have low ionization potentials.
- The holes so created can move along the molecule, i.e., the polymer becomes electrically conductive.
- Thus, when an electron is removed from the top of the valence band of a conjugated polymer, such as

polyacetylene or polypyrrole, a valence (hole or radical cation) is created, causing partial delocalization, extending over several monomeric units.

- iv. The radical cation is called 'polaron'. It stabilizes itself by polarizing the medium around it and hence the name.
- v. The polarons are mobile and can move along the polymer chain by rearrangement of double and single bonds and hence the polymer become conducting.



2. Doping through reduction :

- i. In this type of doping some electrons are introduced into the polymer having conjugate double bonds as they have high electron affinities.
- ii. This process is brought about by adding Lewis bases.
- iii. It should be noted that polyaniline exists in four oxidation states of which, only the emeraldine salt is conducting which require protonic doping of the imine nitrogen.



2. Conductive element-filled polymer :

- a. These are the polymers which are filled with conducting elements, such as carbon black, metallic fibres, metal oxides etc.
- b. The polymer acts as a binder to hold the conducting elements together. These polymers possess reasonable conductivity.
- c. Moreover, these are low in cost, light in weight and mechanically durable and strong. Carbon black which is used as filler is special conducting grade carbon.
- d. This carbon has very high surface area and is highly porous. However, the addition of the filler affects the properties of the polymer such as tensile strength, and impact strength etc.
- e. This problem can be overcome by the use of blended conducting polymers.

- 3. **Blended conducting polymer :** Conducting polymers can be blended with the conventional polymers to produce blends. These blends so formed possess better physical, chemical and mechanical properties.

Engineering applications of conducting polymers :

Potential applications of conductive polymers are quite significant. This is due to the fact that these are generally lighter, more flexible and easier to fabricate than many of the materials, which are conventionally used.

Some of the promising applications include :

- i. **Rechargeable batteries :** The use of conducting polymers as cathodes and solid electrolytes in batteries for automotive and other applications is highly advantageous as an alternative to lead acid batteries. The polymeric batteries have high reliability, light weight, nonleakage of electrolyte solution and are small in size.
- ii. Some conducting polymers like polyaniline show different colours in different oxidation forms. This electrochromic property can be used to produce "smart windows," and electrochromic displays. (Smart windows are the windows which change colour in response to sunlight or temperature changes).
- iii. These are also used in electroluminescence displays like in mobile phones etc.
- iv. Other possible uses of conductive polymers include analytical sensors.
- v. These can also be used in Light Emitting Diodes (LEDs), electromagnetic shielding and non-linear optical material.
- vi. Can also be used in photovoltaic devices.

Difference between thermoplastic and thermosetting polymers :

Refer Q. 2.9, Page 63H, Unit-2.

Que 2.13. Define biodegradable polymers. Write down the applications of biodegradable polymers.

Answer

Biodegradable polymers :

Biodegradable polymers are those polymers which get decomposed by the process of biodegradation. Biodegradation is defined as a process carried out by biological systems (usually fungi or bacteria) wherein a polymer chain is cleaved via enzymatic activity.

Requirements of biodegradation :

There are essentially following three elements for the biodegradation process which needs to be simultaneously present :

- a. **Micro-organisms :** These micro-organisms must exist with the appropriate biochemical machinery to synthesize enzymes specific for the target polymer to initiate to depolymerization process.
- b. **Environment :** The following environmental factors must be tuned in a given environment within the window of acceptability for the organisms producing the appropriate enzymes to degrade the target polymer :
 - i. Temperature,

- ii. Pressure,
- iii. Moisture,
- iv. Oxygen,
- v. Type and concentration of salts,
- vi. Light etc.

c. **Substrate** : Here the substrate refers to biodegradable polymer. It must have following essential features for biodegradation process to be successful :

- i. **Suitable functional groups** : The polymer chain must contain suitable functional groups or linkages (like ester groups) which are susceptible to hydrolysis or oxidation by micro-organisms (or enzymes) for the initiation of the biodegradation process.
- ii. **Hydrophilicity** : Greater the hydrophilicity of the polymer, usually larger is rate of biodegradation.
- iii. **Low molecular weights** : Polymers with low molecular weights are more susceptible towards biodegradation.
- iv. **Less crystallinity** : As the crystalline domains are difficult to be accessed by the enzymes for the degradation process to start so lesser the degree of crystallinity, more will be the biodegradation.

Types of biodegradable polymers :

Broadly, biodegradable polymers can be classified into two types : Natural and Synthetic. In general, naturally occurring polymers are more biodegradable than synthetic polymers.

- a. **Natural biodegradable polymers** : Natural rubber, collagen, lignin, poly(γ -amino-glutamic acid) are some of the examples of natural biodegradable polymers.
- b. **Synthetic biodegradable polymers** : Poly(vinyl alcohol, polyanhydrides, poly-(3-Hydroxybutyrate-CO-3-Hydroxyvalerate) or PHBV are some of the examples of synthetic biodegradable polymers.

Need for biodegradable polymers :

The problems with traditional, non-biodegradable polymers are :

- i. Solid waste problems, particularly with regard to decreasing availability of landfills,
- ii. Litter problems, and
- iii. Entrapment or ingenious hazards to marine life.

Biodegradable polymers are a particularly attractive option for addressing the solid waste and marine pollution concerns. Biodegradable polymers do not need to be land filled, they will re-enter normal geochemical cycles over time and many of the polymers are derived from renewable resources.

Applications of biodegradable polymers :

- i. Poly (β -hydroxy butyrate) or PHB : PHB is used in the manufacture of shampoo bottles.
- ii. β -hydroxy butyrate-b-hydroxyvalerate or HB-HV copolymers : The HB-HV copolymers are suitable as matrices for controlled release of drugs due to their favourable biocompatibility and biodegradation properties.
- iii. Poly (lactic acid) or PLA. As PLA breaks down in the environment back to lactic acid, which can be metabolized, it has found commercial use in medical applications such as sutures, drug-delivery systems and wound clips. It is also used in some agricultural applications, such as timed-release coatings for fertilizers and pesticides.

Limitations of biodegradable polymers :

- i. Biodegradation and recycling are two major approaches to plastic waste management. However, biodegradable polymers are not suitable candidates in the recycling of commingled plastics.
- ii. Generally, biodegradable polymers are very expensive.
- iii. Broadly speaking, biodegradable polymers are not easily available.
- iv. In order to store potentially hazardous materials, landfills are built to be free of moisture and airtight. These anaerobic conditions which serve to guard against the release of hazardous chemicals from landfills, also retard biodegradation.

Que 2.14. How do natural biodegradable polymers undergo biodegradation ?

UPTU 2014-15, Marks 05

Answer

1. They are a specific type of polymers that break down after intended purpose to result in natural byproducts such as gases (CO_2 , N_2), water, biomass, and inorganic salts.
2. These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and other functional groups.
3. Their properties and breakdown mechanism are determined by their exact structure.
4. These polymers are often synthesized by condensation reactions, ring opening polymerization, and metal catalysts.

Que 2.15. Discuss biomedical polymers.

UPTU 2012-13, Marks 04

Answer

1. Biomedical polymers are thermoplastic, low-melting polymeric implant materials based on lactide / caprolactone-monomers. The polymer properties can be varied in wide ranges i.e., properties can be tailored according to the needed application.
2. Typically, this polymer is low melting. For example at 48°C, and thereafter it solidifies at body temperature and becomes a solid, plastic-like material.
3. At molten stage, temperature sensitive active agents can be easily blended into the polymer, which will then be released at a controlled release rate based on diffusion.
4. Several basic studies of this polymer with different active agents have shown that it functions with many of the active agents significantly better than for example polylactide.
5. The degradation times of these polymers are typically in the range of 3 – 12 months. Biodegradable polymers which have medical applications are also termed as biomedical polymers.

Medical applications of biodegradable polymers: Wound management, dental applications, orthopaedic devices, cardiovascular applications, intestinal applications.

Biodegradable polymers used for medical applications:**i. Natural polymers:**

- a. Fibrin
- b. Collagen
- c. Chitosan
- d. Gelatin
- d. Hyaluronan

ii. Synthetic polymers:

- a. PLA, PGA, PLGA, PCL, Polyorthoesters
- b. Poly(dioxanone)
- c. Poly(anhydrides)
- d. Poly(trimethylene carbonate)
- e. Polyphosphazenes

PART-2

Preparations and Applications of Some Industrially Important Polymers (Buna N, Buna S, Neoprene, Nylon 6, 6, Terylene).

CONCEPT OUTLINE : PART-2**Some industrially important polymers are:**

1. Buna N
 2. Buna S
 3. Neoprene
 4. Nylon 6
 5. Nylon 6, 6
 6. Terylene
- **Buna N:** It is prepared by copolymerization of butadiene and acrylonitrile in emulsion system.
 - **Buna S:** It is prepared by the copolymerization of butadiene and styrene in an emulsion system at 50° C in the presence of cumene hydroperoxide as catalyst.
 - **Neoprene:** It is a polymer of chloroprene and is also called polychloroprene.
 - **Nylon 6:** It is a condensation polymer of only one type of monomer molecules containing six carbon atoms.
 - **Nylon 6, 6:** It is a condensation polymer of two types of monomer molecules each containing six carbon atoms.

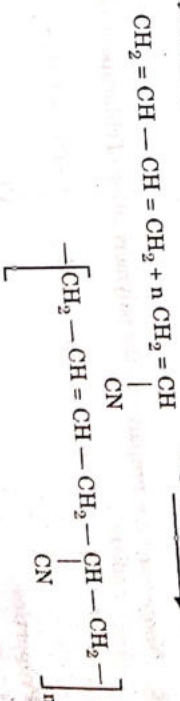
Questions-Answers**Long Answer Type and Medium Answer Type Questions**

Que 2.16. Give the preparation, structure and applications of following polymers:

1. Buna N
2. Buna S
3. Neoprene

Answer**1. Nitrile Rubber (GR-A, BUNA-N or NBR)**

Preparation: It is prepared by the copolymerization of butadiene and acrylonitrile.

**Properties:**

1. Resistant to acids, heat and oils.

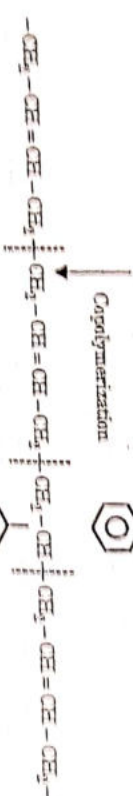
1. In their immigration and absorption policies.

Application: It is used for:

1. Conveyer belts.
1. Adhesives.
3. Airmobiles parts and high altitude aircraft components.
4. Coatings.
3. Printing rollers.
3. Oil resistance films.

4 Styrene Rubber (GR-S, Buna-S or SBR)

Preparation: It is prepared by the copolymerization of 75% butadiene and 25% styrene at 50° C in the presence of cumene hydroperoxide as catalyst.



(Styrene Butadiene Rubber (SBR) having repeating units of mainly 1, 4 addition product.

Properties:

1. High abrasion resistance.
2. High load bearing capacity.
3. Swells in oils and solvents.
4. Low oxidation resistance.

Application : It is used for :

1. Shoe soles.
2. Wire and cable insulations.
3. Motor tyres.
4. Gaskets.
5. Adhesives.
6. Carpet backing.

40

Neoprene: It is prepared by the polymerization of chloroprene (2-chloro-1,3-butadiene).



Properties:

1. Resistance to vegetable and mineral oils

2. Soluble in polar solvents.
 3. Resistance to degradation.
- Application: It is used for:

Application:

1. Damping vibrations in aircrafts.
2. Lining of vessels.
3. Tyres.
- 4.

4. *Yes.*

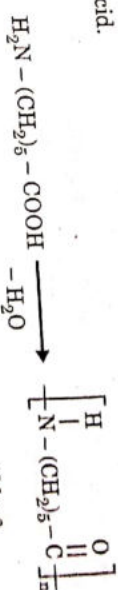
Que 2.17. Give the preparation, properties, structure and following polyamides:

Nylon 6, Nylon 6, 6, and terylene

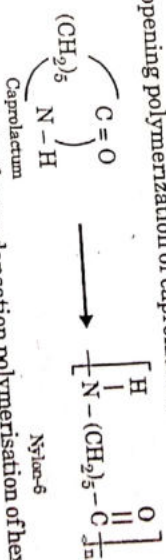
Answer

Answer Synthetic fiber forming polyamides are also termed as 'Nylons'. The important of this category are discussed below :

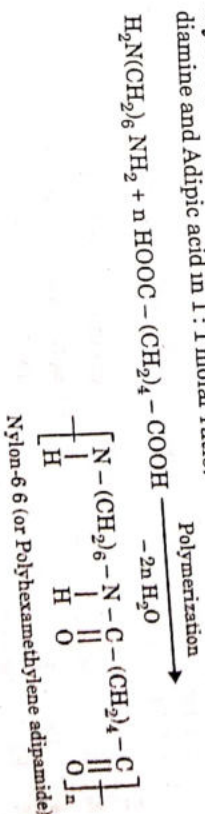
polymers of ϵ -caproic acid.



or by ring opening polymerization of caprolactam
[H



Nylon-6, 6: It is made by the condensation polymerisation of hexamethylene diamine and Adipic acid in 1:1 molar ratio.



Properties:

- a. The structure of nylons are linear that permits strong intermolecular forces. The chains are held together by hydrogen bonds.

The structure of nylons are crystalline. The molecular chains are held together by hydrogen bonds. Moreover, the molecular chains are highly crystalline which imparts high strength, high melting point, elasticity, toughness, abrasion resistance and retention of good mechanical properties upto 125°C.

- b. They are also sterilisable.

- c. Since nylons are polar polymers they have good hydrocarbon resistance. Larger the number of carbon atoms, greater will be ease of processing and hydrocarbon and moisture resistance.

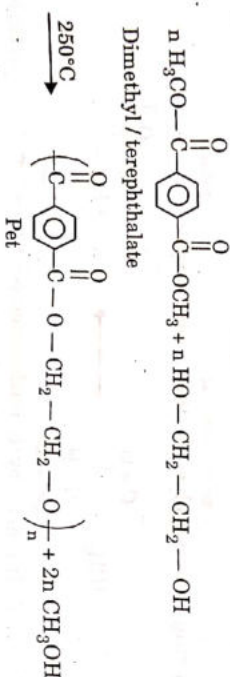
Applications:

- a. Nylon-6,6 is primarily used for fibers, which find use in making socks, tinder-garments, carpets etc.
- b. Nylon-6,6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cams etc. Apart from advantageous properties listed above, Nylon moving parts may be frequently operated without lubrication. They are silent running and may often be moulded in one piece when previously a metal part required assembling of several parts or alternatively extensive machining with consequent waste of material.
- c. Mouldings having application in medicine and pharmacy because of sterility.
- d. Durable (but costly) hair combs.

Chemically terylene is polyethylene terephthalate.

Polyethylene Terephthalate (PET):

PET is a commercial polyester product also known as terylene or dactron and it is obtained by condensation reaction between ethylene glycol and dimethyl terephthalate at high temperature.

**Properties:**

1. It forms crystalline polymer because of symmetrical structure and polar ester groups in chain.
2. It can be easily converted to fine fibers of very good tensile strength.
3. It has good impact strength and better thermal stability.
4. Fibres of PET are crease resistant, low moisture absorbing.
5. PET is resistant to O_2 and acids but is attacked by alkali.

Applications:

1. It is the most common synthetic fabric material.
2. It can be blended with cotton, viscose, wool, silk to get better fabrics.
3. It is useful for making magnetic recording tapes.
4. It can be converted to films and bottles.
5. It is used for making buttons knobs.

PART-3

*General Methods of Synthesis of Organometallic Compound
(Grignard Reagent) and their applications in Polymerization.*

CONCEPT OUTLINE : PART-3

- **Organometallic compounds:** The compounds in which the carbon atoms of organic group are bound to metal atoms are known as organometallic compounds.
 - **Grignard reagent:** The organomagnesium halides are known as Grignard reagent. It is represented by R-Mg-X , where $\text{R} = \text{alkyl / aryl / alkenyl / allyl group}$
 $\text{X} = \text{Cl / Br / I}$
 - **Classification of organometallics:** Organometallic compounds are classified on the basis of bonding between organic group metal atom.
- They are mentioned below:**
1. Ionic Organometallic Compounds
 2. Sigma-Bonded Organometallic Compounds
 3. Non-classically Bonded Organometallic Compounds

Questions-Answers**Long Answer Type and Medium Answer Type Questions**

Que 2.18. What is organometallic compound? Give classification of organometallic compounds.

Answer

Organometallic compounds: The compounds in which the carbon atoms of organic group are bound to metal atoms are known as organometallic compounds.

For example, alkoxide such as RM(OR) is considered to be an organometallic compound because the organic group (R) is bound to metal (M) and a metal-to-carbon bond is present, whereas (RO), M is not an organometallic compound. This is because the organic group (R) is bound to metal (M) by oxygen (O).

Classification of organometallics compound:

Organometallic compounds can be classified on the basis of bonding between organic group and metal atom. Broadly, there are following three types of organometallics:

i Ionic organometallic compounds : The organometallics in which the organic group (*R*) is bound to highly electropositive metals (like Na, Ca etc.) are known as ionic organometallics. In fact, these are metal salts of carbanions. Their general chemical formula is (*R*)_{*x*} *M*^{+*x*}.

$$a \quad (C_6H_5)_3C-Na^+$$

- a. $(\text{C}_6\text{H}_5)_3\text{C}-\text{N}_3$
- b. $(\text{C}_5\text{H}_5)_2\text{Ca}^{2+}$

Ionic organometallic compounds are usually ionic, insoluble in hydrocarbon solvents, and are very reactive toward air, water etc.

ii. **Sigma-bonded organometallic compounds** : In these compounds the organic group (*R*) is bound to a metal atom (of lower electropositivity) by a normal two-electron covalent bond.

iii. **Non-classically bonded organometallic compounds**: Here the bonding is not explained in terms of ionic or electron-pair sigma bonds. Broadly these are of two sub-types:

- a. Alkyl of Li, Be and Al have bridging Alkyl groups. Bonding is multicenter type and there is electron deficiency as in boron hydrides.
- b. Compounds of transition metals with alkenes, alkynes, benzene, and other ring systems such as $C_6H_6^-$.

Que 2.19. Define the term organometallic compounds. Explain general methods of synthesis of organometallic compound preparation and applications with suitable examples.

Answer

Organometallic compounds: Refer Q. 2.18, Page 77H, Unit-2

Methods: General methods of synthesis of organometallic compounds:

Organometallic compounds can be synthesized by the following methods:

- i. **Direct reactions of metals :** Direct reactions of metals (M) with alkyl halides (RX) or alkyl halides (C_6H_5X) in ether lead to the formation of alkyl or aryl or aryl metal halides.



Here M can be Li, Na, K, Mg, Ca, Zn and Cd

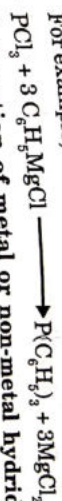
Grignard reagents (RMgX) are synthesized by this method. For example,



ii. **Use of alkylating agents:** Here alkylating agents are used to make organometallic compounds. Alkylating agents can be Grignard and lithium reagents, aluminium and mercury alkyls etc.

The alkylation is generally done either in ether or hydrocarbon solvents

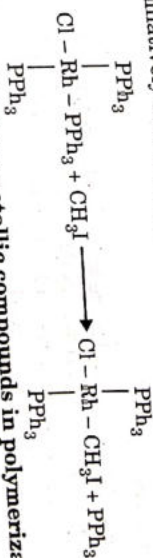
For example,



iii. **Interaction of metal or non-metal hydrides with alkenes or alkynes:** Hydroboration reaction is one of the best example for such synthesis. It can also be regarded as insertion of alkene in M-H bond.



iv. **Oxidative addition reactions or oxad reactions** : Here metal-carbon bonds are made by the addition of alkyl or aryl halides to coordinatively unsaturated transition metal compounds. For example,

$$\text{PPh}_3$$


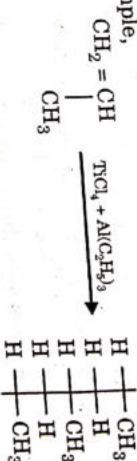
Applications of organometallic compounds in polymerizations and catalysis :

i. Lithium alkyls are widely used as stereospecific catalysts for the polymerization of alkenes. For example, polymerization of isoprene with

ii. The alkyls of aluminum are important because of their industrial use as catalysts for the polymerization of ethylene and propylene. The alkyl of aluminum gives up to 90% of H_2 and C_3H_6 .

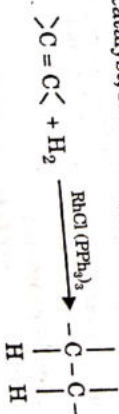
iii. Organo-titanium compounds got importance mainly because of the catalysts for the polymerization of α -olefins. Ethylene can be polymerized in discovery by Ziegler and Natta that ethylene can be polymerized in a hydrocarbon solvent at a mixture of TiCl_4 and AlEt_3 in a hydrocarbon solvent at a mixture and atmospheric pressure.

For example,



Isotactic polypropylene
Propylene

iv. **Propylene** Isotactic polypropylene for the selective hydrogenation of $C = C$ bonds that are not sterically hindered using Wilkinson's catalyst, $RhCl(PPh_3)_3$



v. Hydroformylation reaction using rhodium catalyst : The hydroformylation reaction is the addition of hydrogen (H_2) and carbon

monoxide (CO) [or formally of H and the formyl group, HCO] to an alkene [generally a terminal or 1-alkene] to form an aldehyde product. For example,



Que 2.20. What is organometallic compound? Explain various methods of preparation of Grignard reagent and also write at least five applications of Grignard reagent. **[UPTU 2013-14, Marks 05]**

Answer

Organometallic compound : Refer Q. 2.18, Page 77H, Unit-2.

Grignard reagent :

1. The organomagnesium halides are known as Grignard reagents. These are extremely important reagents developed by the French chemist François Auguste Victor Grignard, who was awarded the Nobel Prize in 1912 in Chemistry for this work.
2. The Grignard reagent is represented as R-Mg-X, where
R = alkyl / aryl / alkenyl / allyl group
X = Cl / Br / I

3. The reactions involving Grignard reagents, as sources of nucleophiles, are usually referred to as Grignard reactions.

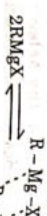
Preparations of Grignard reagent :

- i. The Grignard reagents are prepared by the action of activated magnesium (Rieke magnesium) on organic halides in suitable solvents like Diethyl ether, Et₂O or Tetrahydrofuran, THF in anhydrous conditions.



- ii. This is an oxidation, insertion of magnesium between carbon and halogen bond, which involves oxidation of Mg(0) to Mg(II).

The Grignard reagents are in equilibrium with the dialkylmagnesium species R₂Mg and MgX₂.

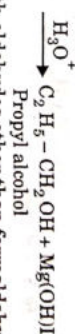
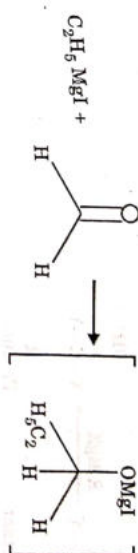


- iv. In the formation of Grignard reagent, the polarity of carbon attached to unpoling.

Applications of Grignard reagent :

1. The addition of Grignard reagents to formaldehyde furnishes primary alcohols.

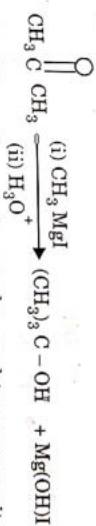
Example,



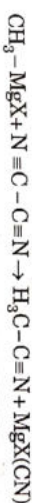
2. The Grignard reaction with aldehydes other than formaldehyde gives secondary alcohols.



The addition of Grignard reagent to ketones furnishes tertiary alcohols.



3. The Grignard reagents are also used to prepare nitriles by reacting them with cyanogen or cyanogen chloride.



4. Amines can be prepared by reacting these reagents with Chloramine, NH₂Cl.



5. The alkyl iodides can be prepared via Grignard reagents. The alkylmagnesium chlorides or bromides are treated with iodine to get corresponding alkyl iodides.



Que 2.21. How is Grignard reagent prepared? How will CH₃CH₂MgBr react with HCHO, CH₃CHO and (CH₃)₂CO?

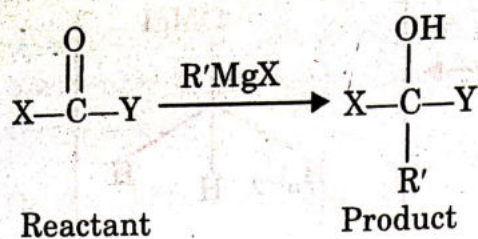
[UPTU 2014-15, Marks 05]

Answer

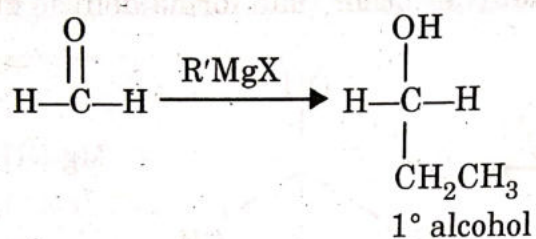
Preparations of Grignard reagent : Refer Q. 2.20, Page 80H, Unit-2.

Reaction :

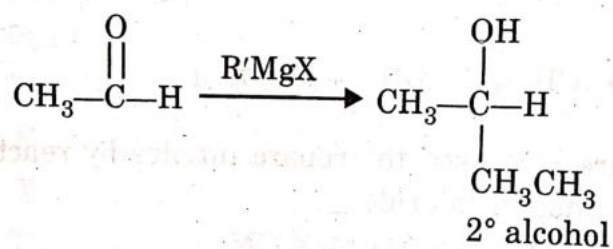




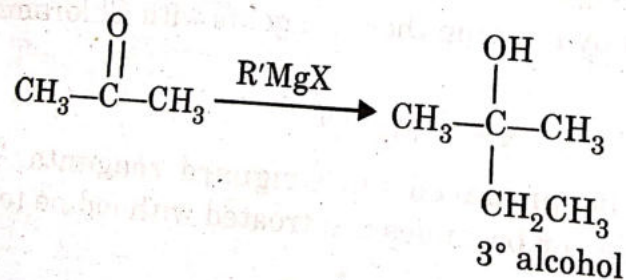
If $\text{X} = \text{H}$, $\text{Y} = \text{H}$ then,



If $\text{X} = \text{CH}_3$, $\text{Y} = \text{H}$ then,



If $\text{X} = \text{CH}_3$, $\text{Y} = \text{CH}_3$ then,



UNIT 3

3 UNIT

Electrochemistry

Part-1 (84H - 98H)

- *Electrochemistry : Galvanic cell*
- *Electrode Potential*
- *Lead Storage Battery*

A. *Concept Outline : Part-1* 84H
 B. *Long and Medium Answer Type Questions* 84H

Part-2 (98H - 110H)

- *Corrosion*
- *Causes and its Prevention*

A. *Concept Outline : Part-2* 98H
 B. *Long and Medium Answer Type Questions* 99H

Part-3 (110H - 128H)

- *Setting and Hardening of Cement*
- *Applications of Cement*
- *Plaster of Paris*
- *Lubricants-Classification, Mechanism and Applications*

A. *Concept Outline : Part-3* 110H
 B. *Long and Medium Answer Type Questions* 111H

PART-1

Electrochemistry : Galvanic Cell, Electrode Potential, Lead Storage Battery.

CONCEPT OUTLINE : PART-1

- **Electrochemistry** : It is defined as the branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions.
- **The three main aspects of study of electrochemistry are** :
 1. Electrolysis
 2. Electrolytic conduction
 3. Galvanic cells / Electrochemical cells / Voltaic cells
- **Electrochemical cells** : It is a device for the conversion of chemical energy into electrical energy or vice-versa.
- **Depending upon the types of electrochemical processes, there are two types of cells** :
 1. Galvanic cell / Electrochemical cell
 2. Electrolytic cell
- **Electrode potential** : The tendency of an electrode to lose or gain electrons is called electrode potential.
- **Lead storage battery** : It is also known as the automobile battery. It is an example of secondary electrochemical cell, since it can be recharged.

Questions-Answers**Long Answer Type and Medium Answer Type Questions**

Que 3.1. Define electrochemistry. Give its importance in practical life.

Answer**Electrochemistry :**

1. It is a branch of physical chemistry that studies the relationship between chemical and electrical phenomena and the laws of their interaction.
2. On passing electric current through an electrolyte solution, a chemical reaction takes place.
3. In other words, an electric current can cause a chemical reaction to take place under suitable conditions.
4. The phenomenon is called electrolysis.

5. The reverse is also true i.e., we can generate electric current by the use of a chemical reaction.
6. Hence, depending upon these two types of electrochemical processes, there are following two types of cells :

a. Electrolytic cells :

- i. A device in which electrical energy is converted into chemical energy by passing an electric current to produce the desired chemical change is called an electrolytic cell and the process is called electrolysis.
- ii. The refining of metals, electroplating with silver, gold and chromium or production of many chemical substances such as chlorine, sodium hydroxide, hydrogen peroxide etc., are carried out in electrolytic cells.
- iii. The charging of storage batteries is also based on electrolytic cells.

b. Electrochemical cells :

- i. An electrochemical cell is a device which converts chemical energy into electrical energy.
- ii. It is also called galvanic cell. Daniel cell is a well known example of galvanic cell.

Importance of electrochemistry : The subject of electrochemistry has numerous theoretical as well as practical importance. For example,

1. A number of metals such as Na, Mg, Ca and Al and a number of chemicals such as NaOH, Cl_2 , F_2 etc., are commercially produced by electrochemical methods.
2. Batteries and cells used in various instruments and other devices convert chemical energy into electrical energy.
3. The sensory signals sent to the brain through the cells and vice versa and also the communication among different cells.

Que 3.2. What are redox / half reactions ?

Answer

1. Various chemical reactions occur through redistribution of electrons among the reacting substances.
2. Any substance that loses electrons is said to be oxidized and the one which gains electrons is said to be reduced.
3. However, in a chemical reaction, a substance can lose electrons only if there is another substance present, which can gain electrons.
4. This implies that oxidation can take place only if reduction also occurs at the same time or vice versa.

5. These reactions in which reduction and oxidation both take place are called redox reaction.

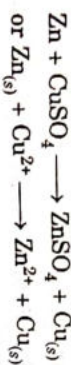
6. In this, $\text{Zn}_{(s)}$ loses two electrons whereas Cu^{2+} gains two electrons, and hence this is a redox reaction.

7. The redox reaction are of two types :

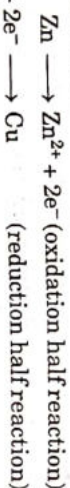
a. Direct redox reactions :

i. The redox reactions in which oxidation and reduction take place in the same vessel are called direct redox reactions.

ii. For example, displacement of copper from CuSO_4 solution when a zinc rod is dipped in it.



iii. The above reaction can be split into two halves :



b. Indirect redox reaction :

i. If redox reaction is allowed to take place in such a way that oxidation reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by former will be taken by latter and a current will flow.

ii. These indirect redox reactions form the basis of electrochemical cells.

Que 3.3. Write a short note on galvanic cell.

Answer

- The galvanic cell is a device used for the conversion of chemical energy into electrical energy.
- Examples of galvanic cell are dry cell or lead storage battery.
- In galvanic cell, the cathode has a higher potential than the anode.
- This is because the species undergoing reduction at cathode withdraws electrons from it.
- This leads to a development of positive charge on it, corresponding to a high potential.
- Oxidation at the anode results in the transfer of electrons to it, so giving it a relative negative charge.
- The practical application of galvanic cell is Daniel cell.
- It consists of zinc electrode, dipped in ZnSO_4 solution (say 1 M) and a copper electrode, dipped in CuSO_4 solution (say 1 M) taken in two different beakers.

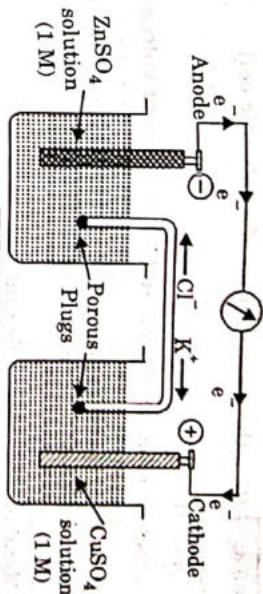


Fig. 3.3.1 Daniel cell.

- The two solutions are connected by means of a salt bridge.
- Salt bridge is an inverted U-tube containing an aqueous solution of electrolyte such as KCl , KNO_3 , or K_2SO_4 (which does not react chemically during the process).
- The moment the two electrodes are connected by a wire the following reactions occur at different electrodes :
- At anode : $\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$ (oxidation half reaction)
- At cathode : $\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$ (reduction half reaction)
- $\text{Zn}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$ (The complete cell reaction)
- Oxidation takes place at the anode and reduction takes place at the cathode.
- The electrons flow from anode to cathode.
- The transference of electrons from Zn anode to Cu cathode leads to the accumulation of positive charge around the anode due to the formation of Zn^{2+} ions and the accumulation of negative charge around cathode due to deposition of Cu^{2+} ions as copper on the cathode.
- The positive charge so accumulated around the anode will prevent the flow of electrons from it.
- Similarly, accumulation of negative charge around the cathode will prevent the acceptance of electrons from the anode.
- As the transference of electrons stops, the current in the electrical circuit also stops.
- At this stage, the salt bridge comes to the aid and restores the electrical neutrality of the solution in the two half cells.
- When the concentration of Zn^{2+} ions around the anode increases, sufficient number of Cl^- ions migrates from the salt bridge to the anode half cell.
- Similarly, sufficient number of K^+ ions migrate from the salt bridge to the cathode half cell for neutralizing excess negative charge due to the additional SO_4^{2-} ions in the cathode half cell.

Que 3.4. Give the construction of a galvanic cell.

Answer

Construction of galvanic cell and calculation of voltage :

The cell is formed with two electrodes and its emf is measured, at 25° C.

1. **Reference electrode (half cell) :** Calomel electrode $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{Cl}^-$ is used as reference electrode and its standard reduction potential is taken as + 0.2415 volts.

2. **Metal or alloy electrode (half cell) :**

a. The metal or alloy in its practically used form is taken as electrode and it is dipped in sea water medium.

b. The two half cells are connected and the cell emf is measured at 25° C.

c. If the metal-sea water electrode system acts as anode, then its standard reduction potential is calculated as,

$$E_{\text{cell}}^{\circ} = (E_{\text{ref}}^{\circ})_{\text{cathode}} - (E_{\text{ref}}^{\circ})_{\text{metal}} = 0.2422 - (E_{\text{ref}}^{\circ})_{\text{metal}}$$

$$\therefore (E_{\text{red}}^{\circ})_{\text{metal}} = (0.2422 - E_{\text{cell}}^{\circ}) \text{ volts}$$

d. If the metal-sea water electrode system acts as cathode, then its standard reduction potential is calculated as,

$$E_{\text{cell}}^{\circ} = (E_{\text{red}}^{\circ})_{\text{metal}} - (E_{\text{ref}}^{\circ})_{\text{anode}} = (E_{\text{red}}^{\circ})_{\text{metal}} - 0.2422$$

$$\therefore (E_{\text{red}}^{\circ})_{\text{metal}} = E_{\text{cell}}^{\circ} + 0.2422$$

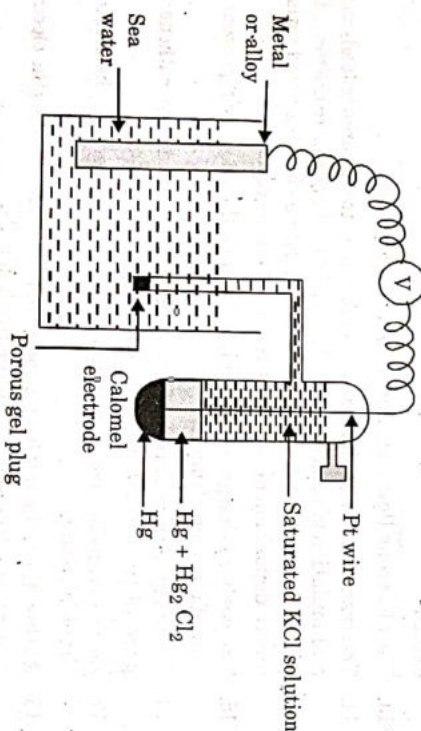


Fig. 3.4.1. Metal or alloy electrode potential.

Que 3.5.

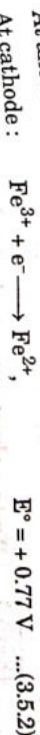
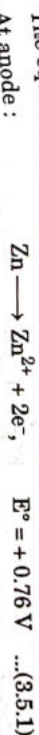
For the cell: $\text{Zn} | \text{Zn}^{2+} (1 \text{ M}) || \text{Fe}^{2+} (1 \text{ M}), \text{Fe}^{3+} (1 \text{ M}) | \text{Pt}$.

Given $E^{\circ}(\text{Fe}^{3+} | \text{Fe}^{2+}) = +0.77 \text{ V}$ and $E^{\circ}(\text{Zn} | \text{Zn}^{2+}) = +0.76 \text{ V}$.

Write the cell reaction and calculate the value of E°_{cell} for the above cell.

Answer

1. The equations for the half-reactions are :



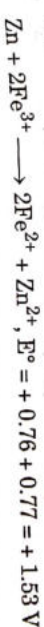
To obtain the equation for the cell reaction, the equation for the $\text{Fe}^{3+} | \text{Fe}^{2+}$ half-reaction must be multiplied by 2 (to obtain 2 mol electron) and combined with the $\text{Zn} | \text{Zn}^{2+}$ half reaction.

3. It is to be noted that potential does not depend on the quantity of substance undergoing reaction, so the value of the half-cell potential is not multiplied by 2.

4. Thus, reaction at cathode is re-written as :



5. And now adding equations (3.5.1) and (3.5.3), we get desired cell reaction as :



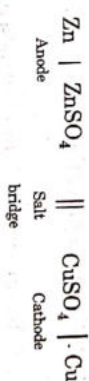
6. A positive sign of E°_{cell} means that the reaction is spontaneous as written.

Que 3.6. Calculate the standard EMF of the following at 25° C,

writing its half cell reaction and net cell reaction $\text{Zn} | \text{ZnSO}_4 || \text{CuSO}_4 | \text{Cu}$. Standard potentials of Cu and Zn electrodes are + 0.34 and - 0.76 V respectively.

Answer

Given cell diagram is,



Oxidation half cell Reduction half cell

The half-cell reactions are :



Now adding equations (3.6.1) and (3.6.2), we get net cell reaction as :



Let the standard EMF of the cell = E°_{cell}

Given, standard potential of cathode = $E^{\circ}_{\text{cathode}} = E^{\circ}_{\text{Cu}^{2+} | \text{Cu}} = +0.34 \text{ V}$

and standard potential of anode = $E^{\circ}_{\text{anode}} = E^{\circ}_{\text{Zn}^{2+} | \text{Zn}} = -0.76 \text{ V}$

As

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}}^{\circ} | \text{Cu} - E_{\text{Zn}^{2+}}^{\circ} | \text{Zn}$$

 $\Rightarrow$

$$E_{\text{cell}}^{\circ} = (+0.34) - (-0.76)$$

 $\Rightarrow$

$$E_{\text{cell}}^{\circ} = 1.10 \text{ V}$$

Que 3.7. Write a short note on electrode potential.

Answer

1. A metal rod or plate in contact with its own ions is called electrode.
2. When a metal is in contact with the solution of its own ions, it can undergo oxidation or reduction.
3. The tendency of an electrode to lose or gain electrons is called electrode potential.
4. Since, each electrode represents a half cell, therefore, electrode potential is also called potential for half cell.
5. Consider a copper rod dipped in the solution of its own ions, i.e., Cu^{2+} ions.
6. The copper rod has a tendency to lose electrons to form Cu^{2+} ions which pass into the solution.
7. Thus, copper rod acquires a net negative charge as electrons which are released, get accumulated around the Cu rod. These electrons will attract Cu^{2+} ions from the solution.
8. This indicates that copper will soon be established.



9. When such an equilibrium is reached, a separation of positive and negative charges would occur.
10. This separation creates a potential difference between metal rod and the solution.
11. This potential difference is called the electrode potential.
12. Thus, electrode potential of a metal is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with its own salt.
13. Its magnitude depends upon :
 - a. The nature of metal and ions
 - b. Concentration of ions
 - c. Temperature
14. Electrode potential measured under standard conditions i.e., 1 molar concentration of metal ions and a temperature of 298 K is called standard electrode potential and is denoted by $E_{\circ}$.

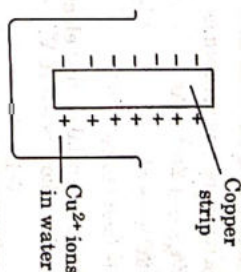


Fig. 3.7.1. Development of a potential difference between metal and its ions.

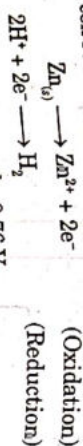
Que 3.8. How to measure the electrode potential ?

Answer

1. The electrochemical cell consists of two half cells.
2. The potential of a single electrode in a half cell is called the single electrode potential.
3. It is impossible to know the absolute value of a single electrode potential because neither oxidation nor reduction takes place independently.
4. However, we can measure the potential difference between the two electrodes with the help of potentiometer, by combining the two electrodes to form a complete cell.
5. The electrode, whose potential is arbitrarily fixed, is called reference electrode.
6. The potential of the reference electrode is arbitrarily assigned a zero value and the potentials of all other electrodes are then referred to it.
7. The reference electrode so chosen is the standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE).
8. In order to measure the electrode potential of the given electrode, the electrode is coupled with SHE.
9. The e.m.f. of the complete cell is then measured using voltmeter.
10. The measured e.m.f. would give the electrode potential of the given electrode because electrode potential of SHE is arbitrarily fixed as zero.
11. The direction of the flow of current further indicates whether oxidation takes place or reduction takes place at the electrode under investigation with respect to SHE.
12. Accordingly, the electrode potential is termed as oxidation or reduction potential.
13. For example, suppose it is desired to measure and determine the electrode potential of zinc electrode, Zn/ZnSO_4 .

14. The electrode is connected with the SHE as shown in Fig. 3.8.1.

15. The two half cell reactions are represented as :



16. The EMF of the cell is found to be 0.76 V.

17. Therefore, the oxidation potential of zinc electrode is taken as 0.76 V and reduction potential is taken as -0.76 V.

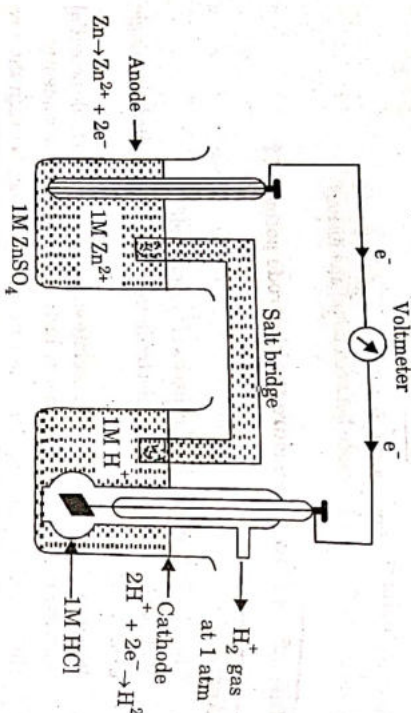


Fig. 3.8.1. Standard electrode potential (reduction potential) of zinc by combining with SHE.

Que 3.9. What is Nernst equation for a cell ?

Answer

1. The concentration of the electrolyte in half cell influences its electrode potential.
2. The concentration dependence of EMF can be obtained from thermodynamic considerations.
3. Consider a general cell reaction :

$$M_{(aq)}^{n+} + ne^- \longrightarrow M_{(s)}$$
4. The decrease in free energy - ΔG , accompanying the process is given by the well known thermodynamic equation,

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{products}}}{a_{\text{reactants}}} \quad \dots (3.9.1)$$

where ΔG° refers to the free energy change for the reaction in the standard state i.e., when the activities of the reactants and products are all unity, a_{product} and a_{reactant} represent the activities of the reactants and

the products under a given set of conditions, R is the gas constant and T is the temperature.

$$\Delta G = -nFE \text{ and } \Delta G^\circ = -nFE^\circ$$

5. Since, where n is the number of electrons liberated at one electrode and F is Faraday of electricity (1F = 96500 coulombs) and E and E° are the electrode potential under the operating conditions and standard conditions respectively.

6. Hence, substituting the value of ΔG in equation (3.9.1) we get,

$$-nEF = -nE^\circ F + RT \ln \frac{a_{\text{products}}}{a_{\text{reactants}}} \quad \dots (3.9.2)$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_p}{a_r} \quad \dots (3.9.3)$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \left(\frac{a_{\text{products}}}{a_{\text{reactants}}} \right) \quad \dots (3.9.4)$$

7. Equation (3.9.4) is known as Nernst equation and gives the dependence of the electrode or cell potential in terms of activities of the reactants and products.

8. The quantity E° is known as standard EMF of the cell and is the cell potential when the activities are all unity.

9. At $T = 298$ K, equation (3.9.4) reduces to :

$$E = E^\circ - \frac{(8.314)(298)(2.303)}{n(96485)} \log \frac{a_{\text{products}}}{a_{\text{reactants}}}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{a_{\text{products}}}{a_{\text{reactants}}} \quad \dots (3.9.5)$$

10. In dilute solutions, the activities may be replaced by molar concentration terms,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[M_{(s)}]}{[M_{(aq)}^{n+}]} \quad \dots (3.9.6)$$

For pure solids, $[M_{(s)}] = 1$

11. Hence, equation (3.9.6) can be written as :

$$E = E^\circ - \frac{0.0591}{n} \log \left[\frac{1}{M_{(aq)}^{n+}} \right] \quad \dots (3.9.7)$$

12. Equation (3.9.7) is the Nernst equation for pure solids at 298 K. For any other temperature, it can be written as :

$$E = E^\circ - \frac{2.303RT}{n} \log \left[\frac{1}{M_{(aq)}^{n+}} \right] \quad \dots (3.9.8)$$

13. For a cell reaction,



14. The Nernst equation can be written as :

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{[L]^l [M]^m}{[A]^a [B]^b} \quad \dots (3.9)$$

$$\text{or } E = E^{\circ} + \frac{2.303RT}{nF} \log \frac{[A]^a [B]^b}{[L]^l [M]^m} \quad \dots (3.10)$$

15. It is seen from the Nernst equation that :

- If the product of the molar concentration of the product is greater than the product of the molar concentration of the reactants, the EMF is less than the standard EMF of the cell.
- The electrode potential (E) decreases as temperature is increased.

Que 3.10. Discuss one type of reversible electrode.

UPTU 2013-14, Marks 04

Answer

Calomel electrode is commonly used as a secondary reference electrode for potential measurements.

Construction :

- Calomel electrode consists of a tube, at the bottom of which a small amount of mercury is placed.

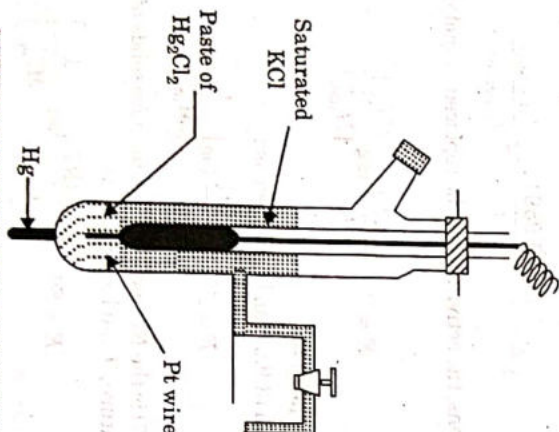


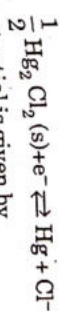
Fig. 3.10.1. Saturated calomel electrode.

It is covered with a paste of solid mercurous chloride, Hg_2Cl_2 (calomel).

- A solution of potassium chloride is then placed over the paste.
- A platinum wire, dipping into the mercury layer, is used for making electrical contact.
- The side tube is used for making electrical contact with a salt bridge.

Working :

- The electrode reaction when the cell acts as cathode is :



and its potential is given by

$$E = E^{\circ} - \frac{RT}{nF} \ln (a_{\text{Cl}^-})$$

- Thus, the potential of calomel electrode depends on the activity of the chloride ions (a_{Cl^-}) and increases as the activity of the chloride ions decreases.

- It has been found that the potential of the calomel electrode vary with the concentration of the potassium chloride solution used.

- The reduction potentials of the calomel electrode (on the hydrogen scale) at 298 K for various KCl concentrations are :

[KCl]	Saturated	10 N	0.1 N
Electrode potential (in Volt)	0.2422	0.2810	0.3335

- When the KCl solution is saturated, 1.0 N and 0.1 N, it is respectively called as Saturated Calomel Electrode (SCE), Normal Calomel Electrode (NCE) and Decinormal Calomel Electrode (DNCE).

Que 3.11. What do you mean by EMF ?

Answer

EMF of an electrochemical cell is the maximum potential difference between two electrodes of a cell. The e.m.f., of a cell is measured with the help of potentiometer.

EMF of cell = Reduction potential of cathode (written on right-hand side) - Reduction potential of anode (written on left-hand side)

$$\Rightarrow E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$\Rightarrow E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

The cell reaction is feasible only when E_{cell} has positive value.

Que 3.12. What is lead storage battery ? Give its construction and working.

Answer

In 1859, the French physicist Gaston Plante (1834-89) invented a device called the lead-acid accumulator, which is still used today as motor car battery with minor changes. It is an example of secondary electrochemical cell, since it can be recharged.

Construction :

1. The cell consists of a lead grid filled with a spongy lead as anode and a lead grid packed with lead oxide as cathode.
2. A solution of H_2SO_4 (38 % by mass) is used as an electrolyte.
3. This is the battery acid which one can buy at service stations.
4. The battery consists of 6 such cells connected in series, each cell having an emf of about 2 V, giving 12 V as the overall emf of the battery.

Working :

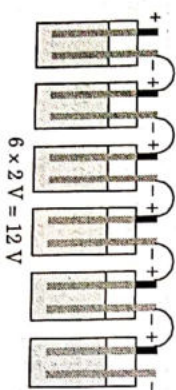
1. When the battery is discharging, i.e., when it is supplying a current, the reactions are :



At the cathode :



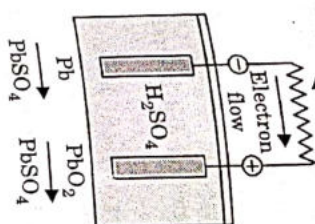
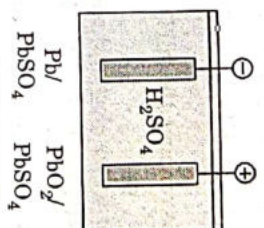
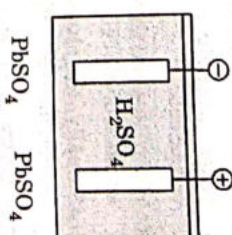
The overall reaction (during discharge) is, therefore,

**Fig. 3.12.1.**

2. Note that the electrolyte is sulphuric acid (H_2SO_4), which is gradually used up.
3. Both electrodes become coated with an insoluble layer of lead sulphate, which, being an insulator, would eventually ruin the battery.
4. As the battery provides energy, it is discharged and this lead to the gradual formation of lead sulphate at the electrodes, and a steady decrease in the concentration of the sulphuric acid.
5. If the battery is totally discharged, both electrodes will have been converted to lead sulphate.
6. It will no longer be able to provide a current, and cannot be recharged. It is only good for scrap.

Discharging

Conventional current flow

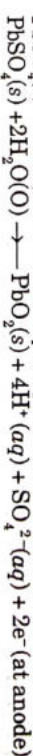
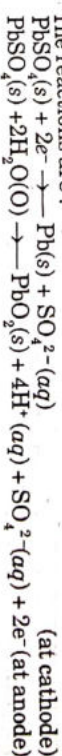
**Discharging/ discharged****Fully discharge****Fig. 3.12.2.**

7. When the battery is being charged (using a battery charger or the motor car's alternator), electrons are supplied to the anode of the battery and this converts the lead sulphate to lead.

8. At the same time, the lead sulphate at the anode is converted to lead dioxide.

9. That is, the cell reactions are reversed and the cell operates like an electrochemical cell.

10. The reactions are :

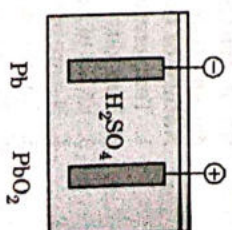
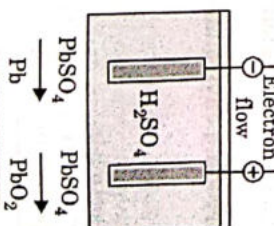
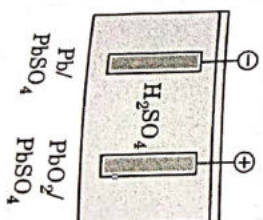


Partially discharged

Charging

Conventional current flow

Battery charger

**Fig. 3.12.3.**

11. The concentration of H_2SO_4 decreases during discharging whereas it increases during charging.
12. Thus, the extent to which the battery is discharged can be checked by measuring the density of H_2SO_4 by hydrometer.
13. The lead storage cell is both a voltaic cell and an electrolytic cell.
14. When electricity is being drawn from the cell to start the car, it acts as voltaic cell.
15. Whereas when the car is running, the cell is being recharged, it acts as an electrolytic cell.
16. Actually, the alternator forces electrical energy generated due to its motion into the cell causing electrolytic reaction to take place.

Que 3.13. Discuss the reactions involved in charging and discharging of a lead storage cell. UPTU 2012-13, Marks 08

Answer

Refer Q. 3.12, Page 95H, Unit-3.

PART-2

Corrosion, Causes and its Prevention.

CONCEPT OUTLINE : PART-2

- **Corrosion :** It is the process of gradual deterioration of a metal from its surface due to the unwanted chemical or electrochemical interaction of metal with its environment.
- **Effects of corrosion :**
 1. Production related consequences
 2. Health and safety related consequences
- **Dry/Chemical corrosion :** It occurs in dry condition. It involves the direct chemical attack of the metal by environment.
- **Wet/Electrochemical corrosion :** It takes place mostly under wet or moist conditions through the formation of short-circuited galvanic cells.
- **Nature of the corroding environment :**
 1. Temperature
 2. Humidity
 3. Effect of pH
 4. Nature of the electrolyte
 5. Formation of oxygen concentration cell
 6. Presence of impurities in atmosphere, etc.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.14. Define corrosion. How does it differ from rusting ?

UPTU 2012-13, Marks 02

OR

Discuss the electrochemical theory of corrosion. How does this theory explain the mechanism of rusting ?

UPTU 2012-13, Marks 04

OR

What is electrochemical corrosion ? Outline the mechanism involved in electrochemical corrosion.

UPTU 2012-13, Marks 04

UPTU 2013-14, Marks 05

OR

Explain the mechanism of hydrogen evolution and oxygen absorption in electrochemical corrosion. UPTU 2011-12, Marks 05

OR

What is electrochemical corrosion ? Write down the mechanism involved in electrochemical corrosion. UPTU 2012-13, Marks 04

UPTU 2013-14, Marks 05

OR

Explain the mechanism of electrochemical corrosion of iron with absorption of oxygen. How can anodic and cathodic metallic coatings help in protection against corrosion ? UPTU 2014-15, Marks 05

Answer

Corrosion :

1. Corrosion is the process of gradual deterioration of a metal from its surface due to the unwanted chemical or electrochemical interaction of metal with its environment.

2. For examples :

- a. Formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron, also known as "rusting of iron".

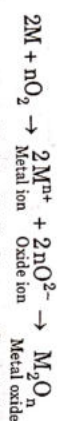
- b. Formation of a layer of black coating on the surface of silver, when it is exposed to atmosphere. It is known as tarnishing of silver.

Types of corrosion :

1. Chemical or dry corrosion :

When metal surface is in immediate proximity to atmospheric gases or anhydrous liquid, a direct chemical interaction between the two leads to chemical or dry corrosion. It is of following types :

- a. Corrosion by O_2 (oxidation corrosion) : It generally takes place in absence of moisture via,



At low temperatures, alkali and alkaline earth metals are oxidized and at high temperatures, except Ag, Au and Pt, all other metals get oxidized. A thin layer of oxide formed at the surface of metal can be,

- i. Stable
- ii. Unstable
- iii. Volatile
- iv. Porous

b. Corrosion by other gases :

- i. Depending on the chemical affinity between metal and gas and the formation of protective or non-protective layer on metal surface, some gases like Cl_2 , H_2 , S etc. exert corrosive effect to different extent.

- ii. For example,



AgCl film is protective and thus protects the metal from further attack of chlorine on silver.

2. Electrochemical or wet corrosion :

- a. It takes place mostly under wet or moist conditions through the formation of short-circuited galvanic cells.
- b. Wet corrosion is more common than dry corrosion.

Mechanism of electrochemical or WET corrosion :

1. Electrochemical corrosion involves :
 - a. Separate 'anodic' and 'cathodic' parts/areas between which current flows through the conducting medium.
 - b. Non-metallic ions like OH^- or O^{2-} are formed at cathodic areas.
 - c. Occurrence of oxidation (corrosion) at anodic areas which generates metallic ions, and
 - d. Diffusion of metallic and non-metallic ions towards each other through conducting medium and formation of corrosion product somewhere between anodic and cathodic areas.
2. For example, rusting of iron in neutral aqueous solution of electrolyte

in the presence of oxygen or in acidic environment with the evolution of hydrogen.

3. Fe^{2+} ions originate at anode and OH^- ions originate from cathode.
4. Smaller Fe^{2+} ions diffuse more rapidly than the larger OH^- ions, so corrosion occurs at the anode, but rust is deposited near cathode.
5. The electrons released at the anode are conducted to the cathode and are responsible for various cathodic reactions such as :

a. Oxygen absorption : In presence of dissolved oxygen

- i. In acidic medium :

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O$$

- ii. In neutral or weak alkaline medium :

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

b. Hydrogen evolution : In absence of O_2

- i. In acidic medium :

$$2H^+ + 2e^- \rightarrow H_2$$

- ii. In neutral or alkaline medium :

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

- c. Electroplating : At the cathode, metal ions collect the electrons and get deposited on the cathode surface.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Metallic coatings : There are two types of metallic coatings :

1. Anodic coatings :
 - a. In these coatings, the metal which is used for coating is more "anodic" than the metal which is to be protected (i.e., the base metal).
 - b. Anodic coatings protect the underlying base metal sacrificially.
 - c. For example, coating of Al, Cd and Zn on steel surface.

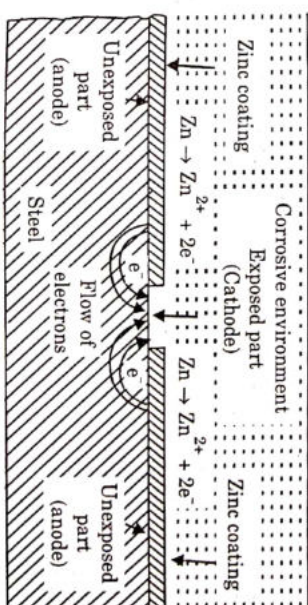


Fig. 3.14.1. Functioning of anodic coating. In galvanized steel, Zn serves as an anode, while iron of steel serves as the cathode. Therefore, the iron is protected, even if it is exposed.

- d. Now galvanized steel is protected from corrosion by following method. Here, Zn is coating metal and steel is base metal. Zn being anodic is attacked, leaving the underlying cathodic (iron/steel) unattacked.

even if it is exposed when pores, breaks or discontinuities occur in such an anodic coating.

- f. Iron or steel is not corroded, till all the coating metal (Zn) is consumed.

2 Cathodic coatings :

- These coatings protect the underlying base metal, due their noble character and higher corrosion resistance.
- In such coatings, effective protection is possible only when they are completely continuous and free from pores, breaks or discontinuities.
- If pores, breaks or discontinuities occur in such a coating, the corrosion of the base metal is speeded up.
- This is due to the fact that exposed metal acts as anode and coating becomes the cathode.
- A galvanic cell is set up and an intense localized attack at the small exposed part occurs.
- This result in severe pitting and perforation of the base metal.



Fig. 3.14.2. Tin-plated steel. The tin protects the iron, when the coating is uniform. When the coating is broken, the iron of the steel becomes the anode and is subjected to intense local corrosion.

Que 3.15. What are the causes of corrosion ?

Answer

Following are the causes of corrosion :

- Metals exist in nature in the form of oxides, sulphides, sulphates and carbonates.
- These chemically combined states of metal known as 'ore' has low energy and is thus thermodynamically stable state for metal.
- A considerable amount of energy is required during metallurgy.
- The extracted metal (in the isolated form) has higher energy and thus it is thermodynamically unstable state.

Thus, it is the natural tendency of metal to go back to the thermodynamically stable state.

5. Metals do this by interacting chemically or electrochemically with their environment to form surface compound and thus undergo corrosion.

6. Metallurgical operation
- Ore of metal (Thermodynamically stable state) + Energy (Thermodynamically unstable state) → Pure metal (Thermodynamically unstable state) → Corroded metal (Comparatively more stable than pure metal)
7. Although, corroded metal is thermodynamically more stable than pure metal but due to corrosion, useful properties of a metal such as malleability, ductility and electrical conductivity are lost.

Que 3.16. State the factors influencing corrosion.

Answer

Rate and extent of corrosion depends on :

- Nature of the metal :
 - Physical state of the metal :
 - Physical state of the metal means orientation of crystal, grain size, stress etc.
 - The larger the grain-size of the metal/alloy, the smaller will be its solubility and hence, lesser will be its corrosion.
 - Nature of the oxide film :
 - The smaller the specific volume ratio $\left(= \frac{\text{Volume of metal oxide}}{\text{Volume of metal}} \right)$, greater is the oxidation corrosion because oxide film formed will be porous, through which oxygen can diffuse and bring about further corrosion.
 - For example, the specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively.
 - Consequently, the rate of corrosion of W is least, even at higher temperatures.
- Relative areas of the anode and cathode :
 - The rate of corrosion of metal is less when the area of the cathode is smaller.
 - When cathodic area is smaller, the demand for electrons will be less and this results in the decreased rate of dissolution of metal at anodic regions.
 - In general,

$$\text{Rate of corrosion of anodic region} \propto \frac{\text{Cathodic area}}{\text{Anodic area}}$$
 - For example, a small steel pipe fitted in a large Cu tank undergoes localised, rapid and severe corrosion.
- Volatility of corrosion products :

- i. Excessive (rapid and continuous) corrosion of metal takes place if corrosion product is volatile.
- ii. This is due to the fact that as soon as corrosion product is formed, it volatilises, thereby, leaving the underlying metal surface for further attack.

2. Nature of the corroding environment :

a. Temperature :

- i. The rate of corrosion increases with rise in temperature.
- ii. This is due to the fact that the anodic attack by the anions, the cathodic evolution of hydrogen gas and solubility of O_2 decreases with the rise of temperature.

b. Humidity :

- i. The greater is humidity, the greater is the rate and extent of corrosion.
- ii. This is due to the fact that moisture acts as a solvent for O_2 , H_2S , SO_2 and $NaCl$ etc., to furnish the electrolyte which is essential for setting up a corrosion cell.
- iii. For example, atmospheric corrosion of iron is slow in dry air as compared to moist air.

c. Presence of impurities in atmosphere :

- i. Corrosion of metals is more in areas near the industry and sea.
- ii. This is due to the fact that corrosive gases like H_2S , SO_2 , CO_2 and fumes of H_2SO_4 and HCl in industrial areas and $NaCl$ of sea water leads to increased conductivity of the liquid in contact with the metal surface, thereby, increases the corrosion rate.

d. Formation of oxygen concentration cell :

- i. Due to differential aeration, oxygen concentration cell sets up and anodic part which has less oxygen concentration suffers corrosion.
- ii. For example, crevice corrosion and waterline corrosion occur due to the formation of differential oxygen concentration cell.

Que 3.17. How can corrosion be minimized by proper design ?

UPTU 2014-15, Marks 05

Answer

Corrosion can be minimized by proper designing in which formation of less oxygenated and more oxygenated area is prohibited. Smooth designs in which joints are less are preferable. If in design, cathode and anode cannot be formed, corrosion stops.

Corrosion can be minimized by using these methods :

1. **Metal cladding:** "Metal cladding is the process of coating of base metal by a dense, homogeneous layer of cladding materials". Cladding materials

2

can be pure metals (which are corrosion-resisting like Ni, Pb, Ag, Pt or Cu) or alloys (like stainless steel or alloys of Ni, Cu or Pb). The choice depends on the environment in which corrosion-resistance is required. Generally, a base metal (example, duralumin) is sandwiched between two layers of cladding materials (example, 99.5 % pure Al), which are then passed through rollers, under the action of heat and pressure to form a clad sheeting which is very widely used in the air-craft industry.

Electroplating: "Electroplating is the process of deposition of coating metal on the base metal by passing a direct current in an electrolytic solution which contains the soluble salt of the coating metal".

Apart from increasing the resistance of metal to corrosion and chemical attack, electroplating also improves physical appearance, hardness, surface properties and aesthetics.

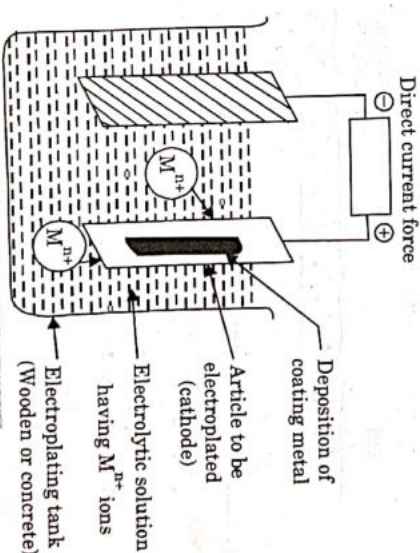


Fig. 3.17.1. Electroplating.

Oils, greases, etc., are first removed from the surface of metal to be electroplated by treatment with organic solvent like tetrachlorethylene. Surface scales, oxides etc., are then removed by treating with HCl (for Ni and Cu plating) or H_2SO_4 (for chromium plating). The cleaned metal is then made cathode of an electrolytic cell. The anode is either an inert material of good electrical conductivity (like graphite) or coating metal (pure) itself. The electrolyte is a solution of a soluble salt of a metal (to be deposited). The anode and cathode are dipped in an electrolytic solution kept in an electroplating tank.

When direct current is passed, coating metal ions migrate to the cathode and get deposited there in the form of thin-layer.

3. Cathodic protection :

Cathodic protection or electrochemical protection : For the structures immersed in soils or electrically-conducting liquids, the cathodic protection is the best way to control corrosion. Cathodic protection is to

force the metal to be protected to behave like a cathode as a result of which it is not corroded.

Cathodic protection can be achieved in two ways :

a. Galvanic protection : In galvanic protection of sacrificial anodic protection, the metal structure to be protected is made the cathode by connecting it by a wire to a more anodic material. As a result, the corrosion takes place at anodic material and the metal structure is saved from corrosion. The more active metal used for the purpose is known as sacrificial anode. The sacrificial anode is replaced by a fresh one when it gets corroded or consumed from time to time. Most commonly metals used for sacrificial anodic protection are Mg, Zn, Al and their alloys.

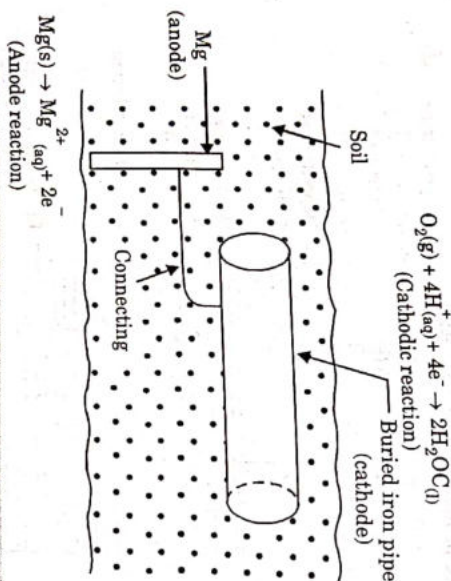


Fig. 3.17.2. Galvanic protection using sacrificial anode.

- The application of cathodic protection include :
- Protection of buried pipelines, underground cables.
 - Protection of marine structures, ship hulls etc.
 - Magnesium rods are inserted into domestic water boilers or tanks to prevent rusting.

b. Impressed current cathodic protection : This method known as electrolytic method of cathodic protection, the object to be protected is made cathode by connecting it to negative terminal of DC source. The positive terminal is connected to an insoluble anode like graphite, scrap iron or platinum. The objective is to apply the current from an external source (insoluble anode) in the opposite direction to that of the corrosion current. The insoluble anode is buried in the soil or in the conducting medium adjacent to the metal which is to be protected (Fig. 3.17.3.). These are placed in such a manner that a uniform potential is obtained over the entire metal surface. The electrons flow to the metal structure

and as a result it act as cathode and is protected. The anode has to be replaced periodically. The impressed current cathodic protection has been applied to protect.

- Buried pipelines, transmission line towers.
 - Water pipes, water tanks, marine piers etc.
- This kind of technique is particularly useful for large structures which require long term applications.

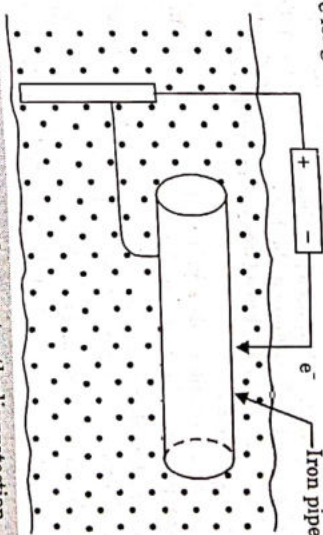


Fig. 3.17.3. Impressed current cathodic protection.

2. Anodic protection :

- Anodic protection is applicable to the metals which can be passivated by the deposition of oxide films.
 - In anodic protection, oxide film is grown on the surface of the metal structure to be protected.
 - This is done by electrochemical means i.e., by applying current in a direction that makes the metal structure more anodic.
 - Under these conditions, the metal structure is passivated when the required potential is maintained and hence rate of corrosion decreases.
- Anodic protection has been applied in case of steel, stainless steel aluminium and chromium.
- It must be remembered that potential has to be accurately maintained so that it just induces passivity.

Que 3.18. How much rust ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) will be formed when 100 kg of iron have rusted away ?

Answer



214 g of rust contains = 112 g Fe

112 g of Fe produces = 214 g rust

100 kg of Fe produces = $\frac{214 \times 100}{112} = 191.07 \text{ kg rust}$

Que 3.19. What are corrosion inhibitors ? Explain the mechanism of their action.

UPTU 2012-13, Marks 02

Answer

Corrosion inhibitors are the substances which when added in small quantities to the corrosive environments decrease the corrosion rate. Inhibitors are organic as well as inorganic substances that dissolve in the corroding medium. Inhibitors are generally classified on the basis of electrode at which their action is predominant. Thus, we have two types of inhibitors :

1. Anodic inhibitors :

- The anodic reaction takes place when the ions from the anodic metal pass into the solution (for example, $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$).
- The anodic inhibitors are the compounds which react with these metal ions to produce insoluble compounds.
- This insoluble compound get adsorbed on the metal surface forming a film or a protective barrier, thereby, reducing the corrosion rate.
- The examples of anodic inhibitors include molybdates, phosphates and chromates of alkali and transition elements.
- Substances like Na_2CrO_4 , NaNO_3 , act as anodic inhibitors either by forming less soluble compounds with the anodic metal ions or they may also retard the corrosion by oxidative repair of the oxide film.
- The organic compounds can also act as anodic inhibitors and example include sodium benzoate.

2. Cathodic inhibitors :

- The cathodic reaction in acidic medium is represented by :
 $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$
- Thus, corrosion can be controlled by slowing down the diffusion of H^+ ions to the cathode.
- The diffusion of H^+ ions is considerably reduced by organic inhibitors such as amines, mercaptans, heavy metal soaps, substituted ureas and thioureas.
- These substances are capable of being adsorbed at the metal surfaces and thus restrict the diffusion of H^+ ions.
- Antimony or arsenic oxides are used as cathodic inhibitors because of the formation of adherent film on the surface on the surface of the metal.
- Compared to anodic inhibitors, cathodic inhibitors are quite safe.
- This is because, even if they are used in concentrations less than required for complete protection, the partially covered cathodic sites decrease the surface of the cathode, whereas anodic area

remains practically the same. Thus, corrosion decreases due to area effect.

3. Vapour phase inhibitors :

- These are the inhibitors which readily vapourize and form a protective layer of inhibitor on the metal surface.
- Vapour phase inhibitors (VPI) are used to prevent corrosion in enclosed spaces and also during storage, packing, shipping etc.
- Small metals are protected from corrosion by keeping them in the envelopes made from paper impregnated with a suitable vapour phase inhibitor.
- Dicyclohexylammonium nitrile and cyclohexyl amine carbonate are amongst the most widely use VPIs.

Que 3.20. Compare chemical corrosion and electrochemical corrosion.

Answer

Sno	Chemical corrosion	Electrochemical corrosion
1.	It occurs in dry condition.	It occurs in wet condition.
2.	It involves the direct chemical attack of the metal by environment.	It involves the setting up of a large number of galvanic cells.
3.	It is explained by absorption mechanism.	It is explained by mechanism of electrochemical reactions.
4.	It occurs on both homogeneous and heterogeneous surfaces.	It occurs only on heterogeneous metal surface.
5.	Corrosion is uniform.	Corrosion is not uniform. If the anode area is small, pitting is more frequent.
6.	It is a slow process.	It is a fast process.
7.	Corrosion products accumulate at the same place where corrosion occurs.	Corrosion occurs at the anode, but products accumulate near the cathode.

Que 3.21. Explain four methods for prevention of corrosion.

OR

Explain sacrificial anodic and impressed cathodic protection method for protection of corrosion.

UPTU 2013-14, Marks 01

Answer

Refer Q. 3.17, Page 104H, Unit-3.

Que 3.22. Explain why a pure metal rod half immersed vertically in water starts corroding at the bottom. **UPTU 2011-12, Marks 05**

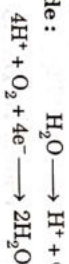
Answer

A pure metal rod half immersed vertically in water starts corroding at the bottom because O_2 concentration is much less there. The area above the water line is highly oxygenated and hence, acts as cathode area consequently it does not corrode.

Reaction at anode :



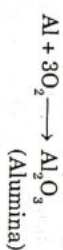
Reaction at cathode :



Que 3.23. Distinguish between the corrosion of aluminium and magnesium. **UPTU 2011-12, Marks 05**

Answer

Aluminium reacts with oxygen to form stable layer which further prevents corrosion and aluminium gets prevented from corrosion while magnesium forms porous layer from which oxygen can further diffuse from the pores and the metal get corroded further.



Stable layer



PART-3

Setting and Hardening of Cement, Applications of Cement, Plaster of Paris, Lubricants-Classification, Mechanism and Applications.

CONCEPT OUTLINE : PART-3

- **Cement** : It is a material having adhesive and cohesive properties.
- **Types of cement** :
 1. Natural
 2. Puzzolana
 3. Slag
 4. Portland
- **Plaster of Paris** : It is a building material used for cooling walls and ceilings.

- **Lubricants** : It is a substance which reduces friction between two moving parts.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.24. What is cement ? Classify various types of cement ?

Answer

Cement : Cement is the binding material used for binding bricks, gravel, tile and for plaster on walls. Most commonly used type of cement is portland cement. Portland cement is the binding material which sets and hardens very strongly even under water. Cement is a material having adhesive and cohesive properties. It gets settled and hardens under water, hence even known as hydraulic cement.

S.No	Type	Preparation	Properties and applications
1.	Natural	Made by calcining a naturally occurring argillaceous lime-stone at high temperature and then pulverising the calcined mass.	Relatively low strength, quick setting and hydraulic. In making mortars, large masses of concrete.
2.	Puzzolana	Cement which is formed by mixing puzzolana (the substance mix with lime form hydraulic without heat) and slaked lime.	Hydraulic when mixed with portland.
3.	Slag	By mixing hydrated slag and lime.	Low strength, slow setting, abrasion-resistant and used for making concrete.
4.	Portland	An extremely finely ground product obtained by calcining together at 1500°C , an intimate and properly proportioned mixture of argillaceous and calcereous raw materials.	Important and reliable use in making strong structures.

Que 3.25. Write the chemical composition of portland cement.

UPTU 2013-14, Marks 02

Answer

Chemical composition of portland cement :

1. Portland cement is made from three principal constituents i.e., lime, silica and alumina.
2. In addition to these, small amount of iron oxide, magnesium oxide, sulphur trioxide, alkalies and other materials are added during cement manufacture.
3. The average chemical composition of portland cement as per ISI specifications is given as :

Oxide	Percentage
Lime (CaO)	60 – 67
Silica (SiO ₂)	17 – 25
Alumina (Al ₂ O ₃)	3 – 8
Iron oxide (Fe ₂ O ₃)	0.5 – 6
Magnesia (MgO)	0.1 – 4
Sulphur trioxide (SO ₃)	1 – 3
Soda and Potash (Na ₂ O + K ₂ O)	0.5 – 1.5

Que 3.26. What is the role of each compound in cement during strengthening ?

Answer

Characteristics of compounds in portland cement :

The properties of cement depend upon the relative proportion of the compounds present as each of them have different characteristics properties, for example, strength developed by different compounds in cement with time is different.

1. **Tricalcium silicate (C₃S) :**
 - a. Its rate of hydrolysis is medium.
 - b. It develops very high strength quite early and its ultimate strength is also highest among all constituents.
 - c. It is mainly responsible for ultimate strength.
 - d. Its heat of hydration is about 120 cal/gm.

e. Rate of hydration is 75.5 %.

2. **Dicalcium silicate (C₂S) :**

- a. It hydrates very slowly.
- b. Thus, its early strength is quite low, but develops ultimate strength almost of the same order as that of C₃S.
- c. Its heat of hydration is the lowest among all constitutional compounds and is about 60 cal/gm.
- d. Rate of hydration is 37.5 %.

3. **Tricalcium aluminate (C₃A) :**

- a. It hydrates at very fast and responsible for initial set called flash set.
- b. Its early strength is good but ultimate strength is quite low.
- c. The heat of hydration is about 210 cal/gm, the highest among all compounds in cement.
- d. Highest rate of hydration among all the constitutional compounds which is 82.5 %.

4. **Tetracalcium alumina ferrite (C₄AF) :**

- a. It hydrates slowly.
- b. Its early and ultimate strength are poor and lowest among all other constitutional compounds.
- c. The heat of hydration is about 100 cal/gm.
- d. Rate of hydration is 57 %.

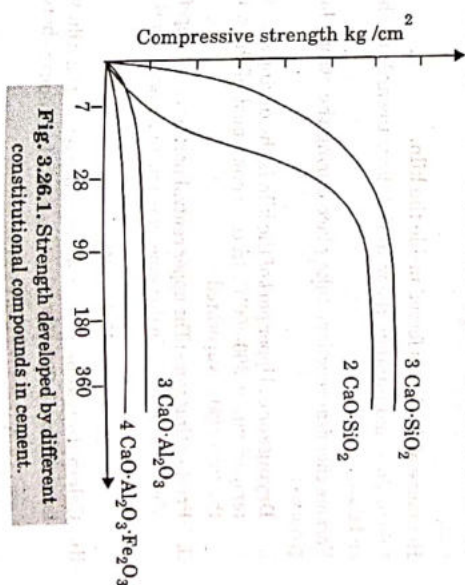


Fig. 3.26.1. Strength developed by different constitutional compounds in cement.

Que 3.27. Describe the process of manufacturing of Portland cement with the help of schematic diagram.

UPTU 2014-15, Marks 05

Answer

The process of manufacturing of portland cement :

Wet process:

1. Mixing:

a. The various materials required for cement manufacture, are separately crushed, powdered, washed with water and stored in tanks.

b. They are intimately mixed in correct proportions and taken as slurry in water to a grinding mill.

2 Grinding:

- a. The raw material is then ground to fine in tube mills, along with 30-40% water.

b. The grinding consumes major part of electrical consumption.

c. Finer the raw material particles, better is the cement produced.

3. Burning :

a. The slurry is fed to a kiln at its upper end.

b. The kiln is inclined, very long and rotating.

The kiln is heated by coal powder or fuel oil introduced from other end.

Hot flame of the fuel is forced inside the kiln.

Due to slope and rotation, the material flows towards the hottest end slowly.

f. Various chemical reactions take place during the strong heating given as :

1. Drying zone: Upper part of the kiln is the drying zone where temperature is 300-400°C. In the zone, most of the water in the slurry gets evaporated.

II. **Pre-heating zone:** The upper central part having temperature of about 400-700°C. In this zone, clay and magnesium carbonate decomposes.

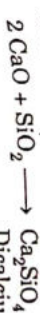
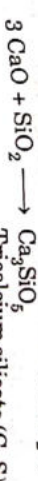


iii. **Calcination zone :** It is the central part of the kiln where temperature is 700-1000°C. Limestone decomposes here.

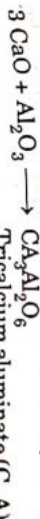


iv. **Clinkering zone** : It is the lower portion of the kiln where temperature is from 1200-1500°C. Here, lime reacts with silica,

alumina and iron oxide in various ways and the materials melt in this zone. The major reactions taking place are :

Dicalcium silicate (C_2S)

Tricalcium silicate (C_3S)

Tricalcium aluminate (C_3A)

F, formed are in molten form.

the C_2S , C_3S , C_3A , C_4AF , formed are in molten form.

g. When cooled by air, there is formation of small hard, greyish stones called as clinkers.

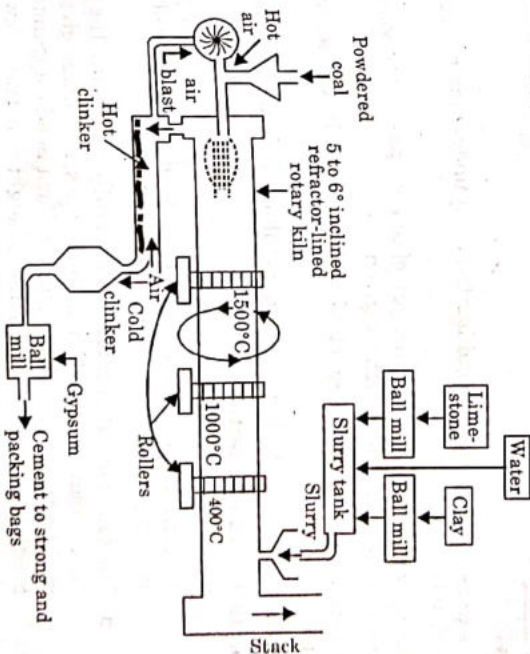


Fig. 3.27.1. Rotary cement kiln.

4. Cooling of clinkers:

- a. The hot clinkers are cooled by use of rotary coolers, planetary coolers or by air quench coolers.

- b. The quality of cement depends upon the rate of cooling of clinkers.
- c. The cooling rate should be such that the definite degree of crystallization occurs in the clinker.

d If the rate of cooling of clinker is very slow, then the crystals of C_2S are converted to fine and such C_2S has no good property of binding. Such cooling results in 'dusting'.

e. If the rate of cooling is fast then almost all alumina and iron oxide solidify and crystalline compounds C_3A and C_4AF formation is badly affected.

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- f. If the cooling rate is medium, then the liquid inside clinkers turn to crystalline C_3S which gives the highest strength to cement mass during setting hardening.
5. **Grinding:** The cooled clinkers are ground to fine powder. During grinding, 2-4 % of gypsum is added.
6. **Packing:** The portland cement powder is packed in 50 kg bags with the help of machines.

Que 3.28. What is Portland cement? Give the chemical reactions involved during setting and hardening of cement.

UPTU 2013-14, Marks 05

Answer

1. The cement which can set and harden even under water is called as portland cement.
2. Setting is the process of solidification of cement paste with some early strength and takes the cast/shape given.
3. Hardening means development of high strength in the set mass of cement.
4. The setting and hardening of cement is taking place in three stages:
 - a. **Initial (flash) setting:**
 - i. When water is added to cement powder, it forms a plastic, semisolid paste like mass, which can be given shape easily while working.
 - ii. The time for initial setting is generally half hour. The plastic mass solidifies in half hour and takes the shape given. The initial setting time can be tested by Vicat needle apparatus. The needle released from the definite height penetrates few mm in the initially set mass, known as setting of cement.
 - iii. Initial setting involves hydration of C_3A to form crystals of tricalcium aluminate hydrate.

$$C_3A + 6H_2O \longrightarrow C_3A \cdot 6H_2O + 880 \text{ kJ/kg}$$

iv. This reaction is very fast and gets completed in about 15 minutes and it is highly exothermic. Side by side, the hydration of C_4AF also goes.

$$C_4AF + 7H_2O \longrightarrow C_4A \cdot 6H_2O + CF \cdot H_2O + 420 \text{ kJ/kg}$$

v. But C_4AF hydration is much slower and requires over an hour to complete.

vi. Hydration of C_3A and C_4AF do not result in developing any appreciable strength.

b. **Final setting or initial hardening:**

- i. The initially set mass of cement or cement mortar gains early strength in 10 hours time.
- ii. This can be tested by Vicat needle apparatus. The needle does not penetrate in the finally set mass but makes just a mark on the surface, is known as hardening.
- iii. In the finally set cement mortar sufficient strength gets developed by hydrolysis of C_3S . The hydrolysis of C_3S is slow and to complete, it requires up to 7 days but in 10 hours, a part of the total C_3S reacts with water and gives the strength.

$$C_3S + (n+1)H_2O \longrightarrow C_2S \cdot nH_2O + Ca(OH)_2 \text{ (gel)}$$
- iv. The tobermonite gel formed is strongly binding in character.

c. Final hardening:

- i. The development of ultimate stiffness or strength in the cement mass is known as final hardening.
- ii. For this stage to complete, sufficient water must be provided (curing).
- iii. Final hardening is due to mainly two chemical reactions i.e., continued hydrolysis of C_3S and hydration of C_2S .

$$C_3S + (n+1)H_2O \longrightarrow C_2S \cdot nH_2O + Ca(OH)_2$$

tobermonite gel crystals

$$C_2S + nH_2O \longrightarrow C_2S \cdot nH_2O$$

gel

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

(from air) (weakly binding)

Que 3.29. What is the role of gypsum in cement?

UPTU 2013-14, Marks 02

Answer

Role of gypsum:

1. Tricalcium aluminate C_3A undergoes hydration quickly and the reaction being highly exothermic (880 kJ/kg) the suddenly liberated heat can cause problems to the setting cement mass i.e., increasing temperature of mass and causing minor cracks to the set cement mass and affect strength. Therefore, the hydration of C_3A should be prolonged or delayed so that the heat liberation takes place in longer time span, and minimize the problems.
2. The quick hydration of C_3A can be delayed by gypsum present in cement. As soon as water is added to the cement powder, most of the C_3A reacts with gypsum, producing calcium sulphoaluminate and this reaction is not high heat liberating.



- This product slowly disintegrates into $C_3A \cdot 6 H_2O$ and thus sudden heat liberation is prolonged by Gypsum up to about half hours.

Que 3.30. Give the applications of cement.

Answer

Following are the applications of cement :

- Cement mass has got very high compressive strength (like rock) but it has not adequate tensile strength.
- To increase the tensile strength, reinforcing material like steel bars, steel network etc. are embodied in it.
- The portland cement is used for the construction of wall, plasters, foundations, reinforced constructions, roads, under water constructions, bridges, etc.

Que 3.31. What is Plaster of Paris ? How it is prepared ?

Answer

Plaster of Paris is the material having formula $CaSO_4 \cdot \frac{1}{2} H_2O$ and it is used for protective or decorative coating on walls and ceilings plaster purpose. It is also used for moulds and casting decorative elements.

- While working, it is mixed with water to make thick paste and then applied on a surface. Its reaction with water liberates heat of crystallization and the hydrated plaster then hardens.
- It is very easy to apply but it is not a strong material. It is suitable only for finishing but not useful for load bearing.

Preparation of Plaster of Paris : It is obtained on heating gypsum mineral at $150^\circ C$.



Gypsum
Plaster of Paris

Que 3.32 What are the properties of POP ? Also, give the applications.

Answer

Properties of POP :

- Setting and hardening with water is the most important property of Plaster of Paris.
- When water is added to Plaster of Paris, slurry is obtained which hardens quickly and sets easily, creating the desired solid shape in a smooth finish.

- Chemically, on mixing with water, Plaster of Paris expands slightly and regains the closely-packed crystalline structure of gypsum.

Process of setting can be accelerated by mixing it with alkali sulphate like K_2SO_4 , which initiates the crystallization process as well as makes it proceed faster.

It is a white coloured powder and light in weight.

The set material is not strong.

It is easy to work and setting time is also conveniently small.

Applications of POP :

- Plaster on wall, ceiling.
- Moulded and casted articles of decoration.
- For orthopedic cast to protect limbs with broken bones.
- It is used for quick sealing.
- At high temperatures, Gypsum loses all the water of crystallization to give anhydrous calcium sulphate.
- It is used in manufacture of H_2SO_4 .
- It is used in making of cement.
- It is used in the preparation of moulds used in surgery and castings.

Que 3.33. What is Lubricant ? Give suitable examples. Classify them and explain any one of the mechanisms of lubrication.

UPTU 2013-14, Marks 05

OR

Define lubricant and lubrication. Explain mechanism of lubrication.

Answer

Lubricant :

- A lubricant is defined as the substance placed between sliding metallic surfaces, to reduce frictional resistance.
- The substance used as lubricant may be solid, semisolid or liquid in state. Sometimes, it is the solution of a solid in a liquid (for example, fatty acid or soap dissolved in mineral oil or water).

Lubrication

- It is the process of reducing friction between two metallic sliding surfaces, by placing a suitable lubricant.

Functions of lubricants :

- It reduces frictional resistance between the metallic surfaces.
- It reduces wear and tear of metal surfaces.
- It decreases the maintenance cost and running cost of machines.

4. It increases the efficiency of machine by minimizing the loss of mechanical, electrical or chemical energy.
5. It minimizes the local heating of sliding metal surfaces, their expansion and jamming.
6. It makes the relative motion of sliding parts smooth and noise free.
7. It acts as coolant for example, in cutting, drilling of metals by tools, transfers the heat from gears to the surface of gear-box for radiation and similarly in transformers.

Mechanism of lubrication : There are mainly three types of mechanism by which lubrication is done :

1. Fluid film or thick film or hydrodynamic lubrication :

- a. **Operating conditions :** This type of lubrication takes place when load is low and speed is high.
- b. Under the condition of low load or high speed, the liquid fills up valleys on both sliding surfaces and can maintain a thick film to separate the surfaces so that there is no direct contact of the surfaces.
- c. The film keeps on moving along with the sliding surface or it is dynamic film.

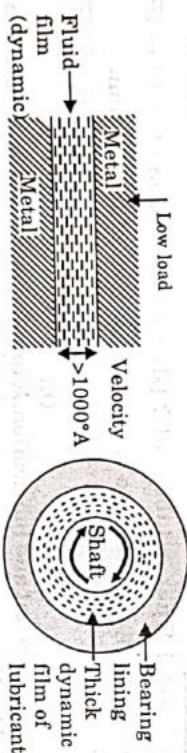


Fig. 3.33.1.

- d. The separation of the two metallic surfaces is at least by $1000 \text{ \AA}$ i.e., the film thickness.
 - e. If the viscosity of lubricant is too high, then the thick lubricant will offer its own resistance to the motion and will not allow free rotation of the delicate parts. Hence, lubricant should not have very high viscosity. Hydrocarbons oils with high molecular weight with some antioxidant are preferred lubricants.
 - f. Examples of machines where this type of lubrication occurs are watches, clocks, locks, gun parts, sewing machine, typewriter, scientific instruments, measuring devices (meters), hinges, light gears, journal bearings, fans, etc.
- ### 2. Boundary lubrication or thin film lubrication or static lubrication :

- a. Under the conditions of boundary lubrication, only a thin film of lubricant of higher oiliness, can be maintained.
- b. The molecules of oil either get chemically adsorbed on the metal surfaces or react to form monomolecular layer or a layer of 2-3 molecules thickness.
- c. The adsorption or reaction takes place in valleys and on asperities of both surface. The adsorbed or reacted lubricant molecules orient at right angle to the surface.
- d. 2-3 molecules thick layer of lubricants between the metallic surfaces is adequate to minimize the metal to metal contact and can reduce the friction in the sliding surfaces.
- e. The coefficient of friction is about 0.05 to 0.15.

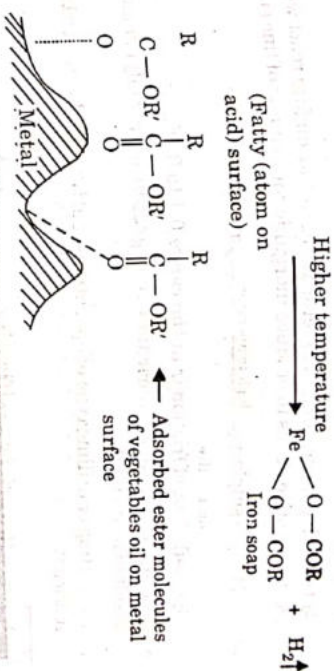


Fig. 3.33.2. The thin film on the surface is stationary or static.

- f. If the temperature of the surfaces increases beyond a limiting value, then the adsorption decreases and fast wear of surfaces begins or the sliding stops due to jamming of the expanded metal parts due to local high temperature.

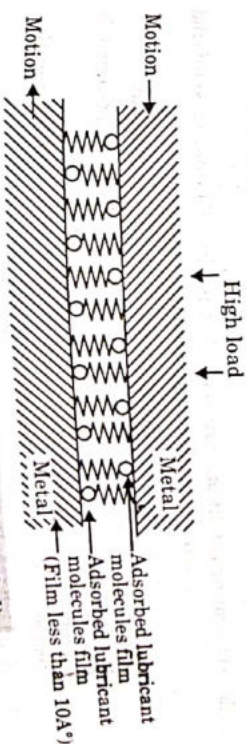


Fig. 3.33.3. Boundary lubrication (magnified).

3. **Extreme pressure lubrication :**
- a. Under the extreme conditions of load and speed, even the best boundary lubricant of fatty acid or metal soap type, fails to work

and there is increase in friction, local temperature and surface damage.

- b. Ordinary lubricant decomposes and evaporates at the high temperature produced. Therefore, effective lubricants are prepared for the purpose by dissolving the long chain organic compounds containing the electronegative atoms (such as Cl or S or P) with mineral oil along with little fatty acid.
- c. The additives dissolved in mineral oil are called as extreme pressure additives and the lubricant is called as extreme pressure lubricant (EP lubricant).
- d. In the beginning, some extent of boundary lubrication takes place but it cannot bring down the friction and shortly a very high temperature is developed.
- e. At the high temperature, the metal atoms of the surface react with electronegative atoms to produce inorganic compounds of fine size.
Metal + sulphur $\xrightarrow{\text{high temperature}}$ metal sulphide
- f. The coefficient of friction is in the range 0.1 to 0.25.
(in additive)
- g. In some cases, solid lubricants like graphite or molybdenum disulphide are used.
- h. For cutting or drilling type of operations, cutting fluids are used as lubricant.

Que 3.34 Give the brief classification of lubricants.

Answer

Lubricants can be classified as :

1. Solid lubricants : Solid lubricants are used in situations such as :

- a. Heavy machinery working on a crude job at very high loads and slow speed.
- b. Operating conditions are such that a film of liquid or semisolid lubricant is not formed or maintained.
- c. Where the parts to be lubricated, are not easily accessible.
- d. Contamination of liquid or semisolid lubricant, with dust or grit, is not desirable for example, open gears.
- e. Combustible lubricants are to be avoided due to high operating temperature and pressure.
- f. Solid lubricants are thermally stable, they do not catch fire under the operating conditions, most of them are smooth and reduce the friction.
- g. Graphite, molybdenum disulphide, talc, soapstone (magnesium silicate), mica are the examples of common solid lubricants. They

are used either in the form of dry powder or mixed with water or oil so that they can firmly adhere to the metal surfaces.

Graphite and molybdenum disulphide are the two important structural solid lubricants used.

Solid lubricants are used for compressors, I.C engines, lathes, pulleys, cranes, railway track joints, open gears, chains, cast iron bearings, food industry, war tanks, etc.

2. Semisolid lubricants :

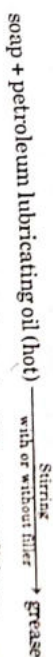
a. The most important semi-solid lubricants are greases, vaselines and waxes.

b. Grease is a semi-solid lubricant obtained on mechanical dispersion of soap in hot petroleum oil. A soap is obtained on reaction of a vegetable oil with an alkali.



c. The alkali used in making soap is NaOH , $\text{Ca}(\text{OH})_2$, LiOH , $\text{Ba}(\text{OH})_2$ etc.

d. The solid soap obtained by reaction of an alkali and a vegetable oil, is used as gelling agent in the liquid medium of petroleum lubricating oil or synthetic oil.



e. Greases are used for lubrication under following conditions :

- i. High pressure condition.
 - ii. High temperature (up to 80°C).
 - iii. In situation where bearing has to be protected against entry of dust, dirt, moisture.
 - iv. In situations where oil cannot remain in place due to low speed, high load or intermittent operation jerks.
 - v. In situations where dripping or spurring of oil is undesirable, for example, machines used in paper, food, textile and dyeing industry.
3. Liquid lubricants :
- a. Liquid lubricants are most common in use and a good liquid lubricant should have following properties :
 - i. High flash and fire point.
 - ii. Required oiliness.
 - iii. Required extent of viscosity.
 - iv. Viscosity should not change appreciably with rise or fall of temperature.

- v. High oxidation resistance.
- vi. High thermal stability and act as cooling medium, sealing agent and corrosion preventer.
- h. Depending upon chemical nature, they are further classified as :
 - i. Mineral or petroleum lubricating oils,
 - ii. Vegetable and animal oils,
 - iii. Blended oils or compounded oils, and
 - iv. Synthetic oils : These oils are manufactured by chemical processes. They possess following distinguishing features :

Que 3.35. What are lubricants ? Give the structure of graphite and explain its lubricating properties.

UPTU 2014-15, Marks 05

Answer

Lubricants : Refer Q. 3.33, Page 119H, Unit-3.

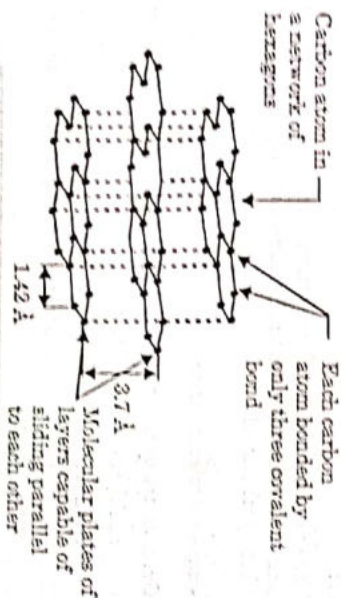


Fig. 3.25.1. Layered structure of graphite.

Properties of graphite :

1. It is the most widely used solid lubricants. It consists of a layered lattice structure.
2. A large number of hexagonally arranged sp^2 hybridized Carbon atoms in graphite are arranged in hexagon in flat parallel layers and each one is linked by covalent bonds to three other atoms but its distance from fourth one is more than double. Hence the fourth valence bond is not fixed and can break and make easily.
3. The two neighbouring parallel graphite molecules are $3.7 \text{ \AA}$ apart and there is a weak Vander Waal force of attraction between them. Therefore, the molecules can slip over each other easily by mechanical force. Hence, graphite powder is easy to touch or very soft and can act as lubricant.
4. It is non-inflammable and does not get oxidised in air below 375°C .

5. It can be used as lubricant at much higher operating temperatures in the absence of air.
6. In presence of moisture, graphite will act as good lubricant.
7. It is used either in powder form or as suspension. The suspension of graphite in oil or water is used with the help of Yarnin as emulsifying agent.
8. The graphite suspension in oil is called as 'oil-dag' and suspension in water is called as 'aqua-dag'.
9. Oil-dag is found useful in I.C. engines. Aqua-dag is useful in air compressors, general machine shop work, lathes and for machinery used in the food industry.
10. Aqua-dag is useful where a lubricant is needed free from oil. It works best in moist air and carbon dioxide whereas it has mediocre lubrication properties in oxygen and nil lubrication properties in nitrogen atmosphere.

Que 3.36. Give an account of the synthetic lubricants.

UPTU 2012-13, Marks 04

Answer

1. Mineral oils cannot be used effectively as they tend to get oxidized at very higher temperatures while wax separation will occur at very low temperatures.
2. So, synthetic lubricants have been developed, which can meet the severe operating conditions such as in aircraft engines.
3. The same lubricants may have to be in the temperature range of -50°C to 250°C .
4. Polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates and silicones are currently used as synthetic lubricants.
5. Few examples : Grease is a semisolid lubricant obtained by thickening liquid lubricating oil through the addition of a metallic soap. The thickness is usually sodium or calcium or lithium soap.
6. **Types of grease :**
 - a. Soda-base grease
 - b. Lime-base grease
 - c. Lithium-soap grease
 - d. Barium-soap grease
 - e. Axle (resin) grease
7. **Graphite :** It consists of a multitude of flat plates, which are held together by weak Vander Waals forces, so the force to shear the crystals parallel to the layers is low.

- It is used either in powder form or as suspension.
- When graphite is dispersed in oil, it is called 'oil-dag' and when graphite is dispersed in water is called 'agua-dag'.
- It is ineffective at above 370 °C. It is used for lubricating internal combustion engines.

8. Molybdenum disulphide :

- It has a sandwich like structure in which a layer of molybdenum atoms lies between two layers of sulphur atoms.
- The weak Vander Waals forces, acting in between the layers, can be destroyed easily.
- MoS_2 can also be used as power or dispersions.
- It is effective upto 800 °C.
- It is used in wire-drawing dies.

Que 3.37. Give applications of lubricants based upon their applications.

Answer

S. No.	Type of machinery	Operating conditions	Properties required in lubricant
1.	Internal combustion engine	High temperature, low to high speed, low to high pressure	- High thermal stability - Non corrosive - High viscosity index - Good oiliness. For example, petroleum oils blended with above 'property improvers'.
2.	Spindles	Low load, high speed	- Low to moderate viscosity - Oxidation resistance - Should contain corrosion inhibitor - Non-volatile For example, thin petroleum oil blended with corrosion inhibitor.
3.	Refrigeration	Low temperature, moderate load	- Low pour point, below -40°F - Moderate viscosity - Low cloud point. For example, naphthenic base oil.

	Circulating system (turbine, hydraulic)	Water or steam contact, high temperature	- High oxidation resistance - Antifoaming character - Antirusting character - Medium viscosity For example, petroleum oils blended with antirust, antifoaming, viscosity index improving additives.
5.	Gears	High pressure, high temperature, low to high speeds	- High oiliness - Proper viscosity (medium to high) - Oxidation resistance is high - High viscosity index For example, proper viscosity petroleum oils blended with antifoam, antioxidant, V.I.
6.	Delicate instruments	Low load, high speed.	- Low to moderate viscosity - Nonvolatile - Low pour point for example, vegetable oils, Animal oils
7.	Steam engine cylinder	Steam contact, high temperature, high pressure	- High oiliness - Less emulsification with water - High viscosity index

Que 3.38. What are flash and fire points ?

UPTU 2014-15, Marks 05

Answer

Flash points :

- An oil's flash point is the temperature at which a flame appears and instantaneously propagates itself over the entire surface.
- The oil flashes because a flammable mixture results when it is heated sufficiently, causing vapours to emerge and mix with oxygen in the air.
- The flash point temperature of oil corresponds roughly to a vapour pressure of 3-5 mm Hg.
- When a small flame (ignition source) is applied to the oil's surface this vapour mixture will burn momentarily and then extinguish if the critical temperature has been reached.
- Naturally, the exact flash point will vary depending on the type and composition of the oil.

Fire points :

1. Continued heating of the oil (typically 50-75° F above the flash point temperature) will cause the fire point to be reached.
2. As the name implies, the fire point is the temperature at which a sustained flame results (longer than four seconds).
3. Naturally, the fire point is always going to be higher than the flash point.



UNIT 4

4 UNIT

Water Treatment

Part-1 (130H - 139H)

- Hardness of Water
- Disadvantages of Hard Water
- Boiler Troubles

A. Concept Outline : Part-1 130H

B. Long and Medium Answer Type Questions 131H

Part-2 (139H - 157H)

- Techniques for Water Softening : Lime-Soda
- Zeolite
- Ion Exchange Resin
- Reverse Osmosis

A. Concept Outline : Part-2 139H

B. Long and Medium Answer Type Questions 140H

Part-3 (158H - 171H)

- Phase Rule and its Application to Water System

A. Concept Outline : Part-3 158H

B. Long and Medium Answer Type Questions 158H

- **Water?** Water is very important for the existence of human beings, animals and plants. It is important in industries. The main sources are :

1. Surface water
2. Underground water
3. Rain water
4. Sea water

- **Hardness of water** : Hardness is defined as the soap consuming capacity of a water sample. Sodium salts of long chain fatty acids present in the soap react with Ca^{++} and Mg^{++} ions of water to form insoluble scums of Ca^{++} and Mg^{++} which do not have any detergent value.

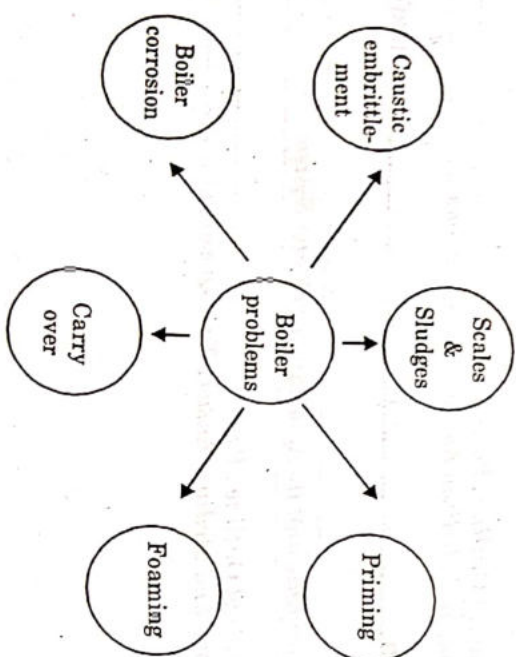
- Hardness are of two types :

1. Temporary hardness
2. Permanent hardness

- **Treatment of water :** For boiler feed, water treatment for hardness is essential. Two types of treatment are there for removal of hardness :
1. External treatment

- ## 2. Internal treatment

- **Boiler problems:**



131 (Sem-1 & 2) H

Long Answer Type and Medium Answer Type Questions

Que 4.1. What is hardness of water? What are its types?

Answer:

1. Hardness is one of the most important characteristic of water. This term was applied to the waters which make cleansing action of the soap difficult.
2. The water which does not form lather with soap and is hard to wash in, is termed as hard water.
3. Hardness of a water sample is a measure of its capacity to precipitate soap or its soap consuming capacity.
4. On the other hand, the water which forms copious lather with soap is termed as soft water.

Cause of hardness :

1. Hardness of water is due to the presence of calcium and magnesium salts. Generally, soaps consist of sodium salts of higher fatty acids such as stearic, oleic, palmitic etc., which are highly soluble in water and thus exert their cleansing action.

2. If calcium and magnesium salts are present in water, these react with soluble sodium soap to form insoluble salts of calcium and magnesium.
3. For example,



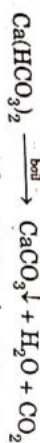
4. Thus, a white scum or precipitate of insoluble soap of calcium and magnesium is formed. Lather is not produced until the cations, Ca^{2+} and Mg^{2+} , are completely precipitated out in the form of insoluble salts.
5. As a result, a large quantity of soap is required to produce lather with hard water. Thus, hardness is rightly defined as soap consuming capacity of water.

Types of hardness :

- a. Temporary hardness
b. Permanent hardness
a. Temporary hardness

1. **Temporary hardness :** Hardness due to the presence of bicarbonate ions of calcium and magnesium is called temporary hardness or carbonate hardness. This is also known as alkaline hardness.

2. This hardness can be removed by mere boiling of water, which converts the bicarbonates into insoluble carbonates or hydroxides.
3. The insoluble carbonates or hydroxides can be removed by filtration.



4. Temporary hardness can also be removed by addition of calculated amount of lime (Ca(OH)_2).



- Permanent hardness :** This type of hardness is also known as non-carbonate hardness. It is due to the presence of sulphates and chlorides of calcium and magnesium. Permanent hardness cannot be removed by boiling.

Que 4.2. Differentiate between hard water and soft water.

Answer

S.No.	Hard water	Soft water
1.	Water which does not produce lather with soap solution readily, but forms a white curd, is called "hard water".	Water which lathers easily on shaking with soap solution, is called "soft water".
2.	Hard water contains dissolved calcium and magnesium salts in it.	Soft water does not contain dissolved calcium and magnesium salts in it.
3.	In hard water, cleansing quality of soap is depressed and a lot of it is wasted during washing and bathing.	In soft water, cleansing quality of soap is not depressed and so soap is not wasted during washing and bathing.
4.	Due to the presence of dissolved hardness producing salts, the boiling point of water is elevated. Consequently, more fuel and time are required for cooking.	Less fuel and time are required for cooking in soft water.

Que 4.3. 200 ml of water sample has a hardness equivalent of 25 ml of 0.08 N MgSO_4 . What is its hardness in ppm?

UPTU 2013-14, Marks 05

Answer

$$\text{Number of gm equivalent} = V \times N = \frac{25}{1000} \times 0.08$$

$$\text{Weight in gms of } \text{MgSO}_4 = \text{number of gm equivalent} \times \text{equivalent weight} \\ = \frac{25}{1000} \times 0.08 \times \text{equivalent weight}$$

$$\text{Weight in gm of } \text{MgSO}_4 \text{ in } 200 \text{ ml} = \frac{25}{1000} \times 0.08 \times \text{equivalent weight}$$

$$\text{in } 1 \text{ ml} = \frac{25}{1000} \times \frac{0.08}{200} \times \text{equivalent weight}$$

$$\text{in } 1000 \text{ ml} = \frac{25}{1000} \times \frac{0.08}{200} \times \text{equivalent weight} \times 10^3 \text{ g}$$

$$\text{in } \text{CaCO}_3 \text{ equivalent} = \frac{25}{1000} \times \frac{0.08}{200} \times \text{equivalent weight} \times 50/$$

$$\text{equivalent weight} \times 10^3 \text{ g} \\ = 0.5 \text{ g/L} = 500 \text{ mg/L}$$

Que 4.4. What are the disadvantages of hardwater?

Answer

In domestic :

1. **Cooking :** Vegetables and other like pulses etc. do not cook well in hard water.
2. **Wastage of soap :** Since, hard water does not form lather with soap readily hence, soap is wasted in removing the Ca^{2+} and Mg^{2+} ions present in water.
3. **Spoiling clothes :** The Ca^{2+} and Mg^{2+} present in hard water combine with soap to form insoluble compound, which sticks to the clothes. It is not easily removed and spoils the clothes.
4. **Consumption of more fuels :** Ca^{2+} and Mg^{2+} salts are deposited inside the boiler. These form a layer as a scale, which are not removed easily. Hence, consumption of fuel is increased and the cooking utensils are spoiled.

In industries :

1. **Textile industry :** The water used in textile and dyeing industries should be free from hardness (Ca^{++} and Mg^{++} ions), organic matter, suspended particles etc. Hard water precipitates basic dyes. Iron and manganese salt produce coloured spots on fabrics.
2. **Sugar industry :** Water should be free from hardness, suspended particles as well as pathogenic micro-organisms. Hard water causes difficulties in the crystallization of sugar from molasses.

3. **Paper and pulp industry :** The water should be free from hardness, suspended particles, iron, manganese etc. Hardness increases the ash contents of paper. Dissolved silica produce cracking tendency of paper. Iron and manganese salts decrease the brightness and colour of paper.
4. **Aluminium industry :** The water should be of high quality. Any type of impurity and hardness make it low grade.
5. **Carbonated beverage industry :** The water should be free from colouring matter, pathogenic micro-organisms, hardness, iron and manganese salts, suspended particles etc. It also should have low alkalinity. Hardness producing salts make it of low grade.
6. **Starch industry :** Water should be free from any type of hardness impurities (organic or inorganic), suspended particles, etc. Iron and manganese salts produce yellow colour, which is undesirable. Hardness producing salts causes the precipitation of salts and accumulates in the starch.
7. **Iron industry :** Hard water makes the iron of low quality. It corrodes the iron and alloy. Water pipes are blocked due to precipitation of salts during boiling of hard water. Hence, water should be free from hardness and impurities.
8. **Fibre industry :** The water used in fibre industry should be of high quality. Silica, salts of iron and manganese, dissolved organic and inorganic materials make the fibre of very low grade. Alkalinity and hardness causing ions are very much harmful for fibres.

Que 4.5. Why do we express hardness of water in terms of CaCO_3 equivalent ?

Answer

Hardness in terms of CaCO_3 equivalents :

1. To compare the hardness of different samples of water, it would be easier, if the hardness caused by different salts can be expressed in terms of single salt.
2. It is customary to express hardness in terms of equivalents of CaCO_3 . The reason for choosing CaCO_3 as the standard for calculating hardness of water is due to :
 - i. Its molecular weight is exactly 100, which makes mathematical calculations easier.
 - ii. It is the most insoluble salt, thus can be easily precipitated in water treatment processes.
3. Now 1 mole of CaCO_3 (or 100 parts by weight) would react with the same amount of soap as 1 mole of CaCl_2 (111 parts by weight), or 1 mole of MgCl_2 (95 parts by weight) because 1 mole of all these salts will produce same number of calcium or magnesium ions (Avogadro's number).

4. Thus, CaCO_3 equivalents for various salts are as follows :

$$\begin{aligned}
 100 \text{ g of } \text{CaCO}_3 &= 111 \text{ g of } \text{CaCl}_2 \\
 &= 136 \text{ g of } \text{CaSO}_4 \\
 &= 95 \text{ g of } \text{MgCl}_2 \\
 &= 120 \text{ g of } \text{MgSO}_4 \\
 &= 162 \text{ g of } \text{Ca}(\text{HCO}_3)_2 \\
 &= 146 \text{ g of } \text{Mg}(\text{HCO}_3)_2 \\
 &= 164 \text{ g of } \text{Ca}(\text{NO}_3)_2 \\
 &= 44 \text{ g of } \text{CO}_2 \\
 &= 148 \text{ g of } \text{Mg}(\text{NO}_3)_2
 \end{aligned}$$

5. If x g of CaCl_2 is present in a water sample, then the amount of CaCl_2 present in terms of its CaCO_3 equivalent will be :

$$\begin{aligned}
 1 \text{ g mole of } \text{CaCl}_2 &= 1 \text{ g mole of } \text{CaCO}_3 \\
 111 \text{ g of } \text{CaCl}_2 &= 100 \text{ g of } \text{CaCO}_3 \\
 55.5 \text{ g of } \text{CaCl}_2 &= 50 \text{ g of } \text{CaCO}_3 \\
 (\because \text{Eq. wt of } \text{CaCO}_3 &= 50 \text{ g Eq. wt of } \text{CaCl}_2 = 55.5 \text{ g}) \\
 x \text{ g of } \text{CaCl}_2 &= \frac{50}{55.5} \times x \text{ g of } \text{CaCO}_3.
 \end{aligned}$$

6. Thus to convert various hardness salts CaCO_3 equivalents we may use,

$$= \frac{\text{Mass of the substance}}{\text{Equivalent weight of the substance}} \times \text{Equivalent weight of } \text{CaCO}_3$$

As equivalent weight of most of the hardness causing substances and that of $\text{CaCO}_3 = \text{Molecular weight}/2$, hence to make mathematical calculations more easier, the above formula can be written in terms of molecular weights i.e.,

$$\text{Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of the substance}}{\text{Molecular mass of the substance} / 2} \times 100 / 2$$

$$\text{or Equivalents of } \text{CaCO}_3 = \frac{\text{Mass of the substance}}{\text{Molecular mass}} \times 100$$

Que 4.6.

Differentiate between temporary and permanent hardness. Calculate temporary and permanent hardness of water sample analysed as : $\text{Ca}(\text{HCO}_3)_2 = 21.0 \text{ mg/L}$, $\text{Mg}(\text{HCO}_3)_2 = 25 \text{ mg/L}$, $\text{CaCl}_2 = 16.4 \text{ mg/L}$ and $\text{MgCl}_2 = 5.2 \text{ mg/L}$. **UPTU 2011-12, Marks 10**

Answer

S.No.	Temporary hardness	Permanent hardness
1.	It is caused by the presence of dissolved bicarbonates of Ca, Mg etc.	It is due to presence of dissolved chlorides and sulphates of Ca, Mg, Fe.
2.	It can be removed by more boiling of water.	It cannot be removed by boiling of water.
3.	For example : $\text{Ca}(\text{HCO}_3)_2$	For example : CaCl_2 , MgCl_2 , FeSO_4 , etc.

Given :

$$\begin{aligned}\text{Ca}(\text{HCO}_3)_2 &= 21.0 \text{ mg/L} \\ \text{Mg}(\text{HCO}_3)_2 &= 25 \text{ mg/L} \\ \text{CaCl}_2 &= 16.4 \text{ mg/L} \\ \text{MgCl}_2 &= 5.2 \text{ mg/L}\end{aligned}$$

Constituent	CaCO_3 equivalent
$\text{Ca}(\text{HCO}_3)_2$	$21 \times \frac{100}{162} = 12.96$
$\text{Mg}(\text{HCO}_3)_2$	$25 \times \frac{100}{146} = 17.12$
CaCl_2	$16.4 \times \frac{100}{111} = 14.77$
MgCl_2	$5.2 \times \frac{100}{95} = 5.473$

Que 4.7. Calculate temporary and total hardness of water sample

of water containing $\text{Mg}(\text{HCO}_3)_2 = 9.3 \text{ mg/L}$, $\text{Ca}(\text{HCO}_3)_2 = 17.4 \text{ mg/L}$,
 $\text{MgCl}_2 = 8.7 \text{ mg/L}$ and $\text{CaSO}_4 = 12.6 \text{ mg/L}$. **UPTU 2013-14, Marks 05**

Answer

$$\begin{aligned}\text{Mg}(\text{HCO}_3)_2 &= 9.3 \text{ mg/L} &= 9.3 \times \frac{100}{146} &= 6.36 \text{ mg/L} \\ \text{Ca}(\text{HCO}_3)_2 &= 17.4 \text{ mg/L} &= 17.4 \times \frac{100}{162} &= 10.74 \text{ mg/L} \\ \text{MgCl}_2 &= 8.7 \text{ mg/L} &= 8.7 \times \frac{100}{95} &= 9.15 \text{ mg/L} \\ \text{CaSO}_4 &= 12.6 \text{ mg/L} &= 12.6 \times \frac{100}{136} &= 9.264 \text{ mg/L}\end{aligned}$$

$$\begin{aligned}\text{Temporary hardness} &= 6.36 + 10.74 = 17.10 \text{ mg/L} \\ \text{Permanent hardness} &= 9.15 + 9.26 = 18.41 \text{ mg/L} \\ \text{Total hardness} &= 35.51 \text{ mg/L}\end{aligned}$$

Que 4.8. 100 ml of water sample has a hardness equivalent of 12.5 ml of 0.08 N MgSO_4 . What is its hardness in ppm?**UPTU 2011-12, Marks 05****Answer**

$$\begin{aligned}\text{Number of gms equivalents of } \text{MgSO}_4 &= \frac{12.5}{1000} \times 0.8 = 10^{-2} \\ &\text{Weight in gms.}\end{aligned}$$

$$\begin{aligned}\text{Number of gms equivalent} &= \frac{\text{Eq. wt. (Equivalent weight)}}{\text{Weight in gms of } \text{MgSO}_4 \text{ present in 100 ml of water sample}} \\ &= (1 \times 10^{-2}) \times \text{Eq. wt. of } \text{MgSO}_4 \\ &\text{Weight in gms of } \text{MgSO}_4 \text{ per L of water} \\ &= (1 \times 10^{-2} \times \text{Eq. wt. of } \text{MgSO}_4) \times \frac{1000}{100} \\ &= 10^{-1} \times \text{Eq. wt.}\end{aligned}$$

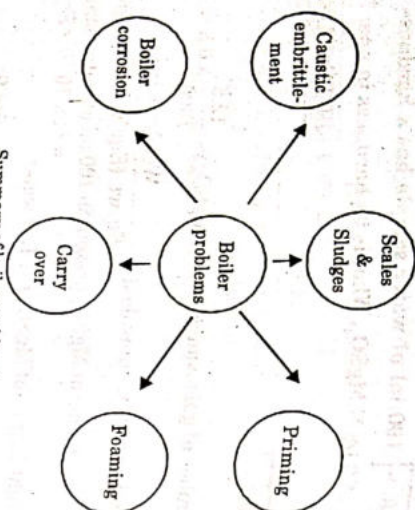
$$\begin{aligned}\text{Hardness} &= \text{Weight in gms of } \text{MgSO}_4 \text{ per L of water} \times \frac{50}{\text{Eq. wt of } \text{MgSO}_4} \\ &= 10^{-1} \times \text{Eq. wt. of } \text{MgSO}_4 \times \frac{50}{\text{Eq. wt of } \text{MgSO}_4} \\ &= 50 \times 10^{-1} \text{ g/L} = 500 \text{ ppm}\end{aligned}$$

Que 4.9. Write a short note on boiler troubles.**Answer**

- Water is mainly used in boilers for the generation of steam (for industries and power houses).
 - For such water all the impurities are not necessarily eliminated, and only those impurities which lead to operational troubles in boilers are eliminated or kept within the tolerable limits.
 - A boiler feed water should correspond with the following composition :
 - Its hardness should be below 0.2 ppm.
 - Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm.
 - Its soda alkalinity (due to Na_2CO_3) should be 0.45 – 1 ppm.
- Excess of impurities, if present in boiler feed water generally cause the following problems :

Scale and sludge formation, corrosion, priming and foaming, caustic embrittlement.

Boiler problems :



Summary of boiler problems

Fig. 4.9.1.

Sludge and scale formation in boilers :

1. In a boiler, water is continuously evaporated to form steam. This increases the concentration of dissolved salts. Finally, a stage is reached when the ionic product of these salts exceeds their solubility product and hence they are thrown out as precipitates.
2. If the precipitates formed are soft, loose and slimy, these are known as sludges; while if the precipitate is hard and adhering on the inner walls, it is called as scale.

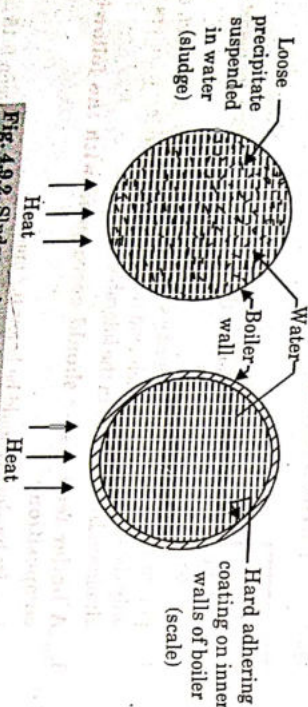


Fig. 4.9.2. Sludge and scale formation in boilers.

Priming and foaming :

1. When steam is produced rapidly in the boilers, some droplets of the liquid water are carried along with the steam. This process of 'wet-steam' formation is called priming.

2. Priming refers to the propulsion of water into the steam drum by extremely rapid, almost explosive boiling of the water at the heating surfaces.
3. Foaming is the formation of small but persistent foam or bubbles at the water surface in boilers, which do not break easily.
4. Foaming is caused by the presence of an oil and alkalis in boiler feed water.
5. Actually oils and alkalis react to form soaps which greatly lower the surface tension of water and thus increase the foaming tendency of the liquid.

Boiler corrosion :

Boiler corrosion is "decay" or "disintegration" of boiler body material either due to chemical or electrochemical reaction with its environment having O_2 , CO_2 and mineral acids.

The disadvantages of corrosion are :

- i. Shortening of boiler life.
- ii. Leakages of the joints and rivets.
- iii. Increased cost of repairs and maintenance.

Corrosion in boilers is due to the following reasons :

Caustic embrittlement :

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of caustic substances. This type of boiler corrosion is caused by the use of highly alkaline water in the high pressure boiler.

Que 4.10. What are the causes and effect of (i) boiler scales (ii) caustic embrittlement?

Answer

Refer Q. 4.9, Page 137H, Unit-4.

UPTU 2011-12, Marks 10

PART-2

Techniques for Water Softening : Lime-Soda, Zeolite, Ion Exchange Resin, Reverse Osmosis.

CONCEPT OUTLINE : PART-2

- Techniques for water softening : It can be done by following methods :
 1. Lime-soda process
 2. Zeolite process

3. Ion exchange process

- **Lime-soda process :** The lime-soda treatment involves the use of lime (calcium hydroxide) and soda (sodium carbonate) to remove hardness from water.
- **Zeolite process :** For the softening of water, the water is percolated through the bed of zeolite packed in a vertical cylinder.
- **Ion exchange process :** It is the process of softening of water by exchanging the harmful ions of water with harmless ions from an ion exchange resin.
- **Reverse osmosis :** In reverse osmosis, the direction of normal osmotic flow of water across the membrane is reversed by applying pressure to the compartment with high concentration.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.11. What do you mean by water softening?

Answer

Water softening :

1. The process whereby we remove or reduce the hardness of water, irrespective of whether it is temporary or permanent is termed as softening of water.
2. It is very essential process since hard water is unsuitable for domestic as well as industrial use.
3. One of the most important applications of water is in steam production for the generation of electricity. For this water need to be fed to industrial boilers.
4. We just cannot feed any water into the industrial boilers because it has been identified that hard water creates large number of problems like scale and sludge formation, priming and foaming etc.
5. The hardness causing salts can be removed from water by following two ways :
 - a. External treatment
 - b. Internal treatment
6. The external treatment of water is carried out before its entry into the boiler.
7. This treatment prevents boiler problems. It can be done by lime-soda, zeolite or ion exchange processes.

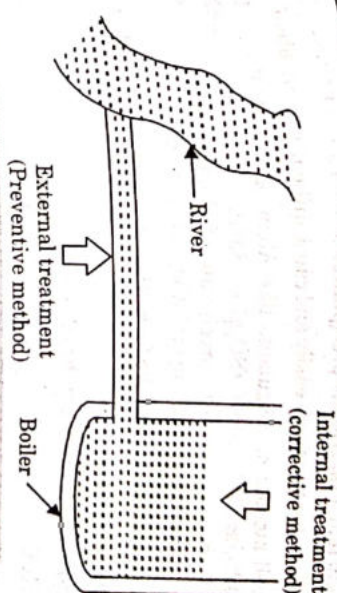
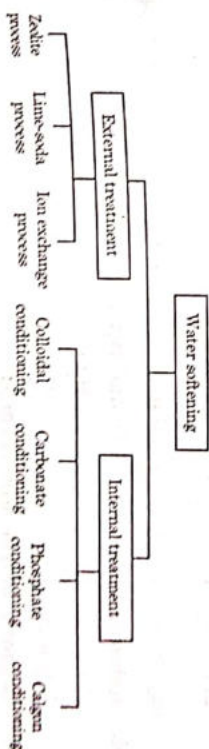


Fig. 4.11.1. Illustration of types of water treatment methods and there point of application.

8. In contrast, the internal treatment of boiler feed water refers to the conditioning of water in the boiler itself by the addition of chemicals.
9. This is essentially a corrective method to remove those salts which are not completely removed by external treatment of water softening.
10. The following conditioning methods are used in the internal treatment : Colloidal, Phosphate, Calgon and Carbonate conditioning.



Que 4.12. Explain the lime-soda process for making soft water from hard water.

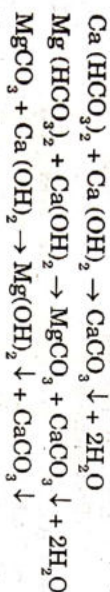
Answer

1. The basic principle of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration.
2. For this purpose, a suspension of milk of lime, Ca(OH)_2 , together with a calculated amount of sodium carbonate, Na_2CO_3 (soda) is added in requisite amount.
3. Proper mixing of the chemicals and water is carried out.
4. Calcium carbonate, CaCO_3 ; magnesium hydroxide, Mg(OH)_2 ; ferric hydroxide, Fe(OH)_3 and aluminium hydroxide, Al(OH)_3 , so precipitates are filtered off.

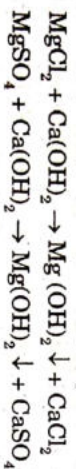
5. At room temperature, the precipitates formed are very fine.
6. They do not settle down easily and cause difficulty in filtration.
7. If small amount of coagulants like Alum [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$], Aluminium sulphate [$Al_2(SO_4)_3$] or Sodium aluminate [$NaAlO_2$] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of $CaCO_3$ and $Mg(OH)_2$.
8. Thus coagulant helps in the formation of coarse precipitate.

Reactions with lime :

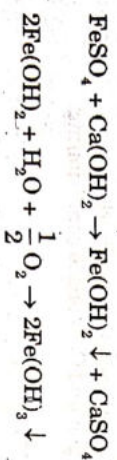
a. Removal of temporary hardness :



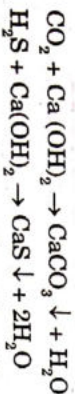
b. Removal of permanent Mg hardness :



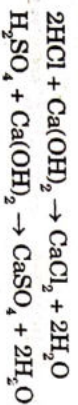
c. Removal of dissolved iron and aluminium salts :



d. Removal of dissolved CO_2 and H_2S :



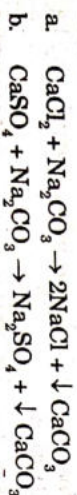
e. Removal of free mineral acids :



f. Reaction with $NaHCO_3$:



Reactions of soda :



It is evident from the above equations that the soluble calcium and magnesium salts are precipitated as insoluble calcium salts and removed by filtration. However, the chemical reactions taking place during lime soda treatment are very slow. Moreover, the precipitates formed are very fine and tend to remain in the solution even after filtration. These may cause troubles by getting deposited on the pipes and boiler tubes later. This problem can be solved by adding coagulants like $Al_2(SO_4)_3$ or $NaAlO_2$ to the treated water.

These coagulants accelerate the coagulation of the fine particles by entrapping them, which subsequently become heavy and settle down.

Advantages of lime-soda process :

The lime-soda process is widely used because of the following advantages :

- i. The process is highly economical.
- ii. The treatment leads to an increase in the pH value of water, thus reducing the corrosion of the distribution pipes.
- iii. This treatment also helps in reducing the total mineral content of water.
- iv. It helps in removing iron and manganese from the water, although to a very small extent.
- v. The increased alkalinity of the treatment water may also help in killing pathogenic bacteria.

Disadvantages of lime-soda process :

There are a few distinct disadvantages of lime-soda process :

- i. A large quantity of sludge is formed in this process, the disposal of which poses a problem. Theoretically each mg/L of calcium hardness removed will produce 1 mg/L of sludge.
- ii. Careful operation and skilled supervision is required to get good results.
- iii. This process cannot produce water having zero hardness. This is because $CaCO_3$ though very slightly, is soluble in water.

Que 4.13: A water sample on analysis gives the following data (in

mg/L):

$Mg(HCO_3)_2 = 73$; $CaSO_4 = 68$;
 $MgCl_2 = 95$; $MgSO_4 = 12$;
 $Ca(HCO_3)_2 = 81$; $NaCl = 4.8$. Calculate the amount of Lime (90 % pure) and Soda (85 % pure) required for softening 20,000 liters of water.

UP T U 2014-15, Marks 05

Answer

$$\text{Lime required} = \frac{74}{100} \left[81 \times \frac{100}{162} + 2 \times 73 \times \frac{100}{146} + 95 \times \frac{100}{95} + 12 \times \frac{100}{120} \right]$$

$$\times \frac{100}{90} \times \frac{20000}{10^6}$$

$$= 4.27 \text{ kg}$$

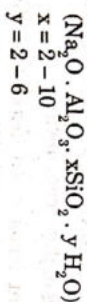
$$\text{Soda required} = \frac{106}{100} \left[68 \times \frac{100}{136} + 95 \times \frac{100}{95} + 12 \times \frac{100}{120} \right] \times \frac{100}{80} \times \frac{20,000}{10^6}$$

$$= 3.99 \text{ kg}$$

Que 4.14: What do you understand by the term zeolite ? Explain the types of zeolite.

Answer

Zeolites are naturally occurring hydrated, sodium aluminosilicate minerals and also known as boiling stone.



Types of zeolites : Zeolites are of two types :

1. **Natural zeolites :** Natural zeolites are non-porous, amorphous and durable.

For example : Natrolite : $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$

2. **Synthetic zeolites :** Synthetic zeolites are porous possess a gel structure and they are prepared by heating together the sodium-carbonate, alumina and silica.

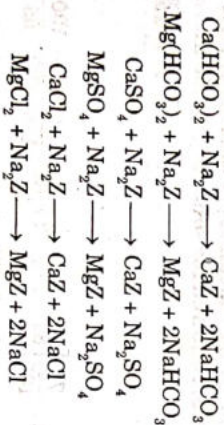
Que 4.15. What is hardness of water ? Describe zeolite process for making soft water from hard water.

UPTU 2013-14, Marks 05

Answer

Hardness of water : Refer Q. 4.1, Page 131H, Unit-4.

1. Zeolites can be represented as Na_2Z , where Z is the insoluble radical framework.
2. When hard water is passed through a bed of active granular Na_2Z , the Ca^{2+} and Mg^{2+} ions of the hard water are exchanged for Na^+ ions of zeolite.
3. The various reactions taking place may be indicated as follows :



4. It is seen from the above reactions that sodium zeolite is converted to calcium and magnesium zeolites.
5. This exchange takes place because the extent of exchange increases with increasing valence of the exchanging ions i.e., monovalent ions are exchanged for divalent ions.

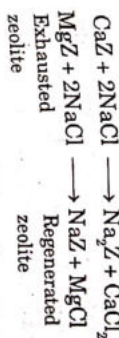
Regeneration :

1. When the zeolite bed gets exhausted i.e., nearly all its Na^+ are exchanged for Ca^{2+} and Mg^{2+} ions, it loses its sodium exchange capacity.

2. The zeolite bed is regenerated by first backwashing it and then by passing a concentrated NaCl solution through it.

3. Though other solutions like NaNO_3 , Na_2SO_4 , KCl etc., can also be used, but brine solution (NaCl solution) is used because it is cheap and also because the products formed by regeneration reactions are CaCl_2 and MgCl_2 which are highly soluble and can be readily rinsed out from the zeolite bed.

4. The following reactions take place during regeneration process :

**Process :**

1. A zeolite softener consists of a steel tank packed with a thick layer of permutit or zeolite.
2. The hard water is percolated at a specified rate through the bed of zeolite.
3. Calcium and magnesium ions present in it are retained by the zeolite in the form of CaZ and MgZ respectively.
4. The outgoing water becomes rich in sodium salts.
5. The softened water is collected from the bottom.
6. When a significant portion of the sodium in the zeolite has been replaced by calcium and magnesium, it is regenerated by first washing it with water by reversing the flow and then treating it with conc. NaCl solution.

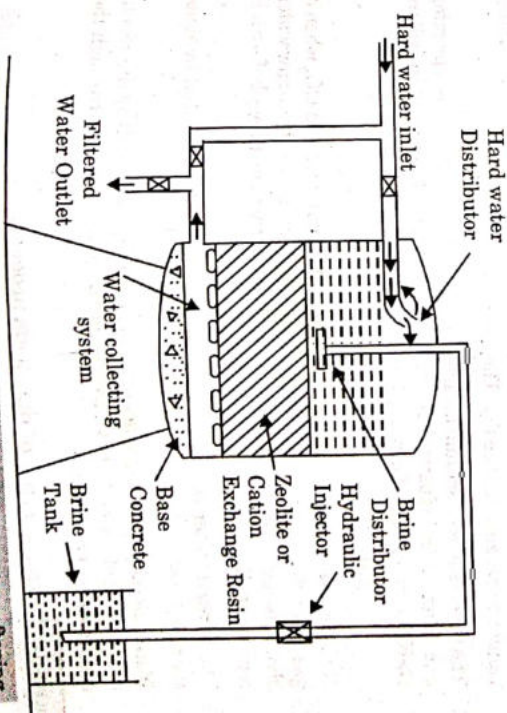


Fig. 4.15.1. Sectional view of Zeolite process for water softening.

7. The soluble CaCl_2 and MgCl_2 so formed in regeneration process are washed with soft water and washings are led to sink.
8. The zeolite bed is ready for use again for softening purpose.
9. Theoretically each mg/L of CaCO_3 hardness requires 1.17 mg/L of NaCl solution.
10. But thrice the amount of theoretically required amount of NaCl is used to make regeneration reaction more efficient.

Advantages of zeolite process :

- i. Water having very low hardness of about 10 ppm hardness is produced. Even water having zero hardness can be produced.
- ii. The plant is compact and occupies less space.
- iii. No sludge is formed and hence there is no problem of sludge disposal.
- iv. The running, maintenance and operation cost is quite less.
- v. The plant can be installed in the water supply line itself, avoiding double pumping.
- vi. It requires less skill for maintenance as well as operation.

Disadvantages of zeolite process :

- i. This process is not suitable for treating highly turbid waters because the turbidity will clog the pores of zeolite bed and thus make zeolite less efficient. Therefore the turbidity must be removed before the water is fed into zeolite.
- ii. Water containing large amounts of Fe and Mn salts when passed through zeolite bed are converted to iron zeolite and manganese zeolite which cannot be regenerated easily. The zeolite is thus wasted.
- iii. The process leaves sodium bicarbonate in water, which causes priming and foaming in industrial or boiler feed waters. Moreover in boilers NaHCO_3 dissociates forming NaOH and CO_2 .
$$\text{NaHCO}_3 \longrightarrow \text{NaOH} + \text{CO}_2$$
- iv. NaOH causes caustic embrittlement of boiler material and CO_2 when it goes with steam renders the water acidic and corrosive. Thus raw water should be subjected to boiling to remove temporary hardness before it is fed into zeolite.
- v. The treated water contains more dissolved salt than treated by lime-soda process.
- vi. Water containing excess of acidity and alkalinity may destroy the zeolite bed. It is preferable to have the pH of the water passing through the zeolite softener around 7.

Que 4.16. Explain types of lime-soda process.

Answer
The lime-soda process can be carried out either in hot or cold.

The lime-soda process :

1. Cold lime-soda process :
In this method, calculated amount of lime and soda are mixed with water at room temperature. There are two types of softeners used for softening water by this process.

a. Intermittent type (batch process) :

- i. Intermittent softener consists of a pair of tanks. Each tank is used in turn for softening of water. Each tank is provided with inlets for raw water and chemicals, outlets for softened water and sludge, and a mechanical stirrer.
- ii. Raw water and the calculated quantities of lime and soda are allowed to run in simultaneously and stirring is started.
- iii. During stirring, some precipitate from the previous treatment is also added in order to form nucleus for the fresh precipitation. By the time tank fills up, the reaction is more or less complete.
- iv. Stirring is stopped and the precipitate formed is allowed to settle down.
- v. At room temperature, the precipitates formed are finely divided, so they do not settle down easily and hence it is essential to add small amounts of coagulants like $\text{Al}_2(\text{SO}_4)_3$, NaAlO_2 , etc.
- vi. The coagulants form gelatinous precipitates of $\text{Al}(\text{OH})_3$ and entraps the fine precipitates.
- vii. Use of sodium aluminate as coagulant also helps the removal of silica as well as oil, if present in water.
- viii. The clear softened water is collected through a pipe and sent to the filtering unit.
- ix. The sludge formed in the tank is removed through the sludge outlet.
- x. When one tank is used for reaction and settling, the other tank supplies soft water.
- xi. Arrangement is such that there is continuous supply of soft water from these tanks.

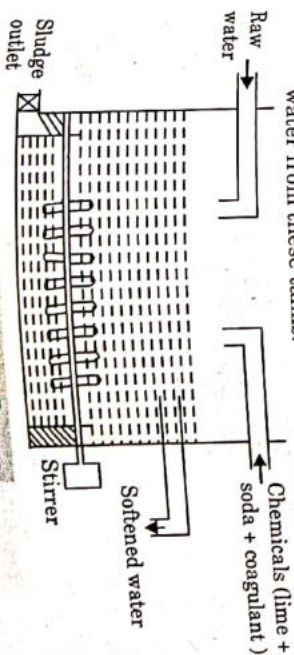


Fig. 4.16.1. Batch Process.

b. Continuous softener :

- i. In continuous softener, there is continuous feed of raw water and chemicals and uninterrupted outflow of soft water is obtained.
- ii. The continuous softener consists of a big steel tank with two chambers.
- iii. The inner chamber is provided with a stirrer, whereas the outer chamber is fitted with a filtering media (usually made of wood fibres).
- iv. Raw water and calculated amount of lime, soda and coagulant are fed through two opposite inlets into the inner chamber at room temperature.
- v. As raw water and chemicals flow down, stirring and mixing takes place.
- vi. Softening of water takes place and the sludge formed settles down at the bottom of the outer chamber.
- vii. The softened water rises upwards, passes through the wood filters to ensure complete removal of sludge.
- viii. Filtered water finally comes out continuously through the outlet provided for the purpose.

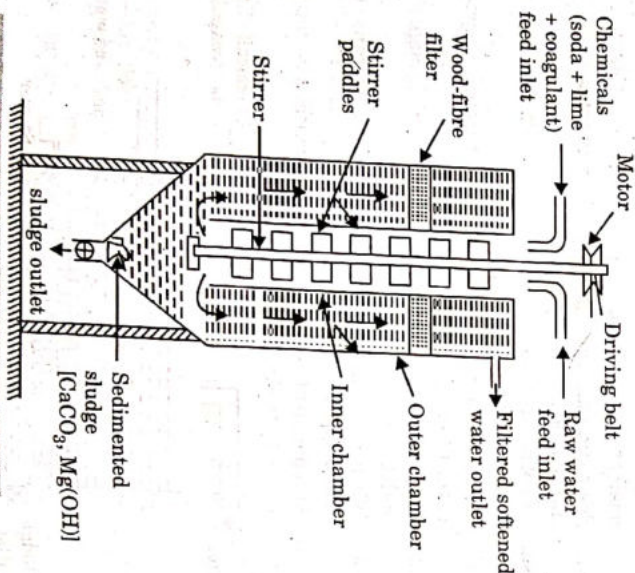


Fig. 4.16.2. Continuous cold lime-soda softener.

Engineering Chemistry**Hot lime-soda process :**

2. This method is exclusively used for the boiler feed waters. This process is much more efficient than cold lime-soda process. The softening reactions are made to occur almost at the boiling point of water. The high temperature :
 - a. increases the rate of precipitation reactions.
 - b. decreases the viscosity of water thereby making settling of the precipitate and filtering easier and rapid.
 - c. eliminates the need of adding coagulants as precipitates settle down quickly.

Two types of softeners are used for hot lime-soda process :

- a. **Intermittent type :** This is exactly similar to what is described under cold lime-soda process. The only difference is that in hot lime-soda process, heating coils are fitted in it for raising the temperature of water.

b. Continuous type :

- i. This type of softening unit consists of three parts-a reaction tank, where raw water, chemicals and steam are mixed, a settling tank, where the precipitates in the form of sludge settle down and a sand filter made up of fine sand and coarse sand, to filter and remove any suspended particle or precipitate.
- ii. Raw water and chemicals are introduced in the settling tank through different inlets.
- iii. A separate opening for steam is also provided which is used to increase the temperature.
- iv. By the time the mixture goes down in the reaction tank, the reaction is complete.
- v. From this tank, the water is fed into settling tank, where sludge settles down.
- vi. Now a days settling tank is combined with reaction tank as shown in Fig. 4.16.3.
- vii. Clear and soft water from the settling tank passes to filter tank where remaining precipitates or suspended particles are removed.

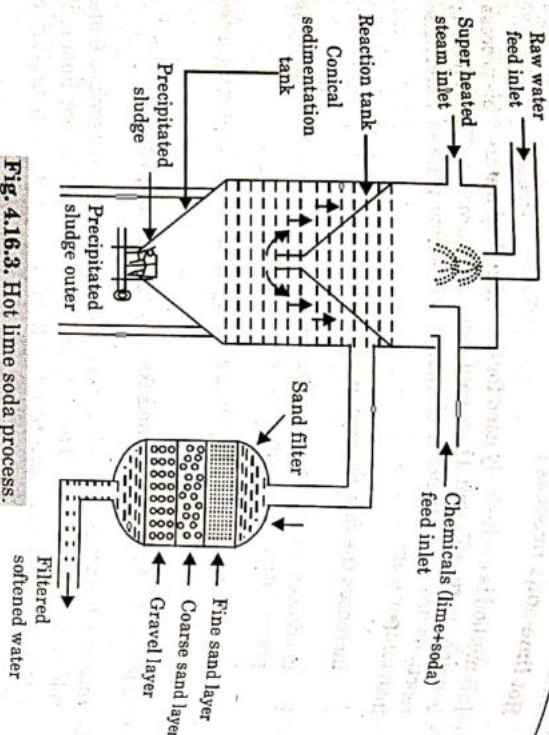


Fig. 4.16.3. Hot lime soda process.

Advantages of hot lime-soda process :

- i. The reaction time is greatly reduced as the precipitation takes place rapidly. It takes about 15 minutes whereas the cold process takes several hours for completion.
- ii. Residual hardness is much less than cold lime-soda process.
- iii. No coagulant is required because the precipitate and sludge formed settle down quickly.
- iv. Most of the dissolved gases like CO_2 and O_2 are also removed.
- v. Less chemicals are required as the softening capacity is high.

Que 4.17. What do you understand by temporary and permanent hardness of water ? Describe the zeolite process for removal of hardness from water. The hardness of 10,000 litres of water sample was removed by passing it through a zeolite softener. The zeolite softener then required 200 litres of sodium chloride solution containing 150 gm/l of NaCl for regeneration. Calculate the hardness of water sample.

UPTU 2014-15, Marks 10

Answer

Temporary and permanent hardness of water : Refer Q. 4.1, Page 131H, Unit-4.

Zeolite process : Refer Q. 4.15, Page 144H, Unit-4.

$$= 150 \text{ gm/L} \times 200 \text{ L} = 30000 \text{ gm of NaCl}$$

$$= 30000 \times \frac{50}{58.5} = \frac{1500000}{58.5} \text{ gm equivalent of } \text{CaCO}_3$$

$$\therefore 10000 \text{ litre of water} = \frac{1500000}{58.5} \text{ gm equivalent of } \text{CaCO}_3$$

$$1 \text{ litre of water} = \frac{1500000 \times 10^3}{58.5 \times 10000} \text{ mg/L } \text{CaCO}_3 \text{ equivalent}$$

$$= 2564 \text{ mg/L of } \text{CaCO}_3 \text{ equivalent}$$

Hence, hardness of water is 2564 ppm.

Que 4.18. Compare lime-soda and zeolite process.

Answer

S.No.	Lime-soda process	Zeolite process
1.	The plant occupies more space.	The plant is compact and occupies less space.
2.	The process requires careful and skilled supervision.	It is automatic and easy to operate.
3.	Turbid water can be treated by this process.	Difficult to treat turbid water as it results in clogging of zeolite.
4.	During the process large quantity of sludge is formed which causes problems of disposal.	No problem of sludge disposal as there is no precipitation taking place.
5.	Operational cost is high as chemicals are consumed in the process.	Exhausted zeolite can be regenerated so operational cost is less.
6.	Involves all the problems related to coagulation, setting, and filtration.	No such treatment is required.
7.	Water of hardness 15-60 ppm can be produced by this process.	Water of very low or zero hardness can be produced by this process.
8.	Treated water contains large amount of Na salts which create problems to be used as feed water to boilers.	Temporary hardness of water sample is completely removed, but NaHCO_3 is present in large amount which is responsible for caustic embrittlement to boilers.
9.	Acidic water can also be treated.	Acidic water cannot be treated by this process as zeolite gets attacked by acidic water.

Que 4.19. What is hardness of water ? Describe ion exchange process for making soft water from hard water.

UPTU 2013-14, Marks 10

OR

What are ion exchange resins ? How will you purify water by using the resins ?

UPTU 2014-15, Marks 10

Answer

Hardness of water : Refer Q. 4.1, Page 131H, Unit-4.

Ion exchange process :

1. Ion exchange resins consist of cross-linked, long chain organic polymers with a microporous structure. The functional groups attached to the polymeric chains are responsible for ion exchange.
2. Resins of suitable chemical compositions and physical properties may be synthesized for specific ion exchange applications. The resins usually consist of styrene-divinylbenzene copolymer. Other polymers like methacrylic acid-divinylbenzene or phenol formaldehyde polymers are also used.
3. The functional groups attached to the resin may be acidic or basic and hence resins can be classified as :
 - a. **Cation exchange resins :**
 - i. Resins containing acidic groups like $-\text{COOH}$ or $-\text{SO}_3\text{H}$ group are termed as cation exchange resins.
 - ii. These are usually styrene divinyl benzene copolymers which on sulphonation or carboxylation become capable of exchanging their H^+ ions with the cations of the solution.
 - iii. A number of synthetic-resin cation exchangers which contain sulphonated phenolic or aromatic hydrocarbons have been prepared.
 - iv. These resins are called H-form cation exchangers.
 - v. It is also possible to convert the H-form cation exchanger to Na-form exchanger by using NaCl.
 - vi. Schematically a cation exchanger can be represented as :

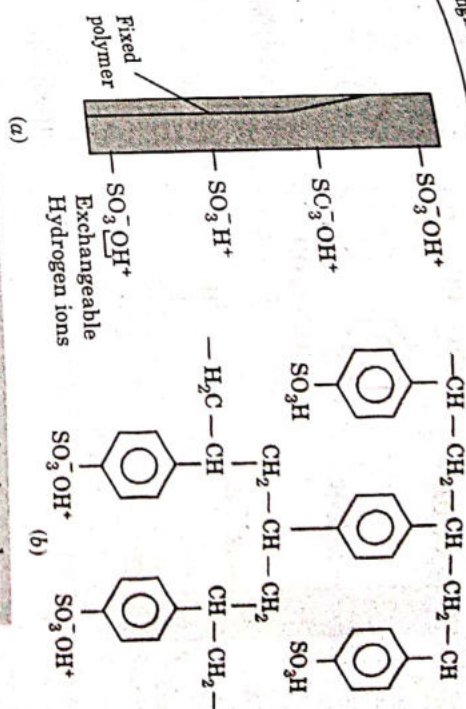
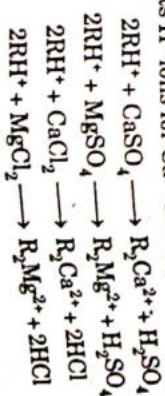


Fig. 4.19.1. Representation of cation exchanger.

- Resins having SO_3H group are termed as strongly acidic resins whereas having $-\text{COOH}$ group are termed as weakly acidic resins.
 - iii. The cation exchange resins can be represented as RH^+ .
 - b. **Anion exchange resins :**
 - i. Resin containing basic functional groups like amine, substituted amine or quaternary ammonium groups as their hydroxide salts is termed as anion exchange resins.
 - ii. There are styrene divinyl benzene complexes which, because of their basic functional groups become capable of exchanging their anions with those present in the solution.
 - iii. Resins having $-\text{NH}_2$, $=\text{NH}$ group are weakly basic whereas those having quaternary ammonium salts are strongly basic.
 - iv. Anion exchange resins are represented as ROH .
- Process :**
1. The ion exchange unit consists of two tanks. Cation exchange resins and anion exchange resins are placed in first and second tank respectively.
 2. First, hard water is made to pass through cation exchange resin which exchanges its H^+ ions for Ca^{2+} and Mg^{2+} ions in water.



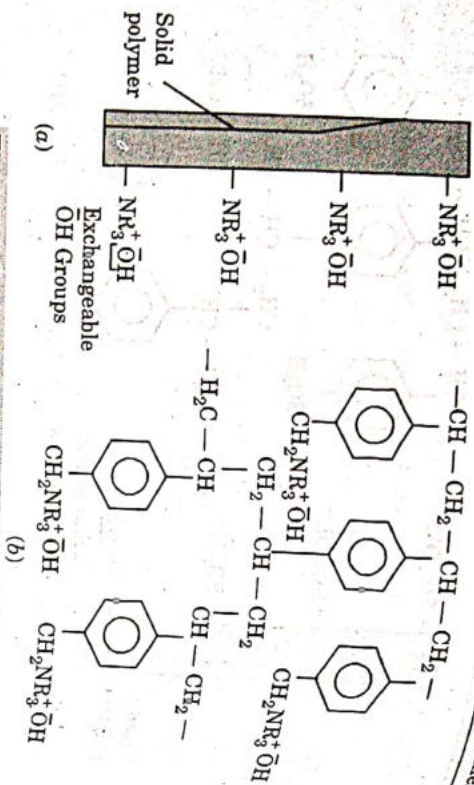


Fig. 4.19.2. Representation of anion exchanger.

- The anions originally associated with Ca^{2+} or Mg^{2+} will be associated with H^+ ions.
- In other words, HCl , H_2SO_4 , H_2CO_3 are formed in amounts equivalent to the anions present in raw water.
- Thus water after passing through cation exchanger is free of Ca^{2+} and Mg^{2+} ions.
- This water is then passed through another column having anion exchange resin.
- Here the anions like SO_4^{2-} , Cl^- etc., present in water are exchanged for OH^- ions of the resin.



- The water coming out of the anion exchanger is completely free from cations and anions responsible for hardness.
- It is known as deionized water or demineralized water. It is as pure as distilled water.
- H^+ released from cation exchanger and $\bar{\text{O}}\text{H}$ released from anion exchanger combine to form unionized water.
- $\text{H}^+ + \bar{\text{O}}\text{H}^- \rightarrow \text{H}_2\text{O}$.

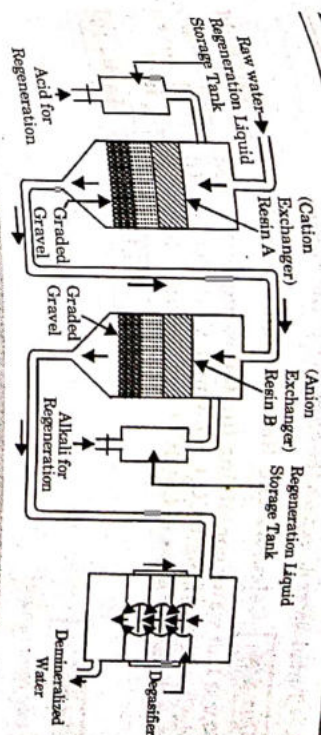


Fig. 4.19.3. Softener for demineralization.

Regeneration :

- After some time the cation and the anion exchangers get exhausted and stop working.
- The cation exchanger is regenerated by first back washing and then passing a 2% H_2SO_4 solution through it. The regeneration reactions can be represented as :

$$\text{R}_2\text{Ca}^{2+} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{RH}^+ + \text{CaSO}_4$$

$$\text{R}_2\text{Mg}^{2+} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{RH}^+ + \text{MgSO}_4$$
 The column is then rinsed with soft water to remove CaSO_4 and MgSO_4 . However if HCl is used for regeneration, MgCl_2 and CaCl_2 are formed.

$$\text{R}_2\text{Ca}^{2+} + 2\text{HCl} \longrightarrow 2\text{RH}^+ + \text{CaCl}_2$$

$$\text{R}_2\text{Mg}^{2+} + 2\text{HCl} \longrightarrow 2\text{RH}^+ + \text{MgCl}_2$$
- HCl is ideally suited for regeneration since CaCl_2 and MgCl_2 are more soluble.
- The anion exchanger is regenerated by back washing and then passing a solution of NaOH . The Na_2SO_4 or NaCl so formed are rinsed with soft water and washing are led to sink.



- The regenerated exchanger is ready for further use.
- Ion exchanger does not remove CO_2 which is removed in degasifier in the deionization process.

Advantages :

- Highly acidic or alkaline water can be softened.
- Water of very low hardness is produced (about 2 ppm).
- Anions as well as cations are removed thereby problems like caustic embrittlement and corrosion are reduced when treated water is used for boiler feed purposes.

Disadvantages :

- The equipments are costly. Moreover costly chemicals are required for regeneration.

- ii. Turbid water decreases the efficiency of the process.

Que 4.20. Calculate the lime and soda needed for softening 50,000 L of water containing the following salts $\text{CaSO}_4 = 13.6 \text{ mg/l}$, $\text{MgCl}_2 = 9.2 \text{ mg/l}$, $\text{Mg}(\text{HCO}_3)_2 = 7.3 \text{ mg/l}$, $\text{Ca}(\text{HCO}_3)_2$ is 16.2 mg/l . Given that the molar mass of $\text{Ca}(\text{HCO}_3)_2$ is 162 and that of MgCl_2 is 95.

UPTU 2014-15, Marks 10

Answer

Lime requirement

$$= 74/100 [16.2 \times 100/162 + 2 \times 7.3 \times 100/146 + 9.5 \times 100/95]$$

$$= 74/100 [10 + 10 + 10] = 22.2 \text{ mg/L}$$

For 50,000L lime required = 1.11 kg

$$\text{Soda requirement} \approx 106/100 [3.6 \times 100/136 + 9.5 \times 100/95]$$

$$= 106/100 [10 + 10]$$

$$= 21.2 \text{ mg/L}$$

For 50,000L soda required = 1.06 kg

Que 4.21. Give comparison between ion exchange, zeolite and lime-soda process.

Answer

S.No.	Characteristic	Ion exchange process	Zeolite process	Lime-soda process
1.	Requirements	Cation and anion exchange	Zeolite	Lime, soda and coagulants
2.	Exchange of ions	Exchange of both cations and anions takes place.	Exchange of only cations takes places.	No exchange of ions.
3.	Capital cost	Very high	High	Low
4.	Operating expenses	High	Low	High
5.	Raw water	(i) Should be non-turbid. (ii) Both acidic or alkaline water can be treated. (iii) Prior knowledge of hardness not required.	(i) Should be non-turbid. (ii) Should not be acidic. (iii) Prior knowledge of hardness not required.	Prior knowledge of hardness is essential.
6.	Automation	Possible	Possible	Not possible
7.	Residual hardness	Least (0-2ppm)	Low (0-15 ppm)	High (15-50 ppm)

Que 4.22. Give an account of reverse osmosis.

OR

UPTU 2012-13, Marks 04
UPTU 2014-15, Marks 05

Explain reverse osmosis process.

Answer

- Reverse osmosis pressurises and passes impure water through a semi-permeable membrane and removes many of the impurities (approximately 90 percent free of mineral and biological contaminants). The quality of the membrane and the pressure of the water help to determine how effectively the water separates the contaminants.
- Reverse osmosis (RO) units remove substantial amount of most inorganic chemicals (such as salts, metals and minerals), micro-organisms and many organic chemicals.
- They do not effectively remove some organic compounds such as nitrate; they will reduce their levels somewhat.
- Reverse osmosis (RO) is a membrane-technology filtration method that removes many types of large molecules and ions from solutions by applying pressure to the solution when it is on one side of a selective membrane.

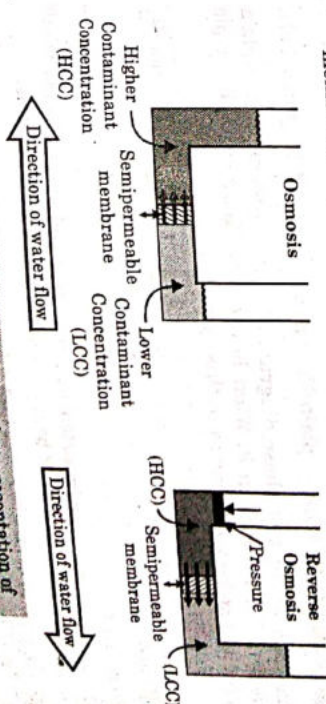


Fig. 4.22.1. Diagrammatic representation of osmosis and reverse osmosis processes.

- f. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side.
- g. To be "selective", this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely.
- h. Reverse osmosis is most commonly known for its use in drinking water purification from seawater, removing the salt and other substances from the water molecules.

PART-3*Phase Rule and its Application to Water System.***CONCEPT OUTLINE : PART-3**

- **Phase rule :** It is an important tool which is used for the quantitative treatment of systems in equilibrium. It helps to predict the specified conditions to exhibit equilibrium. Phase rule is given by J.W. Gibbs in 1876. According to the phase rule, for systems in equilibrium :

$$F = C - P + 2$$

C = Number of components

P = Number of phase

F = Number of degree of freedom

Questions-Answers**Long Answer Type and Medium Answer Type Questions****Que 4.23.**

Define and explain the terms involved in phase rule. Draw a neat labelled phase diagram of water system and explain the areas and curves in it. What is the significance of the triple point and metastable curves in this system?

UPTU 2013-14, Marks 02**Answer****Phase rule :**

1. The phase rule is an important generalization and a versatile tool which is related to the study of behaviour of heterogeneous systems.
2. In general, it may be stated that with the help of phase rule, it has been possible to predict quantitatively the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium by means of a phase diagram.

Phase :

1. A phase is defined as the homogeneous part of the system, which is separated by distinct boundaries and throughout the phase all physical and chemical properties are same.
2. A system may consist only one phase or more than one phase.
3. For example, a water system may consist three phases i.e., solid, liquid and vapour.

Component :

The number of component represent the minimum number of chemical species, may be needed to describe the number concentration of each phase.

1. independent composition of each phase.

$$C = N - E$$

C = Number of component

C = Number of chemical species

N = Number of equilibrium equations

E = Number of water exist in three phases,

For example, water exist in three phases,
Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

2. The composition of each phase can be expressed in terms of H_2O and hence it is one component system.

Degree of freedom :

The number of degree of freedom or variance is defined as the number of independent variables, such as temperatures, pressure and concentration, which must be specified in order to describe the system completely.

2. If a system having degree of freedom 0, 1, 2, 3 then this system is called as invariant, univariant, bivariant and tri-variant respectively.

Advantages of phase rule :

- i. It provides a simple method of classifying equilibrium states of systems such as phases components and degrees of freedom.
- ii. It indicates that different systems having the same number of degrees of freedom behave in like manner.
- iii. It explains the behaviour of systems when allowed to changes in the variables such as pressure temperature and concentration.
- iv. The phase rule is applicable to macroscopic systems. Therefore, it is not compulsory to take into account their molecular structures.
- v. It is applicable to physical as well as chemical equilibria.
- vi. Phase rule predicts that under a given set of conditions :
 - a. Whether various substances would exist together in equilibrium.
 - b. Whether some of the substances would be interconverted.
 - c. Whether some of the substances will completely disappear.

Limitations of phase rule :

- i. As the phase rule is applicable to heterogeneous systems in equilibrium, it is therefore of no use for such systems which are slow in reaching the state of equilibrium.
- ii. As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibrium possible in the system.

- iii. In phase rule the different variables are pressure, temperature and concentration or composition. But phase rule does not consider the other factors like electric and magnetic influences.
- iv. All the phases are required to be present under the same temperature, pressure and gravitational force.
- v. Solid or liquid phases should not be in finely divided form, otherwise vapour pressure may differ from the normal values.
- vi. It does not take into consideration the quality of the phases though it takes into account the number of phases.

Application of phase rule :

1. All the systems are classified on the basis of number of components present.
2. Thus, we may have one, two, three, etc., component systems.
3. The phase rule is perfectly applicable to these systems.
4. The phase diagram is an important medium to clearly indicate the equilibrium conditions between different phases in a system.
5. The phase diagram is helpful for studying and controlling various processes such as phase separation, solidification of metals, the change of structure during heat treatment etc.

Phase diagram of water :

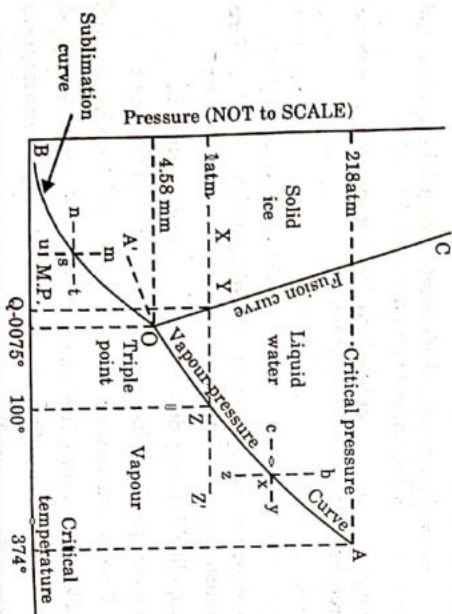


Fig. 4.23.1. The phase diagram for the water system.

1. Under normal conditions the system water is a three phase and one component system.
2. The three phases are liquid, ice and vapour. All these are represented by one chemical entity (H_2O), hence it is one component system.

The three forms of water (ice, water and vapour) constitute the following equilibria:

3. Single phase equilibria:

- i. **Single phase equilibria:**
 - a. Solid (ice) — represented by area BOC.
 - b. Liquid (water) — represented by area AOC.
 - c. Gas (vapour) — represented by area AOB.

ii. Two phase equilibria:

- a. Solid (ice) $\rightleftharpoons$ Liquid (water) — represented by curve OC.
- b. Liquid (water) $\rightleftharpoons$ Gas (water vapour) — represented by curve OA.
- c. Solid (ice) $\rightleftharpoons$ Gas (water vapour) — represented by curve OB.

iii. Three phase equilibria:

Solid (ice) $\rightleftharpoons$ Liquid (water) $\rightleftharpoons$ Gas (vapour) — represented by triple point O.

The phase diagram consists of :

- a. Three areas, BOC, AOC, and AOB.
- b. Three curves, OB, OA and OC.
- c. One triple point, O

The areas :

1. Area BOC represents the solid (ice) phase, which is thermodynamically most stable state under these conditions.
2. Area AOC represents the liquid (water) phase in the system and similarly area AOB represents the gas (vapour) phase in the system.
3. Thus these areas represent one phase equilibria.
4. In order to define the system completely at any point in the area, it is essential to specify both the temperature and pressure.
5. Therefore, areas have two degrees of freedom and are called bivariant systems.
6. It can also be concluded by the phase rule equation :

$$\begin{aligned}
 F &= C - P + 2 \\
 &= 1 - 1 + 2 \\
 &= 2 \text{ (Bivariant system)}
 \end{aligned}$$

The curves :

1. The Curve OC (melting or fusion curve) represents the equilibrium between ice and water (two phase equilibria) and it is known as melting point curve.

2. The very little slope of the curve shows that very high pressure is required to bring about significant changes in melting point of ice.
 3. The Curve OA (Vapour pressure curve) represents the equilibrium between the two phases liquid water and vapour.
 4. Along this curve, water and vapour coexist in equilibrium.
 5. The curve shows the vapour pressure of liquid water at different temperatures.
 6. OA curve is also known as vapour pressure curve of water (l).
 7. This curve terminates at point A. This is the critical point having temperature 374°C and pressure 218 atm.
 8. At this critical point the liquid and vapour are indistinguishable from each other and thus only one phase is left.
 9. Curve OB (sublimation curve) represents the equilibrium between ice and vapour and it is called as sublimation curve of ice.
 10. It shows the vapour pressure of solid ice at different temperatures.
 11. The two phases namely ice and vapour coexists in equilibrium along this curve.
 12. At the lower limit OB curve terminates at absolute (-273°C) where no vapour exists.
 13. Along the curves OC, OA and OB, the number of phases present in equilibrium is two.

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$= 1$$
 14. Hence, system is univariant along the curve.
- Triple point :**
1. The point O where all the three curves OC, OA and OB meet is known as triple point.
 2. At the triple point all the three phases of water system namely solid ice, liquid water, and gas vapour are in equilibrium.
 3. The equilibrium in three phases is attained at .0076°C temperature and 4.58 mm Hg pressure.
 4. Since there are three phases and one component present in the system, the degree of freedom will be,

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$= 0$$
 5. Hence, the system is non-variant. If either the temperature or the pressure or both are changed, the three phases would no longer coexist and at least one of them would disappear.

Engineering Chemistry

Metastable curve OA' :
The dotted curve OA' is the continuation of vapourization curve OA.

1. It is vapour pressure curve of supercooled water.
2. As the water does not always freezes at 0°C, therefore if the vessel containing water and vapour is thoroughly clean and dust free, it is possible to super-cool water several degrees below its freezing point.
3. On slight disturbance, the supercooled water at once changes to ice (solid). This kind of system is a metastable system.

Metastable state :

1. It is the state in which the liquid below its freezing point is in the supercooled state which is not very much stable.

Supercooled liquid $\rightleftharpoons$ Vapour

2. On adding nucleus of ice (stable state), the system reverts to true stable system.

Solid $\rightleftharpoons$ Vapour

Que 4.24. Define the terms : Phase, Components and Degree of freedom. Write the number of components and number of phases and calculate the degree of freedom for the following reactions :



UPTU 2011-12, Marks 10

Answer

Phase, components and degree of freedom : Refer Q. 4.23, Page 163H, Unit-4.

Problem :

$$P = 1$$

$$C = 1$$

$$F + P = C + 2$$

$$F + 1 = 1 + 2$$

$$F = 2$$

Que 4.25. Explain the terms Phase, Component and Degree of freedom. State the phase rule and discuss its application to water, vapour and ice system. Is it possible to have a quadruple point in one component system ?

UPTU 2014-15, Marks 10

Answer

Phase, components and degree of freedom : Refer Q. 4.24, Page 163H, Unit-4.

Phase rule and its application : Refer Q. 4.23, Page 158H, Unit-4.

Problem :

1. No, it is not possible to have a quadruple point on a phase diagram for a one component system.
2. For a quadruple point, the four phases are in equilibrium, therefore, the value of

$$P = 4$$

$$F = C - P + 2$$

$$F = 1 - 4 + 2 = -1$$

3. F can never be a negative value.

Que 4.26. Discuss the application of phase rule to the sulphur system. Draw a labeled diagram.

UPTU 2014-15, Marks 05

Answer

The sulphur system :

It is a one component, four-phase system. The four different phases are :

- i. Rhombic sulphur (S_R)
- ii. Monoclinic Sulphur (S_M)
- iii. Liquid Sulphur (S_L)
- iv. Vapour Sulphur (S_V)

As all the four phases can be represented by only one chemical entity Sulphur (S), it is a one component system.

From the phase rule when $C = 1$,

$$F = C - P + 2$$

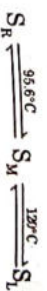
$$= 1 - P + 2$$

$$= 3 - P$$

1. As degree of freedom can not have a minus value, therefore out of four possible phases, only three are present at a time.
2. It is not possible for a single component system to have four phases together at equilibrium.
3. The degree of freedom for different cases will be,
 - when $P = 1$, $F = 3 - P = 3 - 1 = 2$ (bivariant system)
 - $P = 2$, $F = 3 - P = 3 - 2 = 1$ (monovariant system)
 - $P = 3$, $F = 3 - P = 3 - 3 = 0$ (non-variant system)

The two crystalline forms of sulphur are rhombic sulphur and monoclinic sulphur. S_R and S_M exhibit enantiotropy with a transition point at 95.6°C. Below 95.6°C, S_R is stable and above this temperature S_M is the stable variety.

5. Below 95.6°C each form can be gradually transformed to another form and the two forms remain in equilibrium. S_M melts at 120°C
6. At 95.6°C each form can be gradually transformed to another form and the two forms remain in equilibrium. S_M melts at 120°C



Thus,

7. The number of phases at any instant depends upon the temperature-pressure conditions at that instant. The P-T diagram of sulphur system showing various equilibria is given in Fig. 4.26.1.

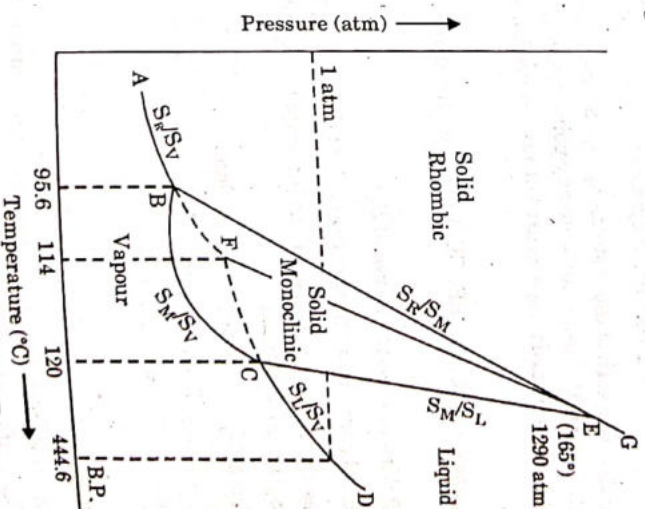


Fig. 4.26.1. Sulphur system

The phase diagram consists of :

- a. Four areas :
 - i. Area ABG (Sulphur rhombic)
 - ii. Area BEC (Sulphur monoclinic)
 - iii. Area GECD (Sulphur liquid)

- iv. Area ABCD (Sulphur vapour)
 b. Six Curves AB, BC, CD, BE, CE, EG
 c. Three triple points B, C and E.

Areas :

1. The phase diagram of sulphur system consists of four areas or regions. Each area represents the single phase system namely, rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour.

2. For each area, $C = 1$ and $P = 1$, and degree of freedom will be,

$$F = C - P + 2$$

$$= 1 - 1 + 2$$

$$= 2 \text{ (Bivariant system)}$$

3. Thus, it is clear that each of the systems S_R , S_M , S_L and S_V are bivariant systems. It means that in order to locate any point in any of these areas, the variables pressure and temperature both is required to be specified.

The curves :

1. The six curves AB, BC, CD, BE, CE, EG divide the diagram into four areas.

2. Curve AB (Vapour Pressure Curve of S_R)

3. Curve AB is the vapour pressure curve of S_R at different temperatures.

4. Along this curve, the two phases rhombic sulphur (S_R) and sulphur vapour (S_V) are in equilibrium.

5. The system S_R/S_V has one degree of freedom.

$$F = C - P + 2$$

$$= 1 - 2 + 2$$

$$= 1$$

Curve BC (Vapour Pressure Curve of S_M) :

1. Curve BC shows the variation of the vapour pressure of monoclinic sulphur (S_M) with temperature.

2. Along this curve S_M and S_V are in equilibrium.

3. The system S_M/S_V is monovariant.

Curve CD (Vapour Pressure Curve of S_L) :

1. Curve CD depicts the variation of the vapour pressure of liquid sulphur (S_L) with temperature.

2. S_L and S_V are in equilibrium along this curve.

The system S_L/S_V is monovariant.

Curve BE (Transition Curve of S_R to S_M) :

3. Curve BE shows the effect of pressure on transition temperature for S_R and S_M . It shows the effect of pressure on transition temperature for S_R and S_M are in equilibrium.

1. Along this curve, the two solid phases S_R and S_M are in equilibrium.

2. The system S_R/S_M is monovariant.

Curve CE (Fusion Curve of S_L) :

3. Curve CE represents the equilibrium between S_M and S_L .

1. Curve CE represents the effect of pressure on the melting point of S_L .

2. It represents the effect of pressure on the melting point of S_L .

3. The system S_M/S_L is monovariant.

Curve EG (Fusion curve of S_R) :

1. The two phases S_R and S_L coexist in equilibrium along this curve. S_R/S_L is monovariant.

Triple point :

1. In the sulphur system there are three triple points B, C and E.

2. All the triple points represent the existence of three phases in equilibrium with each other, therefore,

$$F = C + P + 2$$

$$= 1 - 3 + 2$$

$$= 0$$

The system corresponding to each point is non-variant :

- i. **Triple point B :** At this point the three curves AB, BC and BE meet.

Three phases, S_R , S_M and S_V are in equilibrium at this point B. As, $P = 3$ and $C = 1$, the system is non-variant. At this point B (95.6°C) S_R changes to S_M and the process is reversible.

- ii. **Triple point C :** The three curves BC, CD and CE meet at this point. The three phases S_M , S_L and S_V are in equilibrium at this point. As $P = 3$ and $C = 1$, the system is non-variant. The temperature corresponding to C is 120°C (melting point of S_M).

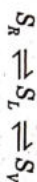
- iii. **Triple point E :** The three curves CE, BE and EG join at this point. The two lines CE and BE have different inclinations away from the pressure axis. The system $S_R/S_M/S_L$ is non-variant at the point E. This point E shows the conditions of existence of the $S_R/S_M/S_L$ at 155°C and 1290 atm pressure.

Metastable equilibria :

1. The transformation of S_R to S_M is a slow process.

2. If enough time is not given for the change and S_R is heated rapidly, it is possible to pass well above the transition point (95.6°C) without obtaining monoclinic sulphur.

3. In that case, there is existence of three phases only.



Que 4.27. Explain why $\text{KCl}-\text{NaCl}-\text{H}_2\text{O}$, should be regarded as a three component system, where as $\text{KCl}-\text{NaBr}-\text{H}_2\text{O}$ should be regarded as a four component system.

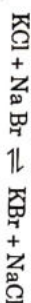
Answer

1. Consider $\text{KCl}-\text{NaCl}-\text{H}_2\text{O}$
2. The number of chemical species are 3, i.e., KCl , NaCl , H_2O and the number of independent equations relating to their concentration is zero.

$$C = N - E$$

$$C = 3 - 0$$

$$C = 3$$
3. Therefore, the number of component is three.
4. Now, consider $\text{KCl}-\text{NaBr}-\text{H}_2\text{O}$
5. The number of chemical species are five i.e., KCl , NaCl , KBr , NaBr , H_2O ($N = 5$) and the number of independent equations relating to these concentrations is one ($E = 1$) i.e.,



$$C = N - E$$

$$= 5 - 1$$

$$= 4$$

6. Therefore, $\text{KCl}-\text{NaCl}-\text{H}_2\text{O}$ is three component system. Whereas $\text{KCl}-\text{NaBr}-\text{H}_2\text{O}$ is a four component system.

Que 4.28. How many components are present in the following systems?

- i. Water $\leftrightarrow$ water vapour
- ii. $\text{Fe}_{(s)} + \text{H}_2\text{O}_{(g)} \leftrightarrow \text{FeO}_{(s)} + \text{H}_{2(g)}$
- iii. $\text{NaCl}_{(s)} \leftrightarrow \text{NaCl}_{(aq)}$

Answer

- i. 1
- ii. 3
- iii. 2

UPTU 2014-15, Marks 05

Que 4.30. What is Gibb's phase rule? Define the term phase, component and degree of freedom. Draw a phase diagram of sulphur system and also give the significance of triple point.

UPTU 2013-14, Marks 10

Answer

Gibb's phase rule: Gibbs phase rule states that if a heterogeneous system is influenced by temperature, pressure and concentration and not by any other action like gravity, electrical, magnetic forces or by surface action, then the sum of number of phases (P) and degrees of freedom (F) is greater than the number of components (C) by two. It is expressed mathematically as follows:

$$P + F = C + 2$$

$$F = C - P + 2$$

or

where, P is the number of phases.

C is the number of degrees of freedom

F is the number of degrees of freedom : Refer Q. 4.23, Page 158H, Phase, component and degree of freedom

Unit-4.
Sulphur system and significance of triple point : Refer Q. 4.26, Page 164H, Unit-4.

Que 4.29. Is it possible to have a quadruple point in a phase diagram for one component system?

Determine the number of degree of freedom on each of the following systems:

- i. Liquid water and water vapour in equilibrium.
- ii. Liquid water and water vapour in equilibrium at a pressure of 1 atm.

UPTU 2011-12, Marks 10

Answer

Quadruple point in a phase diagram for one component system :

Refer Q. 4.25, Page 163H, Unit-4.

- i. Liquid water and water vapour in equilibrium :

Liquid (Water) $\rightleftharpoons$ Water vapour

According to Gibb's formula,

$$F = C - P + 2$$

$$C = 1, P = 2$$

$$F = 1 - 2 + 2 = 1$$

$F = 1$, i.e., one variable temperature or pressure needed to describe the above system.

- ii. Liquid water and water vapour in equilibrium at a pressure of 1 atm :

Liquid (Water) $\rightleftharpoons$ Water vapour at 1 atmospheric pressure

In the above system, the pressure is held constant, the number of degree of freedom reduces by one,

$$F = C - P + 1$$

$$F = 1 - 2 + 1$$

$$F = 0$$

The F value is zero therefore the system under the given conditions is invariant.

Que 4.31. Explain the process of scale and sludge formation in boilers. How can this be prevented? **UPTU 2014-15, Marks 05**

Answer

1. Water is continuously converted into steam results in the concentration of the dissolved impurities until the water becomes saturated.
 2. Then the salts start separating out from the solution in order of their solubility, the least soluble one separates out first.
 3. Some solids separate in the body of the liquid in the form of soft and muddy deposits known as sludges.
 4. And some of the solids deposits on a solid surface to form a sticky and coherent scale.
- Scale and sludges can be prevented by external and internal treatment methods : Refer Q. 4.12, Page 141H and Q. 4.17, Page 150H, Unit-4.

Que 4.32. A water sample having the following data $MgCO_3 = 84 \text{ mg/L}$, $CaCO_3 = 40 \text{ mg/L}$, $CaCl_2 = 5.5 \text{ mg/L}$, $Mg(NO_3)_2 = 37 \text{ mg/L}$, $KCl = 20 \text{ mg/L}$. Calculate the amount of lime (86%) and soda (82% pure) needed for the treatment of 80,000 litres of water.

UPTU 2013-14, Marks 05

Answer

$$Mg(CO_3) = 84 \text{ mg/L } CaCO_3 \\ = 40 \text{ mg/L } CaCl_2 = 5.5 \text{ mg/L}$$

$$Mg(NO_3)_2 = 37 \text{ mg/L } KCl = 20 \text{ mg/L} \\ \text{Vol of water} = 80,000 \text{L, lime} = 86\%, \text{Soda} = 82\%$$

$$\text{Lime required} = \frac{74}{100} (\text{temporary hardness } Ca^{++} + 2 \\ \text{temporary } Mg^{+2}) + \text{permanent } Mg^{+2})$$

$$= \frac{74}{100} \left(\frac{40 \times 100}{100} + 2 \times \left(\frac{84 \times 100}{84} \right) + \left(\frac{37 \times 100}{148} \right) \right) \\ = \frac{74}{100} (40 + 200 + 25) = 196.1 \text{ mg/L}$$

$$\text{Soda required} = \frac{106}{100} (\text{permanent } Ca^{++} + \text{permanent } Mg^{++}) \\ = \frac{106}{100} \left(\frac{5.5 \times 100}{111} + \frac{37 \times 100}{148} \right)$$

$$= \frac{106}{100} (4.95 + 25) = 31.75 \text{ mg/L}$$

$$\text{Amount of lime if } 100\% \text{ pure} \\ 1 \text{ L required} = 196.1 \text{ mg} \\ 80,000 \text{ L required} = 196.1 \times 80,000 \text{ mg}$$

$$\text{if } 86\% \text{ pure} = \frac{196.1 \times 80,000/10^6}{86/100} = 18.24 \text{ kg}$$

$$\text{Amount of soda if } 100\% \text{ pure} \\ 1 \text{ L required} = 31.75 \text{ mg} \\ 80,000 \text{ required} = 31.75 \times 80,000$$

$$\text{if } 82\% \text{ pure} = \frac{31.75 \times 80,000/10^6}{82/100} = 3.097 \text{ kg}$$



UNIT 5

5 UNIT

Fuels and Spectral Techniques

Part-1 (173H - 192H)

- Fuels : Classification of Fuels
- Analysis of Coal
- Determination of Calorific Values (Bomb Calorimeter and Dulong's Method)
- Biogas

A. Concept Outline : Part-1 173H
B. Long and Medium Answer Type Questions 173H

Part-2 (192H - 212H)

- Elementary Ideas and Simple Applications of UV
- Visible
- IR
- ^1H NMR Spectral Techniques

A. Concept Outline : Part-2 192H
B. Long and Medium Answer Type Questions 192H

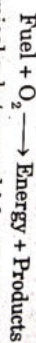
172 (Sem-1 & 2) H

PART-1

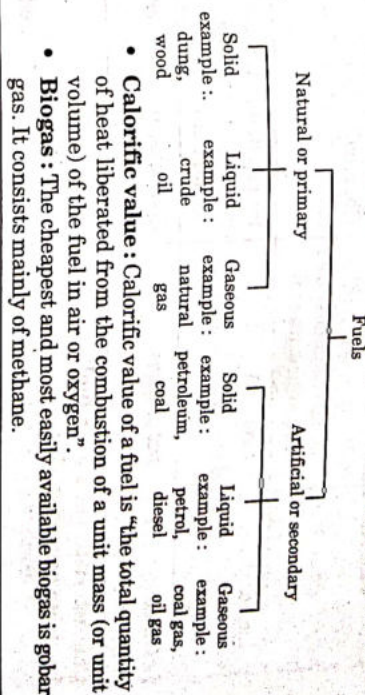
Fuels : Classification of Fuels, Analysis of Coal, Determination of Calorific Values (Bomb Calorimeter and Dulong's Method), Biogas.

CONCEPT OUTLINE : PART-1

- Fuel : Fuel is a combustible substance which may be burnt to supply heat energy without the products of exclusively objectionable by products.



Any chemical substance which produces energy is called fuel.



Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.1. Define fuel. Give its classification and also list the characteristics of a good fuel.

Answer

1. A fuel can be defined as any combustible substance which during combustion gives large amount of industrially and/or domestically useful heat.
2. A chemical fuel can be defined as any combustible substance containing carbon as the main constituent which during combustion gives large amount of industrially and/or domestically useful heat.

Classification : Fuels can be classified :

1. On the basis of their occurrence :

- Natural or primary fuels :** Fuels which are found in nature are called natural fuels, example, wood, coal, peat, petroleum and natural gas.
- Artificial or secondary fuels :** Fuels which are prepared artificially generally from primary fuels are called artificial fuels. Examples of artificial fuels are coke, kerosene oil, petrol, coal gas etc.

- On the basis of physical state of aggregation :** On this basis, there are three types of fuels viz. solid, liquid and gaseous. The important examples of above categories of fuels are tabulated below :

Table 5.1.1. Classifications of chemical fuels

Types of fuel	Natural or Primary	Artificial or Secondary
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, biogas, water gas etc.

Characteristics of a good fuel :

- High calorific value :**
 - Calorific value of a fuel is "the total quantity of heat liberated, from combustion of a unit mass (or volume) of the fuel in air or oxygen."
 - A good fuel should possess high calorific value, since the amount of heat liberated and temperature attained depends upon this property of fuel.
- Moderate ignition temperature :**
 - The lowest temperature to which the fuel must be preheated so that it starts burning smoothly is called ignition temperature.
 - Low ignition temperature (can cause fire hazards) during storage and transport of fuel, on the other hand, fuel with ignition temperature is safe for storage, handling and transport but there might be some difficulty during ignition of fuel.
 - Hence, an ideal fuel should have moderate ignition temperature.
- Low moisture content :** The moisture if present in the fuel reduces its heating value. This ultimately leads to loss of money, because moisture is paid for at the same rate as the fuel. Hence, fuel should have low moisture content.
- Low non-combustible matter content :** The non-combustible matter remains in the form of ash or clinker, after combustion. It also reduces the heating value. There is additional cost of storage, handling and

disposal of the waste involved with it. Hence, a fuel should have low content of non-combustible matter.

5. Moderate rate of combustion :

- If the rate of combustion is low, then a part of the heat liberated may get radiated, instead of raising the temperature. Hence, the required high temperature may not be attained.
- On the other hand, too high combustion rates are also not required because then it gets out of control. For a continuous supply of heat, fuel must burn with a moderate rate.

6. Harmless combustion products :

- They should not pollute the atmosphere by emitting CO , SO_2 , H_2S and other poisonous gases.
- Low cost.
- Easy to transport.
- Low storage cost.
- Controllable combustion so that combustion can be started or stopped when required.
- Uniform size :** In case of solid fuel, the size should be uniform so that combustion is regular.
- A fuel should burn in air with efficiency without much smoke.

Que 5.2. Compare solid, liquid and gaseous fuels.

Answer

Comparison between solid, liquid and gaseous fuels on the basis of their merits and demerits :

S.No.	Solid fuels	Liquid fuels	Gaseous fuels
1.	Transportation is easy.	They can be transported by pipes and tanks.	They can be transported by pipelines only.
2.	Storage is easy.	They must be stored in containers carefully.	They are stored in leak proof tanks.
3.	Cheap and easily available.	Costlier than solid fuels.	Costly.
4.	Slow combustion.	Fast combustion.	Very fast combustion.
5.	High ash content.	Ash is not formed but smoke is produced.	No ash or smoke is produced.
6.	Least calorific value.	High calorific value.	Highest calorific value.
7.	Low risk of fire hazards.	High risk of fire hazards than solid fuels.	High risk of fire hazards than liquid fuels.
8.	Thermal efficiency is low.	High than solid fuels.	High than gaseous fuels.

Que 5.3. Give proximate and ultimate analysis of coal.

Answer

1. Generally, coal is not analyzed by measuring well-defined physico-chemical properties since its composition varies according to the source and age. Mostly consumer-oriented, empirical tests are performed for the sack of comparison and for getting some meaningful insights.

2. In order to ascertain the quality of coal, it is subjected to two types of analysis, viz. proximate and ultimate analysis.

3. Proximate analysis is so called because the data collected vary with the procedure adopted. It gives valuable information about the practical utility of coal. In other words, we can assess the quality of coal by proximate analysis. It includes the determination of moisture, volatile matter, ash and fixed carbon.

3. The ultimate analysis is useful for combustion calculations. It includes the determination of ultimate constituents present in dry coal like Carbon, Hydrogen, Nitrogen, Sulphur, Ash and Oxygen.

1. **Proximate analysis:** This analysis involves following determination:

a. **Moisture content:** The presence of moisture in a coal sample decreases the effective calorific value of coal because when it burns, it takes some of the liberated heat in the form of latent heat of evaporation.

Determination: About 1g of finely powdered and dried sample of coal is taken in a silica crucible and heated in an electric oven for one hour at a temperature 105 – 110°C. Then the crucible is taken out, cooled in a desiccator and weighed. The amount of weight loss is reported as moisture.

$$\% \text{ of moisture} = \frac{\text{loss in weight}}{\text{weight of coal taken}} \times 100$$

b. **Volatile matter:** If coal contains high volatile matter then a large portion of it is left and escapes and burns with smoky flame and has low calorific value.

Determination: The moisture free coal is taken in silica crucible covered with lid and kept in a multiple furnace at 925 ± 25°C for 7 min. Then, crucible is taken out and cooled first in air and then inside the desiccator and weighed again. Loss in weight is reported as volatile matter.

$$\% \text{ of volatile matter} =$$

$$\frac{\text{loss of weight due to removal of volatile matter}}{\text{weight of coal sample taken}} \times 100$$

c. **Ash:** It is a non-combustible matter which left behind when all the combustible substances have been burnt off from coal, which reduces the calorific value.

Determination: It is the weight of residue obtained after burning a weighed amount of dry coal in an open crucible (i.e., in presence of oxygen or air) at 700 – 750° C for half an hour in a muffle furnace. Heating, cooling and weighing is repeated till a constant weight is obtained.

$$\% \text{ of ash} = \frac{\text{Weight of Ash}}{\text{Weight of coal sample taken}} \times 100$$

d. **Fixed carbon:** After the determination of moisture, volatile matter and ash, the remaining material is known as fixed carbon. Higher the % of fixed carbon, greater is the calorific value.

$$\% \text{ of fixed carbon} = 100 - \% \text{ of (moisture + volatile + ash matter)}$$

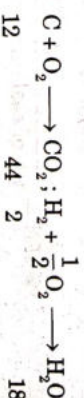
2. **Ultimate analysis:** It includes the exact estimation of carbon, hydrogen, nitrogen, sulphur and oxygen present in fuel.

i. **Determination of C and H:** The amount of C, the major combustible constituent of coal depends on the type of coal and its % increases with rank from lignites to anthracites. Thus, % of C forms the basis of classification of coal.

Greater the % of C and H, better is the coal in quality and calorific value. However, H is mostly associated with the volatile matter and hence, it affects the use to which the coal is put.

Determination: A known quantity of coal (about 1-2 gm) is burnt in a current of dry oxygen when C and H present in coal are oxidized to CO₂ and H₂O respectively.

The gaseous products of combustion are passed through two bulbs. One containing weighed amount of anhydrous CaCl₂ which absorbs water, CaCl₂ + 7 H₂O → CaCl₂ · 7 H₂O and the other containing weighed amount of KOH which absorbs carbon dioxide 2 KOH + CO₂ → K₂CO₃ + H₂O. The weights of CaCl₂ and KOH in the bulbs are then determined. The increase in the weight of CaCl₂ bulb represents the weight of water formed, while the increase in the weight of KOH bulb represents the weight of CO₂ formed.



$$\begin{array}{ccc} 12 & 44 & 2 \\ \text{wt. of Carbon (C)} & & \text{Atm. wt. of C (= 12)} \end{array}$$

$$\frac{\text{wt. of CO}_2 \text{ [= Increase in wt. of KOH tube]}}{\text{wt. of CO}_2 \text{ (= 44)}} = \frac{\text{Mol. wt. of CO}_2 \text{ (= 44)}}{\text{Mol. wt. of C (= 12)}}$$

$$\% C = \frac{\text{wt. of C}}{\text{wt. of coal}} \times 100$$

$$\% \text{ of C} = \frac{\text{Increase in wt. of KOH tube} \times 12}{\text{wt. of coal sample taken} \times 44} \times 100$$

Similar, $\frac{\text{wt. of H}_2\text{O} (= \text{Increase in wt. of CaCl}_2 \text{ tube})}{\text{Mol. wt. of H}_2\text{O} (= 18)}$

$$= \frac{\text{Mol. wt. of H}_2\text{O} (= 18)}{\text{Mol. wt. of H}_2\text{O} (= 18)}$$

$$\% \text{ H} = \frac{\text{wt. of Hydrogen}}{\text{wt. of coal}} \times 100$$

$$\% \text{ of H} = \frac{\text{Increase in wt. of CaCl}_2 \text{ tube} \times 2}{\text{wt. of coal sample taken} \times 18} \times 100$$

ii. **Determination of nitrogen** : Since nitrogen is an inert and incombustible gas, hence its presence is undesirable. Thus, a good quality coal should have very little nitrogen content.

Determination : Nitrogen estimation is carried out by Kjeldahl's method. About 1 gm of accurately weighed powdered coal is heated with conc. H_2SO_4 along with K_2SO_4 and CuSO_4 in a long-necked flask.

2. When clear solution is obtained (i.e., when whole nitrogen is converted into ammonium sulphate) it is treated with excess of NaOH to liberate ammonia.

3. The ammonia thus produced is distilled over and absorbed in a known volume (V_1) of standard H_2SO_4 solution (N/10)



4. The volume of unused H_2SO_4 is then determined by titrating against standard NaOH solution (N/10). Let V_2 mL of 0.1 N NaOH was required to neutralize excess acid.

Thus, the amount of acid neutralized by liberated ammonia (from coal) is determined.

Amount of H_2SO_4 used to neutralize the ammonia evolved,

$$= \text{N}/10 \times V_1 - \text{N}/10 \times V_2 = 0.1 (V_1 - V_2) \text{ millieq.}$$

$$= \frac{0.1 (V_1 - V_2)}{1000} \text{ equivalents}$$

$$\text{wt. of N} = \frac{0.1 (V_1 - V_2)}{1000} \times 14$$

$$\% \text{ of N} = \frac{\text{wt. of coal sample taken (1 gm)}}{\text{wt. of N}} \times 100$$

$$= \frac{0.1 (V_1 - V_2) / 1000}{0.1 (V_1 - V_2) \times 14 \times 100} \times 14 \times 100$$

$$= 0.1 (V_1 - V_2) \times 1.4$$

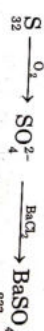
$$\Rightarrow \% \text{ of N} = 0.1 (V_1 - V_2) \times 1.4$$

iii. **Determination of sulphur** : Although sulphur increases the calorific value, on oxidation it produces harmful and corrosion causing SO_2 and SO_3 gases. Oxides of sulphur (formed as combustion products) pollute the atmosphere. S is usually present to the extent of 0.5 to 3% and is

derived from ores like iron pyrites, gypsum, etc. mines along with the coal mines.

Determination : A known amount of coal is burnt completely in bomb calorimeter in a current of oxygen, by which sulphur present in coal is oxidized to sulphates.

The ash from the bomb calorimeter is extracted with dil. hydrochloric acid. The acid extract is then treated with barium chloride solution to precipitate sulphate as BaSO_4 . The ppt. of BaSO_4 is filtered, washed, dried and heated to constant weight.



$$\frac{\text{wt. of S}}{\text{wt. of BaSO}_4} = \frac{\text{atomic wt. of S (32)}}{\text{mol. wt. of BaSO}_4 (233)}$$

Let weight of BaSO_4 precipitate is W_2 gm.

$$\text{Hence, wt. of S} = \frac{32}{233} \times W_2 \text{ gm.}$$

Let wt. of coal taken = W_1 gm

$$\% \text{ of S in coal} = \frac{\text{wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{wt. of coal sample taken in bomb} \times 233}$$

$$\Rightarrow \% \text{ of S in coal} = \frac{W_2}{W_1} \times \frac{32}{233} \times 100$$

iv. **Determination of ash** : Determination is carried out as in proximate analysis.

v. **Determination of oxygen** : Oxygen is present in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than the actual one.

High oxygen content coals have high inherent moisture and low calorific value. An increase in 1% oxygen content decreases the calorific value by about 1.7 %. Thus, a good quality coal should have low % of oxygen.

Determination : It is determined indirectly by deducting the combined % of (C, H, N, S and ash) from 100.

$$\% \text{ of Oxygen} = 100 - \% \text{ of (C + H + N + S + Ash)}$$

Que 5.4. Define calorific value. What are gross and net calorific values ?

UPTU 2014-15, Marks 05

Answer

Calorific value : It is the total amount of heat liberated from the combustion of a unit mass (or volume) of the fuel in air or oxygen.

Higher or Gross calorific value :

1. It is denoted by GCV or HCV.

2. The amount of heat liberated when one unit of fuel is burnt completely and the products of combustion have been cooled at room temperature is termed as gross calorific value of fuel.

3. Because when the calorific value of hydrogen containing fuel is determined, the hydrogen is converted into steam and if products are condensed at room temperature, the latent heat is also included in measured heat which is termed as GCV.

Lower or net calorific value :

1. It is the amount of heat liberated when one unit of fuel is burnt completely and the combustion products are allowed to escape.
2. In this case, water vapours escape as such along with hot combustion gases.

Alternatively, net or lower calorific value (LCV)

$$= \text{HCV} - \text{Latent heat of water vapour formed}$$

Since 1 part by mass of hydrogen produces 9 parts by mass of water.
 $\text{LCV} = \text{HCV} - \text{mass of hydrogen} \times 9 \times \text{Latent heat of steam.}$

The latent heat of steam is 587 kcal/kg or 1,060 B.Th.U./lb of water vapour formed at room temperature (i.e., 15°C).

Units of calorific value :

For solid or liquid fuel : calorie/gram (cal/g) or kilocalorie/kg (kcal/kg);
 British Thermal unit/lb (B.Th.U./lb)

For gaseous fuels : kilocalorie/cubic metre (kcal/m³);
 B.Th.U./Cubic feet (B.Th.U./ft³).

Relation between various units :

$$1 \text{ kcal/kg} = 1.8 \times \text{B.Th.U./lb}; 1 \text{ kcal/m}^3 = 0.1077 \times \text{B.Th.U./ft}^3; 1 \text{ B.Th.U./ft}^3 = 9.3 \text{ kcal/m}^3$$

Que 5.5. With the help of neat sketch, explain construction, principle and working of a bomb calorimeter.

Answer

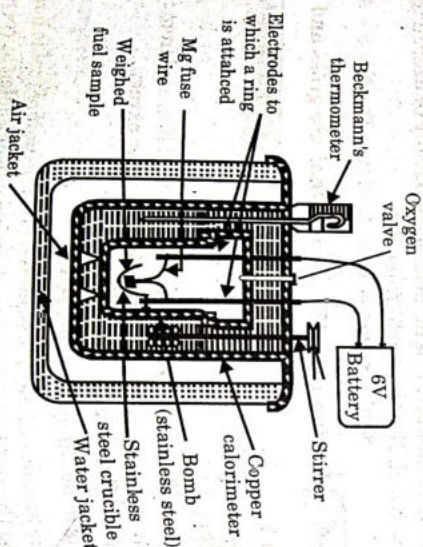


Fig. 5.5.1. Bomb calorimeter.

Principle : A known mass of fuel is burnt and the heat produced is absorbed in water and measured and quantity of heat produced by burning a unit mass of fuel is determined.

Construction :

1. It consists of a strong cylindrical stainless steel bomb capable of with standing high pressure and corrosion resistant.
2. The bomb has lid which can be screwed to the body of bomb to make it perfect seal.
3. The lid contains two stainless steel electrodes and an oxygen inlet valve. A small ring is attached to one of the electrodes which are provided with nickel or stainless steel crucible.
4. The bomb is placed in a copper calorimeter with known weight of water.
5. Calorimeter is surrounded by an air jacket and water jacket to prevent loss of heat.
6. The calorimeter is having an electrical stirrer and Beckmann's thermometer.

Working :

1. A weighed amount (about 0.5 to 1.0 gm) of the given fuel is taken in clean crucible. The crucible is then supported over the ring.
2. A fine Mg wire, touching the fuel sample, is then stretched across the electrodes.
3. The bomb lid is tightly screwed and bomb filled with oxygen to 25-30 atmospheric pressures. The bomb is then lowered into copper calorimeter, containing a known mass of water.
4. The initial temperature of the water is noted after thorough stirring. The electrodes are then connected to 6-volt battery and circuit is then completed.
5. The ignition is initiated by passing a large voltage across a bare fuse wire which has been suitably fixed into the fuel sample.
6. This fixing is normally performed by tying one end of a known mass and length of cotton thread around the fuse and the other and around the sample.
7. The voltage shorts out the fuse which triggers the combustion reaction. The sample burns and heat is liberated which is transferred to water.
8. Uniform stirring of water is continued and the maximum temperature attained is recorded.
9. The calorific value of the fuel can now be calculated as below :

Calculations :

Let x = mass of fuel sample taken in crucible (in gms.) ;

W = mass of water in the calorimeter (in gms.)

w = water equivalent of calorimeter, stirrer,

thermometer, bomb, etc. in gms.

(= wt. of apparatus $\times$ specific heat = $W' \times S$)

T_1 = initial temperature of water in calorimeter ;

T_2 = final temperature of water in calorimeter ;

L = Higher calorific value of fuel (in cal/gm.)

Heat liberated by burning of fuel = $x L$ cal.

and heat absorbed by water, = $(W \times S \times (T_2 - T_1))$

and heat absorbed by apparatus = $(W' \times S \times (T_2 - T_1)) = w (T_2 - T_1)$

since specific heat of water = $1 \frac{\text{cal}}{\text{gm}^\circ\text{C}}$ and $1 \text{ cal} = 4.186 \text{ J}$ or 4.2 J

Hence, total heat absorbed by water, apparatus etc.

$$= [W \times 1 \times (T_2 - T_1) + w \times 1 \times (T_2 - T_1)] = (W + w) \times 1 (T_2 - T_1) \text{ cal}$$

But, heat liberated by the fuel = Heat absorbed by water, apparatus etc.

$$x L = (W + w) (T_2 - T_1) \quad \text{kg} \quad \frac{\text{kcal}}{\text{kg}}$$

or HCV of fuel $(L) = \frac{(W + w)(T_2 - T_1)}{x} \text{ cal/gm or kcal/kg}$

Let H = % of hydrogen in fuel.

$$\text{Then gms of hydrogen present in 1 gm fuel} = 1 \times \frac{H}{100} \text{ gm.}$$

As all fuels contain some hydrogen and when the calorific value of hydrogen containing fuel is determined experimentally, hydrogen is converted into steam according to



i.e., weight of water produced from 1 gm H_2 = 9 gm

Weight of water produced from $\frac{H}{100}$ gm H_2 (or 1 gm fuel) = $9 \times \frac{H}{100}$ gm

= 0.09 H gm

Moreover, Latent heat of steam = 587 cal/gm

$\therefore$ Heat taken by water in forming steam (or Latent heat of water vapour formed),

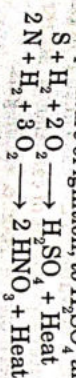
$$= 0.09 H \times 587 \text{ cal}$$

LCV = HCV - Latent heat of water vapour formed
or LCV = (HCV - 0.09 H $\times$ 587) cal/gm

Corrections : To get more accurate results, the following corrections must be considered while calculating the calorific value of a fuel :

i. **Fuse wire correction :** The heat liberated, as measured above, includes the heat given out by ignition of the fuse wire used. Hence, it must be subtracted from the total value.

ii. **Acid correction :** Fuels containing S and N are oxidized, under high pressure and temperature of ignition, to H_2SO_4 and HNO_3 respectively.



iii. **Cooling correction :** Time taken to cool the water in calorimeter from maximum temperature to room temperature is noted. From the rate of cooling (dT/minute) and the actual time taken for cooling (t minutes), the cooling correction of $dT \times t$ is added to the rise in temperature.

iv. **Cotton thread correction :** As cotton thread is used for igniting the fuel, so its burning also generates heat.

$$\text{HCV} = \left\{ (W + w) \left(T_2 - T_1 + \text{Cooling correction} \right) - \left[\begin{array}{l} \text{Fuse wire} \\ \text{correction} \end{array} \right] - \left[\begin{array}{l} \text{Acid} \\ \text{correction} \end{array} \right] + \left[\begin{array}{l} \text{Cotton} \\ \text{thread} \\ \text{correction} \end{array} \right] \right\} \times \frac{1}{\text{Mass of fuel (x)}}$$

Que 5.6. What are the characteristics of a good fuel ?

A sample of coal containing 92% C, 5% H and 3% ash. When this coal tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained :

Weight of coal burnt = 0.95 g
Weight of water taken = 700 g
Water equivalent of calorimeter = 200 g
Rise in temperature = 0.02°C
Fuse wire correction = 10 cal
Acid correction = 60 cal
Calculate the net and gross calorific values of the coal in cal/g.
(Assume the latent heat of condensation of steam is 580 cal/g).

UPTU 2011-12, Marks 10

Answer

Characteristics of a good fuel : Refer Q. 5.1, Page 173H, Unit -5.

$$\text{HCV} = \left\{ (W + w) \left(t_2 - t_1 + \text{cooling correction} \right) - \left[\begin{array}{l} \text{Fuse wire + acid} \\ \text{correction} \end{array} \right] + \left[\begin{array}{l} \text{Cotton thread} \\ \text{correction} \end{array} \right] \right\} \times \frac{1}{0.95}$$

$$\text{HCV} = 7031.578 \text{ cal/g}$$

$$\text{LCV} = 7031.578 - 5 \times 0.09 \times 580$$

$$= 6770.578 \text{ cal/g}$$

Que 5.7.

What is coal ? On what basis the coal should be classified ? 3.25 g of coal was kjeldahlized and NH_3 gas thus evolved was absorbed in 45 ml of 0.1 NH_4SO_4 . To neutralize excess of acid, 11.5 ml of 0.1 NaOH was required. Calculate the % of N in the coal sample.

UPTU 2013-14, Marks 05

Answer**Coal :**

Coal is formed from the fossilized remains of animals and plant. It is mainly composed of C, H, N, O and non-combustible inorganic matter.

There are various types of coal based on carbon content present in it :

Types of coal	Nature	% Carbon	Calorific value (kcal/kg)
Wood	Soft	50	4000 - 4500
Peat	Soft	57	4125 - 5400
Lignite	Soft	67	6500 - 7100
Bituminous	Hard	83	8000 - 8500
Anthracite	Hard	93	8650 - 8700

Numerical :

$$\begin{aligned} \%N &= 0.1 (V_1 - V_2) \times 1.4 N = 0.1 \\ &= \frac{0.1(45 - 11.5) \times 1.4}{3.25} = 1.44\% \end{aligned}$$

Que 5.8 :

A sample of coal was analysed as follows :

Exactly 2.5g was weighed into a silica crucible. After heating for one hour at 110°C, the residue weighed 2.415g. The crucible was then strongly heated for exactly 7 minutes at 950°C. The residue weighed 1.528g. The crucible was then heated until a constant weight was obtained. The last residue was found to be weight 0.245g. Calculate the percentage result of the above analysis.

UPTU 2011-12, Marks 10**Answer :**

$$\begin{aligned} \% \text{ Moisture} &= \frac{2.5 - 2.415}{2.5} \times 100 \\ &= 3.4\% \end{aligned}$$

$$\begin{aligned} \% \text{ Volatile Matter} &= \frac{2.415 - 1.528}{2.5} \times 100 \\ &= 35.48\% \end{aligned}$$

$$\begin{aligned} \% \text{ Ash} &= \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100 \\ &= \frac{0.254}{2.5} \times 100 \end{aligned}$$

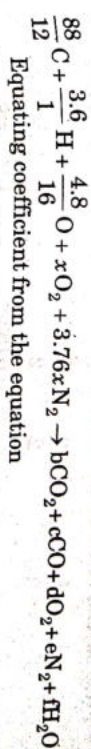
$$\begin{aligned} &= 10.16 \\ \text{Fixed carbon} &= 100 - (3.4 + 35.48 + 10.16) \\ &= 50.96\% \end{aligned}$$

Que 5.9 :

The analysis of the coal in a boiler trial was C = 88%, H = 3.6%, O = 4.8%, other matters 3.6% and the flue gas analysis by volume was CO₂ = 10.9%, CO = 1%, O₂ = 7.1%, N₂ = 81%. Find the proportion of carbon burned to CO and the air required for kg of fuel for the combustion as it actually occurred and also the weight of flue gas per kg of fuel burned.

UPTU 2014-15, Marks 05**Answer :**

Since the fuel analysis is given on mass basis, so let us consider 100 kg of fuel. Let x mole of oxygen are supplied for combustion. The combustion equation on mole basis is given as,



Equating coefficient from the equation

$$\text{Carbon : } \frac{88}{12} = b + c,$$

$$\text{Hydrogen : } \frac{3.6}{1} = 2f$$

$$f = 1.8$$

$$\text{Oxygen : } \frac{4.8}{32} + x = b + \frac{c}{2} + d + \frac{f}{2}; \quad \text{Nitrogen : } 3.76x = e$$

Based on volumetric analysis of dry flue gases,

$$\frac{b}{b + c + d + e} = 0.109 \quad \dots(5.9.1)$$

$$\frac{c}{b + c + d + e} = 0.01 \quad \dots(5.9.2)$$

$$\frac{d}{b + c + d + e} = 0.071 \quad \dots(5.9.3)$$

$$\frac{e}{b + c + d + e} = 0.81 \quad \dots(5.9.4)$$

Dividing eq. (5.9.1) by eq. (5.9.2), we have

$$\frac{b}{c} = \frac{0.109}{0.01} = 10.9$$

$$b = 10.9c$$

$$b + c = \frac{88}{12}$$

$$10.9c + c = \frac{88}{12}$$

$$c = \frac{88}{12 \times 11.9} = 0.61625$$

$$b = 6.7170$$

By eq. (5.9.1) and eq. (5.9.3),

$$\frac{b}{d} = \frac{0.109}{0.071} = 1.55621$$

$$d = 6.7170$$

$$d = 1.53521$$

$$d = 4.375$$

Dividing eq. (5.9.1) by eq. (5.9.4)

$$\frac{b}{e} = \frac{0.109}{0.81} = 0.13456$$

$$e = 6.7170$$

$$e = 0.13456$$

$$e = 49.9153$$

From oxygen balance, we have,

$$\frac{4.8}{32} + x = b + \frac{c}{2} + d + \frac{f}{2}$$

$$x = 6.7170 + \frac{0.61625}{2} + 4.375 + \frac{1.8}{2} - \frac{4.8}{32}$$

$$x = 12.150 \text{ moles}$$

Thus, the mass of oxygen supplied = $12.150 \times 32 = 388.804 \text{ kg}$

The mass of actual air supplied for 100 kg fuel,

$$= \frac{388.804}{232} \times 10^3 = 1675.87 \text{ kg}$$

Therefore, the mass of actual air supplied per kg of fuel,

$$= \frac{1675.873}{100} = 16.75 \text{ kg}$$

Proportion of carbon burned to CO,

$$= \frac{c}{b+c} = \frac{0.61625}{6.717 + 0.61625} = 0.084035 = 8.4035 \%$$

Weight of flue gas 100 kg of fuel burned,

$$= b\text{CO}_2 + c\text{CO} + d\text{O}_2 + e\text{N}_2$$

$$= 6.7170 \times 44 + 0.61625 \times 28 + 4.375 \times 32 + 28 \times 49.9153$$

$$= 1850.4314$$

Weight of the gas per kg of fuel burned,

$$= \frac{1850.4314}{100} = 18.50 \text{ kg}$$

Que 5.10. Calculate the gross and net calorific value of a coal sample containing 84% of carbon, 1.5% sulphur, 6% nitrogen, 5.5% hydrogen and 8.4% oxygen. The calorific values of carbon, hydrogen, sulphur are 8080 kcal/kg, 34500 kcal/kg and 2240 kcal/kg respectively, and latent heat of steam is 587 cal/g.

UPTU 2014-15, Marks 05

Answer

Gross calorific value can be calculated by Dulong's formula,

$$= 1/100[8080(C\%) + 34500(H\% - O\%/8) + 2240(S\%)]$$

$$= 1/100[8080(84) + 34500(5.5 - 8/8) + 2240(1.5)]$$

$$= 8356.05 \text{ kcal/kg}$$

$$\text{NCV} = 8356.05 - 0.09 \times 5.5 \times 587$$

$$= 8065.485 \text{ kcal/kg}$$

Que 5.11.

Calculate the GCV and NCV of coal having the following compositions : C = 85%, H = 7%, S = 1%, N = 2%, ash = 4% and heat capacity of steam = 2458 J/g.

Answer

UPTU 2013-14, Marks 05

By Dulong formula :

$$\text{GCV} = 1/100[8080C + 34500(H - O/8) + 2240S]$$

$$= 1/100[8080 \times 85 + 34500(7 - 1/8) + 2240 \times 1] = 9262.275 \text{ kcal/kg}$$

$$\text{NCV} = \text{GCV} - 0.09 \times H \times \text{latent heat of steam}$$

$$\text{latent heat of steam} = 2458 \text{ J/g} = 2458/4.2 = 585.2 \text{ cal/g}$$

$$\text{NCV} = 9262.275 - 0.09 \times 7 \times 585.2 = 8893.599$$

Que 5.12. A sample of coal contains C = 93%, H = 6% and ash = 1%.

The following data were obtained when the above coal was tested in bomb calorimeter :

1. Wt. of coal burnt = 0.92 g

2. Wt. of water taken = 2200 g

3. Water equivalent of bomb calorimeter = 550 g

4. Rise in temperature = 2.42°C

5. Fuse wire correction = 10.0 cal

6. Acid correction = 50.0 cal

Calculate gross and net calorific values of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Answer

Gross calorific value (GCV)

$$= (W + w)(T_2 - T_1) - (\text{Acid correction} + \text{Fuse wire correction})$$

Given, wt. of coal burnt = $x = 0.92 \text{ gm}$;

Wt. of water taken = $W = 2200 \text{ gm}$;

Water equivalent of bomb calorimeter = $w = 550 \text{ gm}$;

Rise in temperature = $T_2 - T_1 = 2.42^\circ\text{C}$;

Fuse wire correction = 10.0 cal

Acid correction = 50.0 cal

$$\therefore \text{GCV} = \frac{\{2200 + 500(2.42)\} - \{50.0 + 10.0\}}{0.92}$$

$$= 7058.695 \text{ cal/gm} \approx 7058.695 \text{ cal/gm}$$

Now, net calorific value,

$$(\text{NCV}) = \text{GCV} - 0.09 \text{ H} \times 580$$

$$\Rightarrow \text{NCV} = 7058.695 - 0.09 \times 6 \times 580 = 6745.495 \text{ cal/gm.}$$

Que 5.13. 0.72 gm of fuel containing 80 % carbon, when burnt in a bomb calorimeter, increased the temperature of water from 27.3 °C to 29.1 °C. If the calorimeter contains 250 gm of water and its water equivalent is 150 gm, calculate the HCV of fuel.

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Answer

$$x = 0.72 \text{ g}$$

$$t_1 = 27.3^\circ\text{C}$$

$$t_2 = 29.1^\circ\text{C}$$

$$W = 250 \text{ g}$$

$$w = 150 \text{ g}$$

$$\text{HCV} = \frac{(W + w)(t_2 - t_1)}{x}$$

$$= \frac{(250 + 150)(29.1 - 27.3)}{0.72}$$

$$= 1000 \text{ cal/mol}$$

$$= 4200.0 \text{ kJ/kg}$$

Que 5.14. The following data were obtained in a bomb calorimeter experiment.

Weight of coal = 0.85g

Weight of water taken = 750g

Water equivalent of calorimeter = 2000g

Rise in temperature = 0.30 °C

Acid correction = 0.030 °C

If the sample contains 10% H. Calculate net and gross calorific value.

Answer

$$\text{Weight of water (w)} = 750\text{g}$$

$$\text{Water equivalent of Calorimeter (W)} = 2000\text{g}$$

$$\text{Rise in temperature } (t_2 - t_1) = 0.30^\circ\text{C}$$

$$\text{Latent heat of steam} = 587 \text{ cal/g}$$

$$\text{Acid correction } (C_A) = 0.03^\circ\text{C}$$

$$\% \text{ of H} = 10\%$$

$$\text{Mass of fuel (x)} = .85\text{g}$$

$$\text{GCV} = \frac{(W + w)(t_2 - t_1) - (C_A)}{x}$$

$$= \frac{(2000 + 750 \times 30) - (0.030)}{.85}$$

$$\text{GCV} = 970.55 \text{ cal/g}$$

$$\text{HCV} = \text{GCV} - .09 \times \% \text{ of H} \times 587$$

$$= 972.67 - (.09 \times 10 \times 587)$$

$$\text{HCV} = 442.25 \text{ cal/g}$$

Que 5.15. What is dulong formula for calculation of theoretical calorific value of fuel?

Answer

Dulong formula :

The theoretical gross or higher calorific value of a coal sample from ultimate analysis data, can be calculated by dulong formula, on the basis of calorific values of elements ; carbon = 8080 cal/g, hydrogen = 34500 cal/g, and sulphur = 2240 cal/g,

$$\text{GCV in cal/gm} = \frac{1}{100} \left[8080 \text{ C} + 34500 \left(\text{H} - \frac{\text{O}}{8} \right) + 2240 \text{ S} \right] \text{ cal/gm}$$

where C, H, O, S represent the percentages of carbon, hydrogen, oxygen and sulphur respectively in the coal.

Que 5.16. What is biogas ? Discuss the mechanism of biogasification.

UPTU 2013-14, Marks 05

Answer

1. The cheapest and most easily available biogas is gobar gas. It consists mainly of methane. It burns with a blue flame and its average calorific value is about 5300 kcal/m³.

2. The composition of gobar gas is :

Constituent	Methane (CH ₄)	Hydrogen (H ₂)	Carbon dioxide (CO ₂)	Nitrogen (N ₂)
Percentage	55%	7.4%	35%	2.6%

3. Gobar gas is manufactured in gobar gas plant, which consists of :

- A 'well' constructed of masonry work (also known as 'digester'). The digester is usually built below the ground level.
- A 'gas holder' which covers digester and made up of weld steel sheets.
- A 'pipeline', 10 cm in diameter.

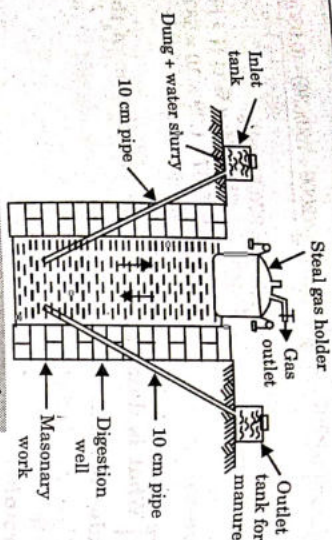


Fig. 5.16.1. Gobar gas plant

Stages involved in production of biogas from cattle dung :

1. Cattle dung in the form of slurry (made by mixing equal parts of water) is poured in digester. Anaerobic bacteria's present in the dung digest this slurry in a process called anaerobic fermentation.
2. The optimum temperature for this fermentation is $34 - 48^\circ\text{C}$. The gas generated, due to continuous decay, is mostly methane and is collected in gas holder.
3. It is interesting to note that in addition to cattle dung gobar gas plant can also digest human refuse, poultry, sweeps etc.

Advantages of biogas :

1. Heat generated by direct burning, 1 kg of dry cattle dung is 23.4 kcal but if the same amount of cattle dung is converted first into gobar gas, [160 l gas per kg dung], it can supply 188 kcal of heat.
2. Gobar gas does not contain poisonous gas, CO as an ingredient.
3. Gobar gas is free from smoke, dust, dirt etc., hence by its use, environment and utensil remain comparatively clean.
4. By producing gobar gas, we in fact are optimally utilizing waste.
5. It can provide the flame temperature of 540°C , with proper burners.

Limitation of biogas : Gobar gas should be used within 10 metres of the gobar gas plant.

Applications biogas :

1. It is used as domestic fuel in many villages.
2. It is also used for lighting and power purposes.
3. Gobar gas also gives simultaneously excellent yield of good manure which has 2% nitrogen content as against 0.75% in farm yard manure.

Que 5.17. What are the essential components of a biogas plant and their function ? List three important application of biogas.

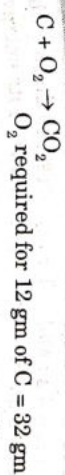
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Answer

Refer Q. 5.16, Page 189H, Unit-5.

Que 5.18. Calculate the weight and volume of air required for combustion of 3 kg of carbon.

UPTU 2011-12, Marks 05

Answer

Weight of oxygen required by 3 kg = $\frac{32}{12} \times 1 \approx 2.67$ kg

Weight of air required = $\frac{100}{23} \times 2.67 = 11.60$ kg

Since 32 gm of oxygen occupies 22.4 litres at NTP

$$34.78 \times 3000 \text{ gm } \text{O}_2 \text{ will occupy } = \frac{100}{23} \times 11.60 \times 3000 = 151304.35 \text{ L}$$

$$\text{Volume of air required} = \frac{100}{21} \times 151304.35 = 720496.90 \text{ L}$$

Que 5.19. What are the characteristics of a good fuel ? List the raw materials which can be utilized for biogas manufacture ? Explain the stages involved in production of biogas from cattle dung.

UPTU 2014-15, Marks 05

Answer

Characteristics of a good fuel : Refer Q. 5.1, Page 173H, Unit - 5.
Biogas : Refer Q. 5.16, Page 189H, Unit - 5.

Que 5.20. What is biomass ?

Answer

1. Biomass is the waste materials of living organisms and plants or living objects like plants and animals.
2. It contains carbon compounds and works as a source of heat energy for domestic purpose.
3. Example : wood, cattle dung, rice barn, bagasses, paddy husk.

4. It can be used directly or is converted into fuel.
5. Wood can be converted into a better fuel called biogas. can be converted into much better fuel called biogas.
6. The energy of biomass can be considered to be another form of indirect use of solar energy as biomass is obtained through the process of photosynthesis.

PART-2

Elementary Ideas and Simple Applications of UV, Visible, IR and ¹H NMR Spectral Techniques.

CONCEPT OUTLINE : PART-2

- **Spectroscopic analysis :** Molecular spectroscopy deals with the transitions that a molecule undergoes between its energy levels after absorption of suitable electromagnetic radiations determined by quantum selection rules.
- **Electromagnetic radiations :** The ordinary white light is the most familiar form of electromagnetic radiation.
- **UV spectroscopy :** It involves the promotion of electrons from ground state to the higher energy state.
- **IR spectroscopy :** IR spectroscopy is used for the identification of functional group of chemical compound.
- **NMR spectroscopy :** NMR spectroscopy involves absorption of electromagnetic radiation in the radio frequency region.

Questions-Answers**Long Answer Type and Medium Answer Type Questions**

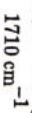
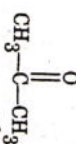
Que 5.21. Define electronic spectroscopy. Explain

Answer

1. It involves the transitions of electron(s) within a molecule or ion from a lower to a higher electronic energy level or vice-versa by the absorption or emission of radiations falling in the UV-visible range of electromagnetic spectrum.
2. While electronic spectra in the visible range span (12,500 - 25,000) cm⁻¹, those in the UV region span (25,000 - 72,000) cm⁻¹.
3. An important principle for the interpretation of electronic spectra was given by Franck and Condon.

Answer**Finger print region :**

1. In this region, numerous peaks are observed and the pattern is complex, due to interacting vibrational modes.
2. A peak to peak match of an unknown spectrum with the spectrum of suspected compound in this region helps to assign its structure.
3. This portion of spectrum is extremely important when it is examined with reference to other regions.
4. Example, if alcoholic or phenolic OH stretching absorption appears in high frequency region and there is an absorption band in 1260-1000 cm⁻¹, due to C - C - O bonding then it makes possible to assign O - H absorption to alcohol or phenol with highly specific structure of compound.

Numerical :

Que 5.40. What is shielding and deshielding?

UPTU 2013-14, Marks 05

Answer

Refer 5.32, Page 203H, Unit-5.

Que 5.41. Write the basic principle of NMR and explain the following terms :

- i. Chemical shift

- ii. Spin-spin splitting

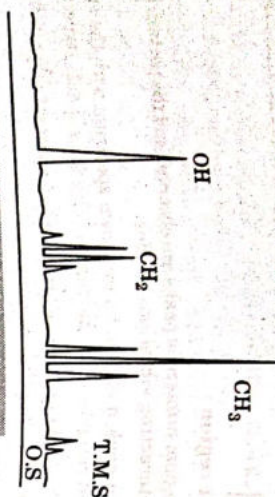
UPTU 2012-13, Marks 06

Answer

Principle of NMR : Refer Q. 5.33, Page 205H, Unit-5.

- i. **Chemical shift :** Refer Q. 5.32, Page 203H, Unit-5.

- ii. **Spin-spin splitting :** An NMR spectrum shows a signals for each kind of proton in a molecule. Generally these signals are splitted by spin-spin coupling. Splitting reflex the environment of the absorbing proton with respect to near by proton. Splitting arises because of a coupling interaction between the neighbouring proton and is related to the number of possible spin orientation that these neighbours can adopt. This is known as (n + 1) rule.

Fig. 5.13.1. δ values (Chemical shift).

Que 5.43. An organic compound C_9H_8O contains a carbonyl group $C=O$. How will its NMR spectrum decide whether it is an aldehyde or ketone?

UPTU 2012-13, Marks 06

Answer C_9H_8O : For aldehyde CH_3CH_2CHO

Signals: a, b, c

Splitting pattern:

a = Triplet

b = Quartet

c = Triplet

For Ketone: CH_3COCH_3

Signals: a,

Splitting pattern: a = singlet

Que 5.43. Discuss the significance of following in relation to IR spectroscopy:

UPTU 2012-13, Marks 06

i. Group frequency region

ii. Fingerprint region.

Answer

i. Group frequency region appears in between 400–1400 cm⁻¹. The patterns of bands in this region are typical of functional present in an organic compound.

ii. Fingerprint region: Refer Q. 5.39, Page 208H, Unit - 5.

Que 5.44. Briefly discuss the structural information obtainable from IR, UV and proton-NMR data.

UPTU 2012-13, Marks 04

Answer

Structural information obtained from:

IR:

1. It can reveal functional groups of a compound.
2. Substitution of aromatic ring.
3. Geometrical configuration isomers (cis and trans).

UV:

1. Extend of conjugation.
2. Substitution of a ring.
3. Value of λ_{max} of a given compound.
4. Presence of chromophore in the group.

NMR:

1. It can predict different protonic environment.
2. It can tell chain length of compound.
3. It tells functional group of system.
4. Can differentiate aromatic system.

Que 5.45. A gaseous hydrocarbon 'A' on passing through a quartz tube heated at 600°C, gave a liquid compound 'B' (molecular weight 78 amu). The latter compound was found to undergo electrophilic substitution reactions. It gave the following data on analysis: The IR spectrum showed a characteristic absorption band at 3040 cm⁻¹ and a UV absorption at 204 nm due to $\pi \rightarrow \pi^*$ transition. The ¹H-NMR spectrum displayed a downfield singlet (6H) at 7.3 τ . Identify the compound A and B and give your reasoning.

UPTU 2012-13, Marks 08

Answer

1. A characteristic absorption band at 3040 cm⁻¹ in the IR spectrum indicates the presence of aromatic C-H bonds in 'B'.
2. A UV absorption, due to $\pi \rightarrow \pi^*$ transition, at 204 nm ($\log \epsilon$ 3.84) indicate the presence of conjugation in 'B'.
3. The ¹H-NMR spectrum of 'B' displaying a downfield singlet at 7.3 τ due to six equivalent protons.
4. It seems that compound 'B' is aromatic having six equivalent protons.
5. Its molecular weight is 78 amu so the compound 'B' is benzene (C₆H₆).
6. It is known that benzene is formed by trimerisation of acetylene, when later is passed through a quartz tube heated at 600°C.
7. Thus, compound 'A' must be acetylene (C₂H₂).

Que 5.46. How many proton signals would you expect in the NMR spectra's of the following compounds ; Cyclobutane and 2-Chloropropane ?

UPTU 2011-12, Marks 05

Answer

Cyclobutane : In cyclobutane, $\begin{array}{cc} \text{CH}_2 & - & \text{CH}_2 \\ | & & | \\ \text{CH}_2 & & \text{CH}_2 \end{array}$ all the hydrogen atoms are

equivalent, only one NMR signal will be observed.

2 - Chloropropane : Refer Q. 5.38, Page 208H, Unit - 5.

Que 5.47. Define chemical shift. What is its significance in the determination of the structure of molecules ?

Two isomers A and B of the molecular formula ($\text{C}_3\text{H}_6\text{O}$) give an IR absorption band at 1650 cm^{-1} and 1710 cm^{-1} respectively. Assign structural formulas to A and B isomers.

UPTU 2011-12, Marks 10

Answer

Chemical shift : Refer Q. 5.32, Page 203H, Unit - 5.

Numerical : Probable isomer structure are,

$\text{CH}_3 - \text{CH}_2 - \text{CHO}$ $\text{CH}_3 - \text{CO} - \text{CH}_3$ $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{OH}$ and cyclopropanol
 1710 cm^{-1} corresponds to ketone group, hence acetone confirmed for compound A = $\text{CH}_3 - \text{CO} - \text{CH}_3$

Allyl alcohol will give band at 1650 cm^{-1} hence B is allyl alcohol

B = $\text{CH}_3 - \text{CH}_2 - \text{CHO}$



SHORT ANSWER QUESTIONS ALL UNITS

1

UNIT

Molecular Orbital Theory

(2 Marks Questions)

Memory Based Questions

1.1. Distinguish between order and molecularity of reaction.

Ans:

S. No.	Molecularity of reaction	Order of reaction
1.	It is the number of reacting species undergoing simultaneous collision in reaction.	It is sum of the power of concentration terms in rate law expression.
2.	It is a theoretical concept.	It is determined experimentally.
3.	It can have integral value only.	It can have fractional value also.
4.	It cannot be zero.	It can be zero.
5.	It does not tell us anything about the mechanism of reaction.	It tells us about the slowest step in mechanism and hence gives some clue about mechanism of reaction.
6.	It does not change with change in temperature and pressure.	It changes with change in temperature and pressure.

1.2. What is the effect of temperature on the conductivity of metals and semimetals?

Ans: With increase in temperature, the conductivity of metals decreases and that of semimetals increases.

1.3. Define hybridization.

Ans: The mixing or redistribution of one or more orbitals of the outermost energy level of an atom to give new orbitals of equivalent energy is

known as hybridization. The newly formed orbitals are termed as hybrid orbitals.

1.4. Why is geometry of NH_3 pyramidal?

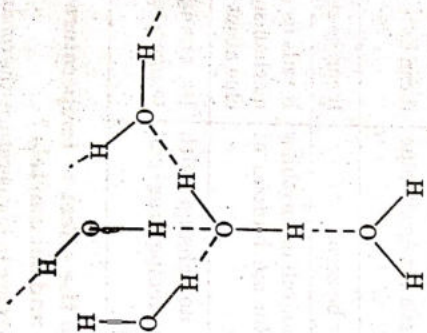
Ans. The central N-atom in NH_3 is surrounded by four electron pairs, so its geometry should be tetrahedral. However, one of the four electron pairs is a lone pair, therefore, the geometry becomes pyramidal.

1.5. Why is sigma-bond stronger than a pi-bond?

Ans. Orbitals can overlap to a greater extent in a sigma-bond, due to their axial orientation, so sigma-bond is quite strong. On the other hand, in a pi-bond, sideways overlapping of orbitals takes place. The sideways overlapping is not to an appreciable extent, due to the already present sigma-bond, which restricts the distance between the involved atoms. Hence, sigma-bond is much stronger than a pi-bond.

1.6. Ice has lower density than water. Why?

Ans. When ice is formed from liquid water, the water molecules arranged themselves in tetrahedral open cage like structure and some air gap is formed so the volume of ice is greater than water hence density is less that is why ice floats on water. When ice melts up to 4°C , density increases. Above 4°C , volume increases hence density decreases.



1.7. What are the shortcomings or drawbacks of valence bond theory in the case of coordination compounds?

Ans. The valence bond theory was fairly successful in explaining the geometry qualitatively and magnetic behaviour of the complexes. But, it could not explain the following:

- The origin of their absorption spectra could not be explained.

ii. Why did different complexes of the same metal show different colours.

iii. Relative stabilities of different complexes could not be explained.

iv. Why should certain ligands form high spin, while others low spin complexes.

1.8. Explain why metals are malleable and ductile.

Ans. Metals can be beaten into thin sheets and can drawn into thin wires, when shear stress is applied on metals the position of positive atomic cores altered without destroying the structure of crystal and relative position of atoms does not change. The layers of kernels get shifted from one part to another but the environment does not change as delocalised electrons are present everywhere.

1.9. On the basis of MO theory, explain why hydrogen forms diatomic molecule while helium remains monoatomic.

Ans. For hydrogen molecule : Refer Q. 1.2, Page 7H, Unit-1.
For helium molecule : Refer Q. 1.4, Page 9H, Unit-1.

1.10. What is metallic luster.

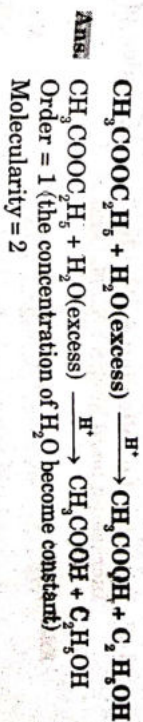
Ans. Metallic luster : Metals are having well definite layered structure. When light strikes on metal surface, the electron between the layers gets excited and when they come back to its original state, the light gets emitted in the form of luster.

Application Based Questions

1.11. On the basis of molecular orbital theory, explain why F_2 is diamagnetic while O_2 is paramagnetic? Calculate their bond orders.

Ans. Refer Q. 1.9, Page 17H, Unit-1.

1.12. Calculate the order and molecularity of the following reaction :



1.13. CaCl_2 will introduce Schottky defect when added to AgCl crystal. Explain.

Ans. CaCl_2 on adding to AgCl introduces impurity defect. The addition of one Ca^{++} ion will replace two Ag^+ ions to maintain electrical conductivity. One of the position of Ag^+ will be occupied by Ca^{++} ion and other will be left as a hole. Thus, the hole is created similar to Schottky defect.

- 1.14. Zinc oxide is white but it turns yellow on heating. Explain.
Ans When ZnO is heated, it loses oxygen as :



The Zn^{++} ions are entrapped in the interstitial sites and electrons are entrapped in the neighbouring interstitial sites to maintain electrical neutrality. This results in metal excess defect. Due to the presence of electrons in the interstitial void, the colour is yellow.

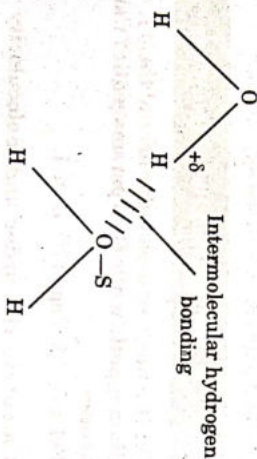
- 1.15. Arrange the covalent bonds $sp^3 - sp^3$, $sp^2 - sp^2$ and $sp - sp$ in increasing order of strength, giving reason.

Ans $sp^3 - sp^3 < sp^2 - sp^2 < sp - sp$.

Reason : The higher the percentage of s-character, the higher is the bond strength. Percentage of s-character is sp , sp^2 and sp^3 are 50, 33.33, 25 respectively.

- 1.16. Explain H_2O is liquid but H_2S is a gas.

Ans H_2O is liquid because it has hydrogen bonding in it by which all the molecules of water gets associated with each other and the density becomes high. While H_2S molecule does not have hydrogen bonding in it, so the density of H_2S is low than density of H_2O . So, H_2O exists as liquid while H_2S as a gas.



- 1.17. Arrange the following molecules/ions in order of their increasing bond length: N_2 , N_2^- and N_2^{2-} .

Ans N_2 : $\text{B.O} = \frac{1}{2} (10 - 4) = 3$

N_2^- : $\text{B.O} = \frac{1}{2} (10 - 5) = 2.5$

N_2^{2-} : $\text{B.O} = \frac{1}{2} (10 - 6) = 2$



Polymers and Organometallics (2 Marks Questions)

Memory Based Questions

- 2.1. Why all simple organic compounds cannot act as monomer during polymerization process ?

Ans Because, for a substance to act as a monomer, it must be at least bifunctional. Thus, organic compounds like (i) Acetic acid (CH_3COOH), (ii) Benzoic acid ($\text{C}_6\text{H}_5 - \text{COOH}$), (iii) Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$), (iv) Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$), (v) Aniline ($\text{C}_6\text{H}_5\text{NH}_2$), (vi) Methyl isocyanate (CH_3NCO) etc. [which have only one functional group present per molecule] cannot act as monomer since they are monofunctional.

- 2.2. Why low density and high density polythene differ in density ?

Ans High density polythene (HDPE) possesses linear unbranched chains. Thus, these chains can be easily packed to form a solid with high density.

Low density polythene (LDPE) possesses several short and long branches which prevent close packing. Thus, LDPE forms a solid with low density.

- 2.3. What is the main purpose of vulcanization ?

Ans Added sulphur combines chemically at the double bonds of different rubber chains, thereby making the product stiff.

- 2.4. Why are plastics indispensable in everyday life ?

Ans Plastics are indispensable due to properties like :

- Light in weight
- Corrosion resistance
- Low fabrication cost
- Good thermal and electrical insulation properties
- Easy and quick moulding etc.

2.5. Why is teflon highly chemical resistant ?

Ans. Due to presence of most electronegative element, F in teflon, there are very strong attractive forces between its different chains. Hence, it possesses extremely high chemical resistance towards most chemicals.

2.6. Why is PVC used in chemical industries ?

Ans. This is because :

- Maintenance of cost of PVC is low.
- High resistance towards chemicals.
- PVC can be processed in any form, even by hot welding.

2.7. Distinguish between homopolymers and copolymers.

Ans.

S.No.	Homopolymer	Copolymer
1.	Only one type of monomer when get polymerized result in homopolymers.	Two or more than two types of monomers results in copolymers.
2.	It is formed by addition polymerization. Example, Polyethylene, PVC.	It can be formed by addition polymerization. Example, NBR, SBR.

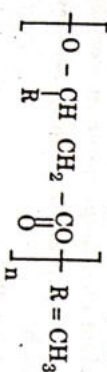
2.8. What is the primary structural feature necessary for a molecule to make it useful in a condensation polymerization reaction ?

Ans. The monomers must be bifunctional, i.e., contains two functional groups.

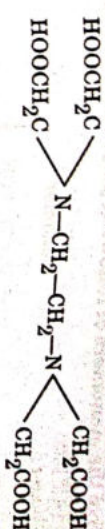
2.9. What is a biodegradable polymer ? Give an example of biodegradable polymer.

Ans. The polymers which are degraded by micro-organisms with in a suitable period so that the polymers and their degraded products do not cause any serious effects on the environment are called biodegradable polymers.

Example : Poly (β -hydroxy butyrate-CO- β hydroxyvalerate) PHBV

**2.10. What is EDTA ? Give its chemical formula.**

Ans. EDTA is a hexadentate ligand and it forms a stable complex with metal ions with its 6 donor sites.
Structure of EDTA :

**2.11. Why can human beings digest starch but cannot digest cellulose although both are made up of D-(+)-Glucose ?**

Ans. Starch ($\text{C}_6\text{H}_{10}\text{O}_5$) is a biodegradable polymer and can degrade in the presence of micro-organisms so can be digestible while cellulose is not a degradable polymer.

2.12. Give two examples of initiators used for free radical polymerization.

Ans. i. Benzoyl peroxide

ii. AIBN (Azobis Iso Butyro Nitrile)

Application Based Questions**2.13. 42 gm of propene was polymerized by radical polymerization process and $\overline{\text{DP}}$ was found to be 1000. Calculate the number of molecules of PP produced.**

Ans. As $\overline{\text{DP}}$ of PP = $\frac{\text{Numbers of Propene molecules}}{\text{Number of PP molecules formed}}$

Hence, number of PP molecules formed

$$= \frac{\text{Numbers of propene molecules}}{\overline{\text{DP of PP}}} = \frac{42 \text{ gm} \times (6.023 \times 10^{23} \text{ molecules/42 gm})}{1000} = 6.023 \times 10^{20} \text{ molecules.}$$

Evaluation Based Questions**2.14. Ethelene polymerises but ethane does not. Why ?**

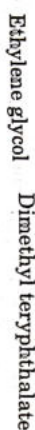
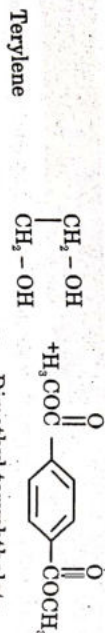
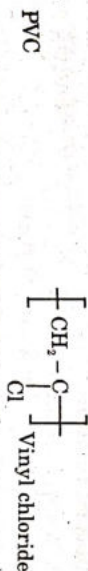
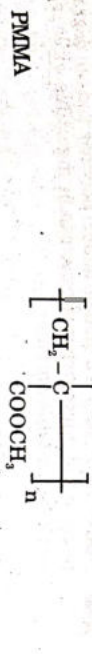
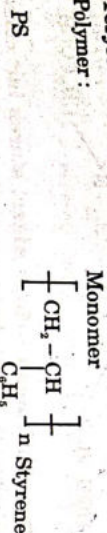
Ans. Ethane can not polymerize because it does not have a property to show functionality. Bonds are not available for combination in ethane while they are available in ethelene.

**2.15. Classify the following as addition and condensation polymers.**

Ans. Terylene, Bakelite, PVC, PE
Terylene and Bakelite : Condensation polymers
PVC & PE : Addition polymers

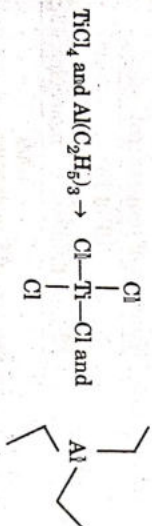
2.16. Give the monomers of following polymers PS, PMMA, PVC, Terylene.

Ans: Polymer:



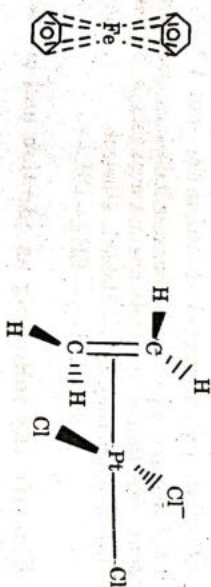
2.17. Write down the structure of Ziegler Natta catalyst.

Ans: It is a combination of transition metal halide (like TiCl_4 or TiCl_3) with an organometallic compound (like triethyl aluminium, trimethyl aluminium).



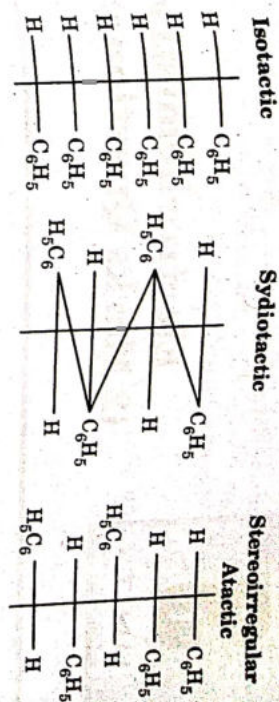
2.18. Write down the structure of Ferrocene and Zeise's salt.

Ans: Ferrocene



2.19. Write the monomers of BUNA-S and Polystyrene.

Ans: BUNA-S: Refer Q. 2.16, Page 73H, Unit-2.
Polystyrene: This question is out of syllabus.



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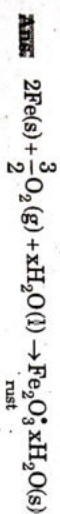
3

UNIT

Electrochemistry (2 Marks Questions)

Memory Based Questions

3.1. Give the reaction of rust formation.



3.2. Give some example of differential metal corrosion

- Ans**
1. Buried iron pipeline connected to Zn bar.
 2. Steel pipe connected to copper plumbing.
 3. Zinc coating on mild steel.
 4. Lead-tin solder around copper wires.

3.3. How does corrosion get effected with temperature ?

Ans The rate of any chemical reaction increases with rise in temperature. Increase in temperature increases the conductance of the medium, reduces passivity of the metal, and thus increases rate of reaction.

3.4. Compare dry and wet process in the preparation of cement.

S.No.	Dry Process	Wet Process
i.	Used when raw material is hard.	Used for all types of raw material.
ii.	Process is slow.	Process is fast.
iii.	Fuel consumption is low.	Fuel consumption is high.
iv.	Inferior quality cement is formed.	Superior quality cement is formed.

3.5. What is the role of Gypsum ?

Ans Gypsum plays a very important role in controlling the rate of hardening of the cement and is added to regulate the process of setting. In the absence of Gypsum, cement would set immediately on mixing with water.

3.6. What are the different functions of lubricant ?

- Ans**
1. To keep moving parts apart.
 2. To reduce friction.
 3. To protect against wear.
 4. To transfer heat.

3.7. Explain why iron is corroded while gold does not.

Ans Iron oxidises in the presence of oxygen and the layer formed is porous in nature and further corrosion occurs while in case of gold, oxidation occurs at primary level, the layer formed is unstable and corrosion is prevented.

3.8. Write the chemical composition of Portland cement.

Ans Refer Q. 3.25, Page 112H, Unit-3.

3.9. What is plaster of paris ? Give reaction for its preparation.

Ans Refer Q. 3.31, Page 118H, Unit-3.

3.10. Why is a block of magnesium attached through an insulated metallic wire to the hull of the ship ?

Ans A block of magnesium is attached through an insulated metallic wire to the hull of the ship because magnesium shows sacrificial anode protection. Mg becomes anode, shows oxidation, gets corroded while ship made up of iron becomes cathode and is protected from corrosion.

3.11. Why ferrous ammonium sulphate is used instead of ferrous sulphate in redox titration ?

Ans Hydrated ferrous ammonium sulphate is used because it is more stable than ferrous sulphate, which oxidises and produces Fe^{+2} ions before the reaction. While ferrous ammonium sulphate is stable enough to produce Fe^{+2} ions at the time of reaction.





Water Treatment (2 Marks Questions)

Memory Based Questions

- 4.1. Why is demineralisation process preferred over zeolite process for softening of water for use in boilers ?

OR

Why is water softened by zeolite process unfit for use in boilers ?

Ans. Because zeolite softened water contains large quantities of sodium salts like NaCl , Na_2SO_4 etc., which can lead to caustic embrittlement.

- 4.2. Write a short note on water quality parameters.

Ans. The quality of water can be decided with the help of certain parameters named as water quality parameters. These are : Colour, pH, Electrical conductivity, Turbidity, Suspended solids, Acidity, Alkalinity, Chlorides, Hardness, Sulphates, Dissolved oxygen, BOD, COD, Residual chloride, Chloride demand, Iron, Nitrogen and Phosphorus compounds, Fluoride and MPN (which indicates bacterial density).

- 4.3. What are the different impurities present in water ?

Ans. The impurities present in water are :

- Biological impurities
- Suspended impurities
- Colloidal impurities
- Dissolved impurities

- 4.4. Define permanent hardness.

Ans. The hardness due to the presence of chlorides and sulphates of Ca and Mg in water is termed as permanent hardness.

- 4.5. What are the different units of hardness ?

Ans. The different units are :

- i. Parts per million (ppm)
- ii. Milligrams per litre (mg/l)
- iii. Degree Clarke ($^{\circ}\text{Cl}$)
- iv. Degree French ($^{\circ}\text{Fr}$).

4.6. Discuss the problems created by hard water in boiler. A sample of hard water has hardness 500 ppm. Express the hardness in $^{\circ}\text{French}$ and $^{\circ}\text{Clark}$.

Ans. Any natural source of water can not provide perfect boiler feed water. In boilers, water boils regularly so it evaporates hence concentration of dissolved salt increases. The two major problems created by hard water in boiler are :

1. **Sludge** : It is a loose, soft and slimy precipitate formed in the boiler.
2. **Scale** : It is hard deposits which stick very firmly to the inner surfaces of the boiler.

$$\text{Hardness} = 500 \text{ ppm}$$

$$1 \text{ ppm} = 0.1^{\circ}\text{Fr} = 0.07^{\circ}\text{Cl}$$

$$\begin{aligned} \text{Hardness in French} &= 500 \times 0.1 \\ &= 50^{\circ}\text{Fr} \end{aligned}$$

$$\begin{aligned} \text{Hardness in Clark} &= 500 \times 0.07 \\ &= 35^{\circ}\text{Cl} \end{aligned}$$

4.7. What is total hardness ?

Ans. The sum of temporary and permanent hardness is termed as total hardness. This hardness is caused due to the presence of CO_3^{2-} , HCO_3^{-} , Cl^{-} , SO_4^{2-} of Ca and Mg.

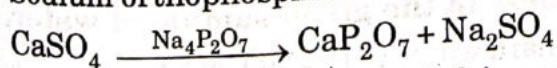
4.8. What are the main boiler troubles ?

Ans. The main boiler troubles are :

- i. Scale and sludge
- ii. Priming and foaming
- iii. Caustic embrittlement
- iv. Boiler corrosion

4.9. Define phosphate treatment.

Ans. Sodium orthophosphate may be added to the boiler water.



Calcium orthophosphate (loose sludge)

4.10. What are the applications of phase rule ?

- Ans.**
1. It applies to physical as well as chemical phase reactions.
 2. It applies to macroscopic systems.
 3. It helps in predicting the behaviour of a system under different conditions of the governing variables.

4.11. What are different phases in sulphur system that exist in equilibrium?

Ans.

The following four phase exist in equilibrium :

- i. Rhombic Sulphur (S_R)
- ii. Monoclinic Sulphur (S_M)
- iii. Liquid Sulphur (S_L)
- iv. Sulphur Vapour (S_V)

4.12. Define the following terms :

i. Water recovery

Ans. Water recovery projects can provide additional water for productive and environmental purposes. The volumes of water saved are in addition to water provided for water users and the environment through the rules in the water sharing plans. Water recovery can be achieved through investing in infrastructure to achieve greater efficiency and through the purchase of water licenses.

ii. Solute rejection

Ans. i. Solutes retained by the membrane :

Lower solubility in water or diffuse more slowly through the membrane

C_p = concentration of solute i in permeate

C_r = concentration of solute i in retentate

ii. Ranges : 1 - 0

When $r_i = 0$, the membrane is completely permeable.

When $r_i = 1$, the membrane is completely impermeable.

4.13. Why the zeolite softener is not recommended for obtaining feed water for high pressure boiler?

Ans.

Zeolites process cannot remove acidic ions like HCO_3^- and CO_3^{--} if water is used in high pressure boilers for steam generation. $NaHCO_3$ if present in water sample liberates CO_2 and causes corrosion.

Application Based Questions

4.14. Standard hard water contains 15 g of $CaCO_3$ per litre. 10 ml of this required 50 ml of EDTA solution. Calculate the temporary hardness in the given sample of water.

Ans.

1 L of standard hard water = 15 g of $CaCO_3$

50 ml of EDTA solution = $15 \times 10^3 \text{ mg/l } CaCO_3$

= 10 ml of the standard hard water

= $10 \times 15 \text{ mg } CaCO_3$

10 ml of the standard hard water = $10 \times 15 / 50 = 3 \text{ mg } CaCO_3$

10 ml of the standard hard water = 50 ml of EDTA solution

1 ml of the standard hard water = $3 \times 50 \text{ mg } CaCO_3$

1 L of standard hard water = $3 \times 50 / 10 = 15 \text{ mg } CaCO_3$

1 L of standard hard water = 15000 ppm

4.15. An exhausted zeolite softener was regenerated by passing 150 litres of NaCl solution, having strength 150 g/litre of NaCl. How many litres of hard water sample having a 600 ppm can be softened using this softener?

Ans.

150 L of NaCl contains = $150 \times (150 \text{ g/L})$ of NaCl

= 22500 gm of NaCl

= $22500 \times \frac{100}{117} \text{ } CaCO_3 \text{ eq.}$

= $1.932 \times 10^6 \text{ gm } CaCO_3 \text{ eq.}$

= $1.932 \times 10^7 \text{ mg } CaCO_3 \text{ eq.}$

The number of litres of hard water = $\frac{1.932 \times 10^7}{600} = 32.2 \text{ litres.}$

4.16. Calculate the degree of freedom at triple point in water system.

Ans. Refer Q. 4.23, Page 158H, Unit-4.

4.17. A sample of water contains 40.5 mg/L $Ca(HCO_3)_2$, 13.6 mg/L $CaSO_4$, 46.5 mg/L of $Mg(HCO_3)_2$, and 27.6 mg/L of $MgSO_4$. Calculate the temporary hardness in the given water sample.

Ans.

$Ca(HCO_3)_2$ $\frac{100}{162} = 25 \text{ mg/L}$

$CaSO_4$ 13.6

$Mg(HCO_3)_2$ $46.5 \times \frac{100}{146} = 31.84 \text{ mg/L}$

$MgSO_4$ 27.6

Temporary hardness = $25 + 31.84 = 56.84 \text{ mg/L or ppm}$





Fuels and Spectral Techniques

(2 Marks Questions)

Memory Based Questions

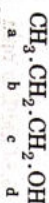
5.1. Give one advantage of NMR spectroscopy over conventional chemical analysis.

Ans. NMR spectroscopy is non destructive technique. Sample is recovered as such after investigation because this technique does not damage the solution.

5.2. Define chemical shift. Show the expected NMR signals and their splitting in the following compounds :



Ans. Chemical shift : The shifts in the position of NMR absorptions which arises due to the shielding or deshielding of protons by the electrons are called chemical shifts.



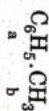
Numbers of signals and splitting

a = Triplet

b = Sextet

c = Triplet

d = Singlet



a = Singlet

b = Singlet

5.3. What is Beer Lambert law in UV-VIS absorption spectroscopy ? A compound having concentration 10^{-3} g/l resulted absorbance value 0.20 at λ_{max} 510 nm using 1.0 cm cell. Calculate its absorptivity and molar absorptivity values. Molecular weight of compound is 500.

Ans. Beer-Lambert law : The intensity of beam of monochromatic radiation decreases exponentially with increase in thickness (l) and concentration of the absorbing medium.

$$\log \frac{I_0}{I} = \epsilon c l \text{ or } A = \epsilon c l$$

where, A or $\log \frac{I_0}{I}$ = Absorbance of the solution

I_0 = Intensity of incident light

I = Intensity of transmitted light

c = concentration

l = length of sample tube

ϵ = absorptivity coefficient

$$\log \frac{I_0}{I} = A = \epsilon \times c \times l$$

Given :

$$l = 1.0 \text{ cm}$$

$$c = 10^{-3} \text{ g/l}$$

$$A = 0.20$$

$$A = \epsilon \cdot c \cdot l$$

$$0.20 = \epsilon \times 1 \times 10^{-3}$$

$$\epsilon = \frac{0.20}{10^{-3} \times 100} = \frac{20}{21^{-1}} = 20 \times 10$$

$$\text{Absorptivity} = 200$$

$$\text{moles} = \frac{\text{wt. in gm/mol}}{\text{wt.}} = \frac{10^{-3}}{500}$$

$$= 2 \times 10^{-6}$$

$$A = \epsilon \cdot x \cdot C$$

$$\text{Molar absorptivity, } \epsilon = \frac{A}{x \cdot C} = \frac{0.20}{1 \times 2 \times 10^{-6}} = 100000$$

5.4. What is the basic difference between adsorption and partition chromatography ?

Ans.

S.No.	Adsorption chromatography	Partition chromatography
1.	Simple technique.	Complex technique.
2.	Large amount of samples can be separated.	Less suitable for large amount of sample.
3.	Less useful for the separation of homogeneous series.	Used for the separation of homologous series.

5.5. What is the use of value of R_f ?

Ans. R_f is used for the identification of compounds since the value of R_f is constant for a compound with a particular solvent at a particular temperature.

5.6. What are the characteristics of a good fuel ?

Ans. A sample of coal containing 92% C, 5% H and 3% ash. When this coal was tested in the laboratory for its calorific value in a bomb calorimeter, the following data were obtained :

Weight of coal burnt	= 0.95g
Weight of water taken	= 700 g
Water equivalent of calorimeter	= 2000 g
Rise in temperature	= 0.02 °C
Fuse wire correction	= 10 cal
Acid correction	= 60 cal

Calculate the net and gross calorific value of the coal in cal/g (Assume the latent heat of condensation of steam is 580 cal/g).

Ans. Characteristics of a good fuel: Refer Q. 5.1, Page 173H, Unit-5.

$$\text{HCV} = \frac{\left\{ (W + w)(t_2 - t_1 + \text{Cooling Correction}) - \left[\begin{array}{l} \text{Fuse wire + Acid} \\ \text{Correction correction} \end{array} \right] \right\} \times 0.95}{[(2000 + 700)(2.48 + 0.02)] - [10 + 60]}$$

$$\text{HCV} = 7031.578 \text{ cal/g}$$

$$= 7031.578 - 5 \times 0.09 \times 580$$

$$= 6670.578 \text{ cal/g}$$

5.7. Define calorific value.

Ans. The calorific value of a fuel is defined as the amount of heat obtainable by the complete combustion of a unit mass of the fuel.

5.8. What are the different units of calorific value ?

Ans. Different calorific value are :

1 cal/g = 1k cal/kg = 1.8 B. Th. U./lb

1 kcal/m³ = 0.1077 B. Th. U./ft³

1 B. Th. U./ft³ = 9.3 kcal/m³

5.9. What are the various forms of coal ?

Wood	50
Peat	57
Lignite	67
Sub bituminous	77
Bituminous	83
Anthracite	93

5.10. Define the terms chromophore and auxochrome.

Ans. Refer Q. 5.23, Page 194H, Unit-5.

5.11. Explain why value of NCV is greater than GCV.

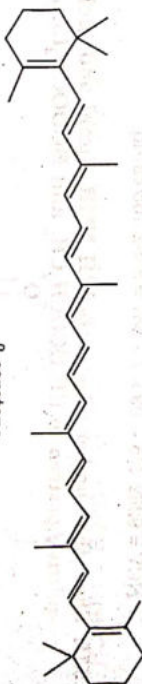
Ans. The G.C.V. is of only theoretical importance because in actual practice, we do not have any provision of cooling the products of combustion during combustion of a fuel in an engine, furnace or any other fuel burning device and the product gases leave with some heat.

A fuel containing hydrogen produces water. on combustion. Out of the total heat produced in combustion of the fuel, the water takes away a considerable portion of the heat for evaporation and actually less heat is available for heating.

There is no any furnace, engine or device designed to collect the heat being taken away by the water vapours. Therefore practically we get lower calorific value than the theoretically expected.

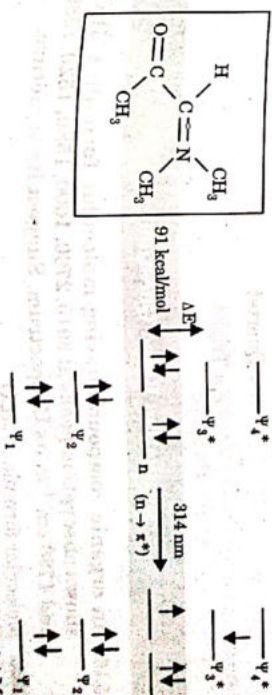
5.12. Why β -carotene absorbs light in visible region ?

Ans. Beta-carotene, with its system of 11 conjugated double bonds, absorbs light with wavelengths in the blue region of the visible spectrum while allowing other visible wavelengths, mainly those in the red-yellow region to be transmitted. This is why carrots are orange.



β -carotene

The conjugated π system in 4-methyl-3-penten-2-one gives rise to strong UV absorbance at 236 nm due to a $\pi - \pi^*$ transition. However, this molecule also absorbs at 314 nm. This second absorbance is due to the transition of a non-bonding (lone pair) electron on the oxygen up to a π^* antibonding MO.



This is referred to as an $n - \pi^*$ transition. The nonbonding (n) MOs are higher in energy than the highest bonding p orbitals, so the energy gap for an $n - \pi^*$ transition is smaller than that of a $\pi - \pi^*$

transition and thus the $n-\pi^*$ peak is at a longer wavelength. In general, $n-\pi^*$ transitions are weaker (less light absorbed) than those due to $\pi-\pi^*$ transitions.

Application Based Questions

5.13. 3.25 gram of coal was Kjeldahlized and NH_3 gas thus evolved was absorbed in 45 ml of 0.1 N H_2SO_4 . To neutralise excess acid, 11.5 ml of 0.1 N NaOH was required.

Determine the percentage of nitrogen in the coal sample.

$$\begin{aligned} \%N &= 0.1 (V_2 - V_1) \times 1.4 N = 0.1 \\ &= \frac{0.1(45 - 11.5) \times 1.4}{3.25} = 1.44\% \end{aligned}$$

5.14. Calculate the GCV of coal having the following composition C = 85%, S = 1%, N = 2% and ash = 4% (Latent heat of water vapour = 587 cal/gm).

Ans.

By Dulong formula :

$$\text{GCV} = \frac{1}{100} [8080C + 34500(H - O/8) + 2240S]$$

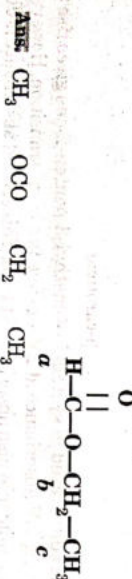
$$= \frac{1}{100} [8080 \times 85 + 34500(7 - 1/8) + 2240 \times 1]$$

$$= 9262.275 \text{ Kcal/Kg}$$

$$\text{NCV} = \text{GCV} - .09 \times H \times \text{latent heat of steam}$$

$$\text{NCV} = 9262.275 - .09 \times 7 \times 587 = 8892.465 \text{ cal/kg}$$

5.15. Show the number of expected ^1H NMR signal and their splitting pattern in $\text{CH}_3\text{OCOCH}_2\text{CH}_3$ and $\text{HCOOCH}_2\text{CH}_3$.



Signals :

$$a = \text{No}$$

$$b = \text{Quartet}$$

$$c = \text{Triplet}$$

Evaluation Based Questions

5.16. An organic compound having molecular formula $\text{C}_7\text{H}_6\text{O}$ shows absorption peaks at 3010, 2700, 1600, 1580, 1520, 1580 and 1720 cm^{-1} in its IR spectrum. Suggest its structure.

Ans.

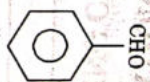
Molecular formula : $\text{C}_7\text{H}_6\text{O}$

Functional group may be OH or $\text{C}=\text{O}$

The peak at 1720 cm^{-1} corresponds to $\text{C}=\text{O}$

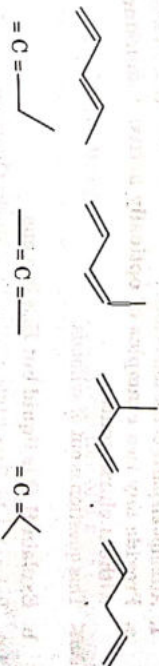
The peak at 2700 cm^{-1} corresponds to C-H

The peak at 3010 cm^{-1} corresponds to benzene ring.
The peaks at 1600, 1580, 1520, 1580 cm^{-1} corresponds to C=C in ring.
The proposed structure is



5.17. Two isomeric compounds A and B having the molecular formula C_5H_8 absorb at $\lambda_{\text{max}} = 223 \text{ nm}$ and $\lambda_{\text{max}} = 178 \text{ nm}$ respectively. Write the structures of the two isomers.

Ans.



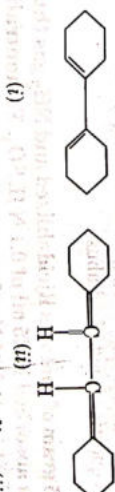
5.18. How many NMR signals are found in $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$?

Ans.



Total signals : Five

5.19. Why the λ_{max} for the diene (i) is observed at a lower nm than (ii)?



Ans. $\lambda_{\text{max}} = 215 \text{ nm}$ in both the molecules but in diene (ii) there is one extra absorption of exocyclic ring of 5 nm so,

$$\begin{aligned} \lambda_{\text{max}} &= \lambda_{\text{basic}} + \lambda_{\text{exocyclic}} \\ &= 215 \text{ nm} + 5 \text{ nm} = 220 \text{ nm} \end{aligned}$$