

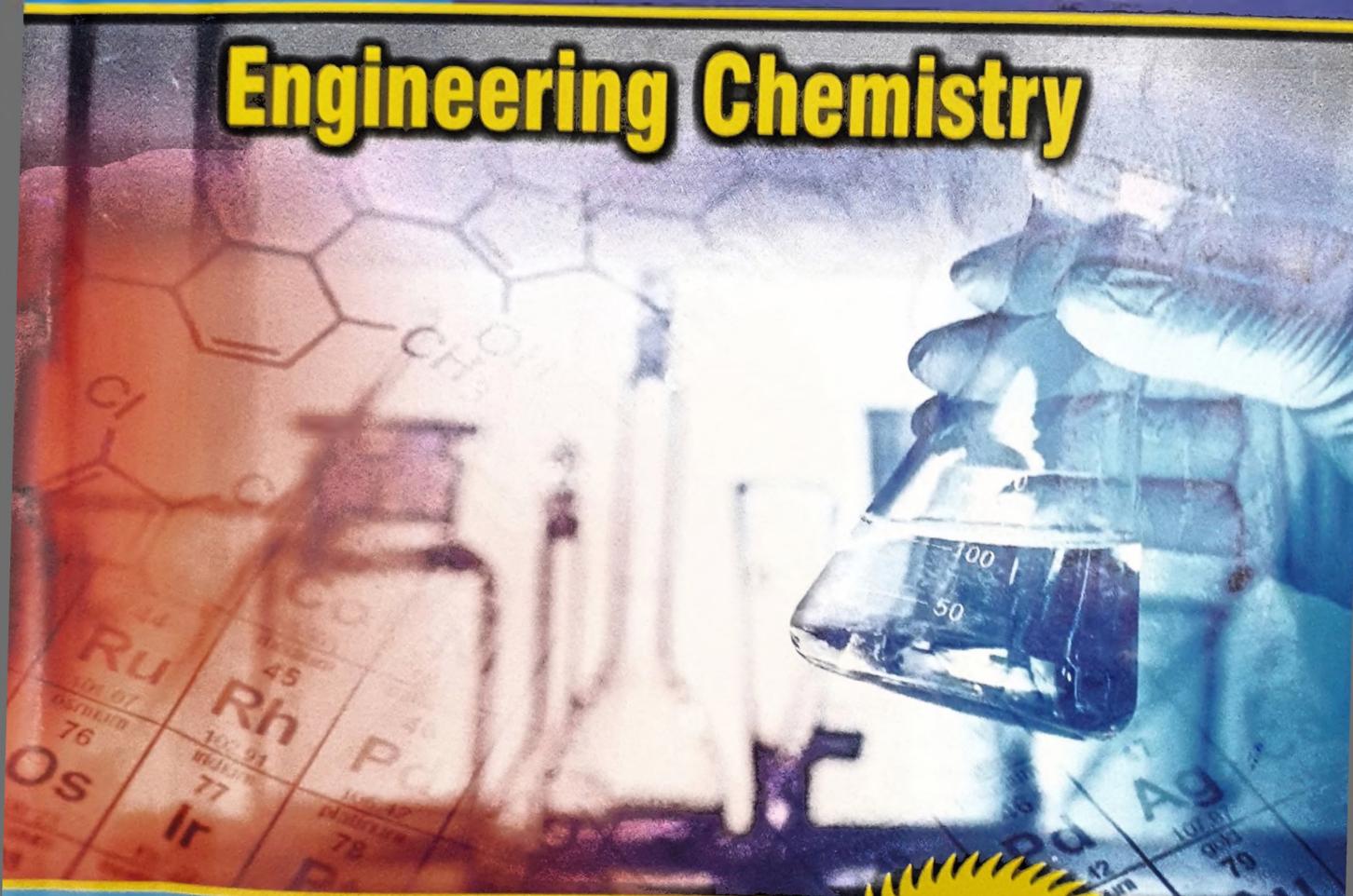


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B.Tech - 1st Year

Common to All Branches

Engineering Chemistry

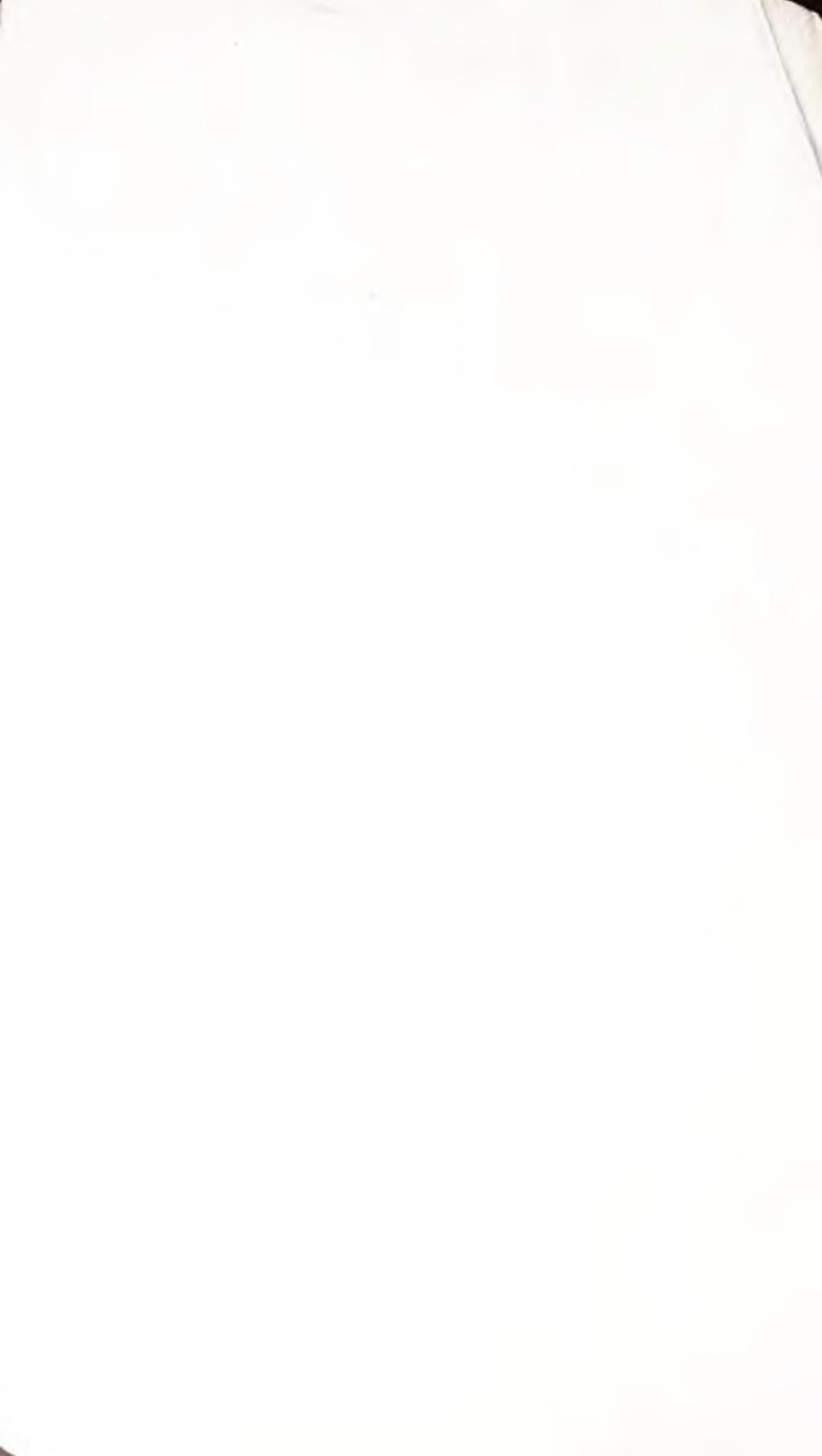


- Topic-wise coverage of entire syllabus in Question-Answer form.
- Short Questions (2 Marks)



Includes solution of following AKTU Question Papers (Odd & Even)

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For

B.Tech Students of First Year
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Dr. A.P.J. Abdul Kalam Technical University,
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Engineering Chemistry

By

Dr. Parul Verma



QUANTUM PAGE PVT. LTD.
Ghaziabad ■ New Delhi

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BAS102 / BAS202 : Engineering Chemistry

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Chemistry of Advanced Materials:

Liquid Crystals; Introduction, Types and Applications of liquid crystals, Industrially important materials used as liquid crystals. Graphite and Fullerene; Introduction, Structure and applications. Nanomaterials; Introduction, Preparation, characteristics of nanomaterials and applications of nanomaterials, Carbon Nano Tubes (CNT).

Green Chemistry: Introduction, 12 principles and importance of green Synthesis, Green Chemicals, Synthesis of typical organic compounds by conventional and Green route (Adipic acid and Paracetamol). Environmental impact of Green Chemistry on society.

UNIT-2 : SPECTROSCOPIC TECHNIQUES & APPLICATIONS

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Stereochemistry: Optical isomerism in compounds without chiral carbon, Geometrical isomerism, Chiral Drugs.

UNIT-3 : ELECTROCHEMISTRY

(3-1 B to 3-32 B)

Electrochemistry and Batteries: Basic concepts of electrochemistry. Batteries, Classification and applications of Primary Cells (Dry Cell) and Secondary Cells (Lead Acid battery).

Corrosion: Introduction to corrosion, Types of corrosion, Cause of corrosion, Corrosion prevention and control, Corrosion issues in specific industries (Power generation, Chemical processing industry, Oil & gas industry and Pulp & paper industries).

Chemistry of Engineering Materials:

Cement; Constituents, manufacturing, hardening and setting, deterioration of cement, Plaster of Paris (POP).

UNIT-4 : WATER TECHNOLOGY, FUEL AND COMBUSTION**(4-1 B to 4-48 B)**

Water Technology: Sources and impurities of water, Hardness of water, Boiler troubles, Techniques for water softening (Lime-Soda, Zeolite, Ion Exchange and Reverse Osmosis process), Determination of Hardness and alkalinity, Numerical problems.

Fuels and Combustion: Definition, Classification, Characteristics of a good fuel, Calorific Values, Gross & Net calorific value, Determination of calorific value by Bomb Calorimeter, Theoretical calculation of calorific value by Dulong's method, Ranking of Coal, Analysis of coal by Proximate and Ultimate analysis method, Numerical problems, Chemistry of Biogas production from organic waste materials and their environmental impact on society.

UNIT-5 : MATERIALS CHEMISTRY**(5-1 B to 5-38 B)**

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Preparation, properties, industrial applications of Teflon, Lucite, Bakelite, Kelvar, Dacron, Thiokol, Nylon, Buna-N and Buna-S and their environmental impact on society, Speciality polymers.

Organometallic Compounds: General methods of preparation and applications of Organometallic compounds (RMgX and LiAlH_4).

SHORT QUESTIONS**(SQ-1 B to SQ-22 B)****SOLVED PAPERS (2017-18 TO 2021-22)****(SP-1 B to SP-26 B)**

1

UNIT

Atomic and Molecular Structure

CONTENTS

- Part-1 :** Molecular Orbital's of Diatomic **1-2B to 1-13B**
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- Part-15 :** Environmental Impact of **1-39B to 1-40B**
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PART-1

Molecular Orbital's of Diatomic Molecules, Band Order Magnetic Characters and Numerical Problem.

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.

OR

Discuss the postulates of Molecular Orbital Theory.

Answer

1. In the molecular orbital (MO) 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.
2. **Postulates of Molecular Orbital Theory :**
 - 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 and 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.
3. For simple homoatomic molecules, the filling of electrons is carried out in a similar fashion as in atomic orbitals. Following rules are followed :
 - a. **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.

- b. **Pauli's Exclusion Principle :** The maximum number of electrons in a molecular orbital cannot exceed two and these should have opposite spins.
- c. **Hund's Rule :** Pairing of electrons takes place only when each molecular orbital of the same energy has at least one electron each.
- d. 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.
- e. **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.

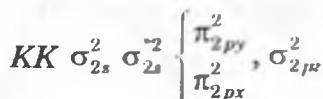
Que 1.2. Draw the Molecular orbital diagram of N_2 molecule. Calculate its bond order and predict its magnetic behavior.

AKTU 2017-18 (Sem-1), Marks 07

Answer

A. Nitrogen Molecule (N_2) :

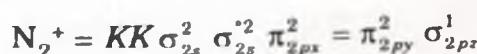
- i. Nitrogen atom has seven electrons. In the formation of N_2 molecule, a total of 14 electrons are arranged in molecular orbitals as :



- ii. Bond order = $\frac{1}{2} (10 - 4) = 3$
- iii. 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.

B. N_2^+ Ion :

- i. N_2^+ ion has one electron less than N_2 molecule. This electron will be lost from $\sigma_{2p\zeta}$ orbital.
- ii. Hence, the molecular electronic configuration :



- iii. Bond order = $\frac{1}{2} (7 - 2) = 2 \frac{1}{2}$
- iv. The ion is paramagnetic due to the presence of unpaired electron.

C. N_2^- Ion :

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

$$\text{N}_2^- = KK \sigma_{2s}^2 \sigma_{2s}^{*2} \pi_{2px}^2 = \pi_{2py}^2 \sigma_{2pz}^2 \pi_{2px}^{*1}$$

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

iv. As it contains one unpaired electron, the ion is paramagnetic.

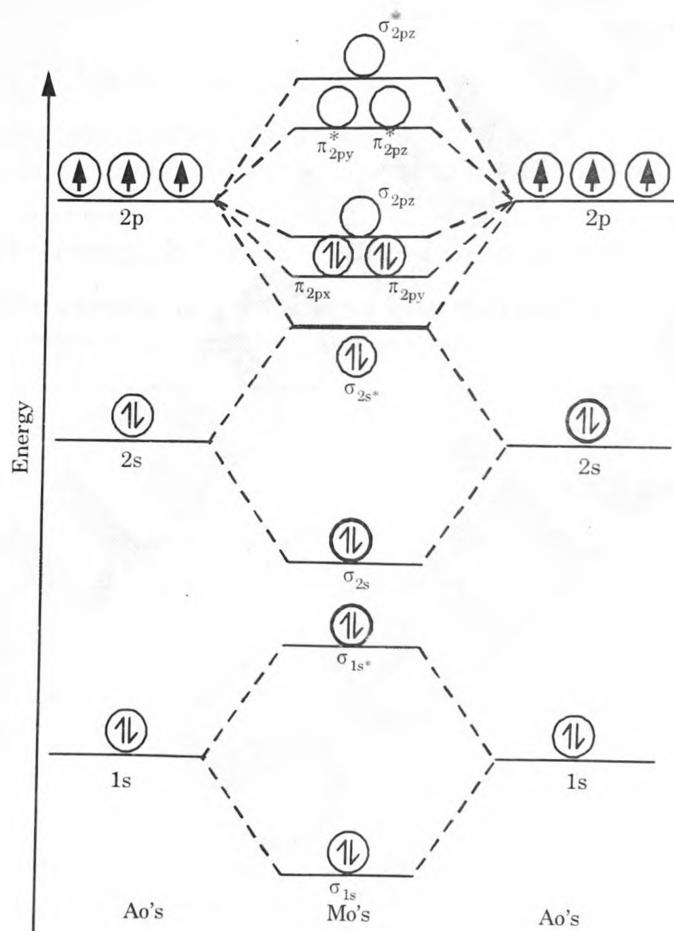
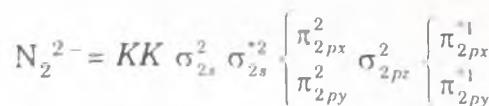


Fig. 1.2.1. Energy level diagram for N_2^- .

D. N_2^{2-} Ion :

- N_2^{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^{2-} ion :



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

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

E. Stability of these species is in the order :



Que 1.3. Draw the molecular orbital diagrams of N_2 and O_2 . Calculate their bond orders.

OR

Explain why O_2 is paramagnetic in nature.

AKTU 2017-18 (Sem-2), Marks 07

On the basis of molecular orbital theory, explain why N_2 is diamagnetic and O_2 is paramagnetic.

OR

With the help of molecular diagram, explain the paramagnetic nature of O_2 and diamagnetic character of N_2 .

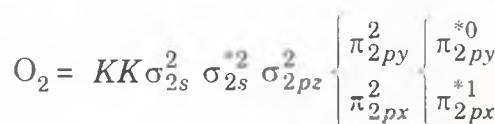
AKTU 2021-22 (Sem-2), Marks 10

Answer

A. Nitrogen Molecule (N_2) : Refer Q. 1.2, Page 1-3B, Unit-1.

B. Oxygen Molecule (O_2) :

- i. 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.
- ii. The molecular electronic configuration will be :

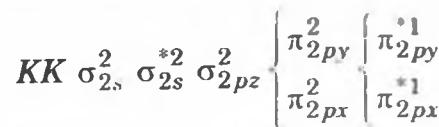


$$\text{Bond order} = \frac{(10 - 6)}{2} = 2$$

- iii. Thus, a double bond is present in the molecule.
- iv. From molecular diagram (Fig. 1.3.1) it is clear that two unpaired electrons are present so molecule is paramagnetic.

C. O_2^- Ion :

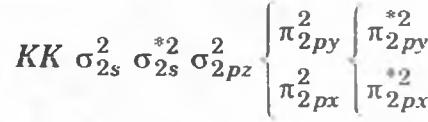
- These superoxide ion O_2^- has 17 electrons i.e., one electron more than O_2 and hence, this extra electron enters the π_{2px}^* or π_{2py}^* orbital.
- The molecular orbital electron configuration becomes :



- Bond order = $\frac{(10 - 7)}{2} = 1\frac{1}{2}$
- The superoxide ion is paramagnetic.

D. O_2^{2-} Ion :

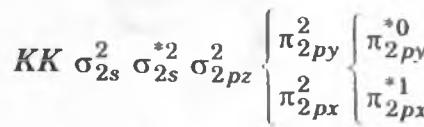
- The peroxide ion O_2^{2-} has 18 electrons and has molecular orbital configuration as :



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

E. O_2^+ Ion :

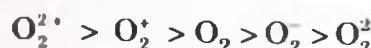
- This ion has 15 electrons.
- The molecular orbital configuration can be written as :



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

F. Order of Bond Strength :

- 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 :



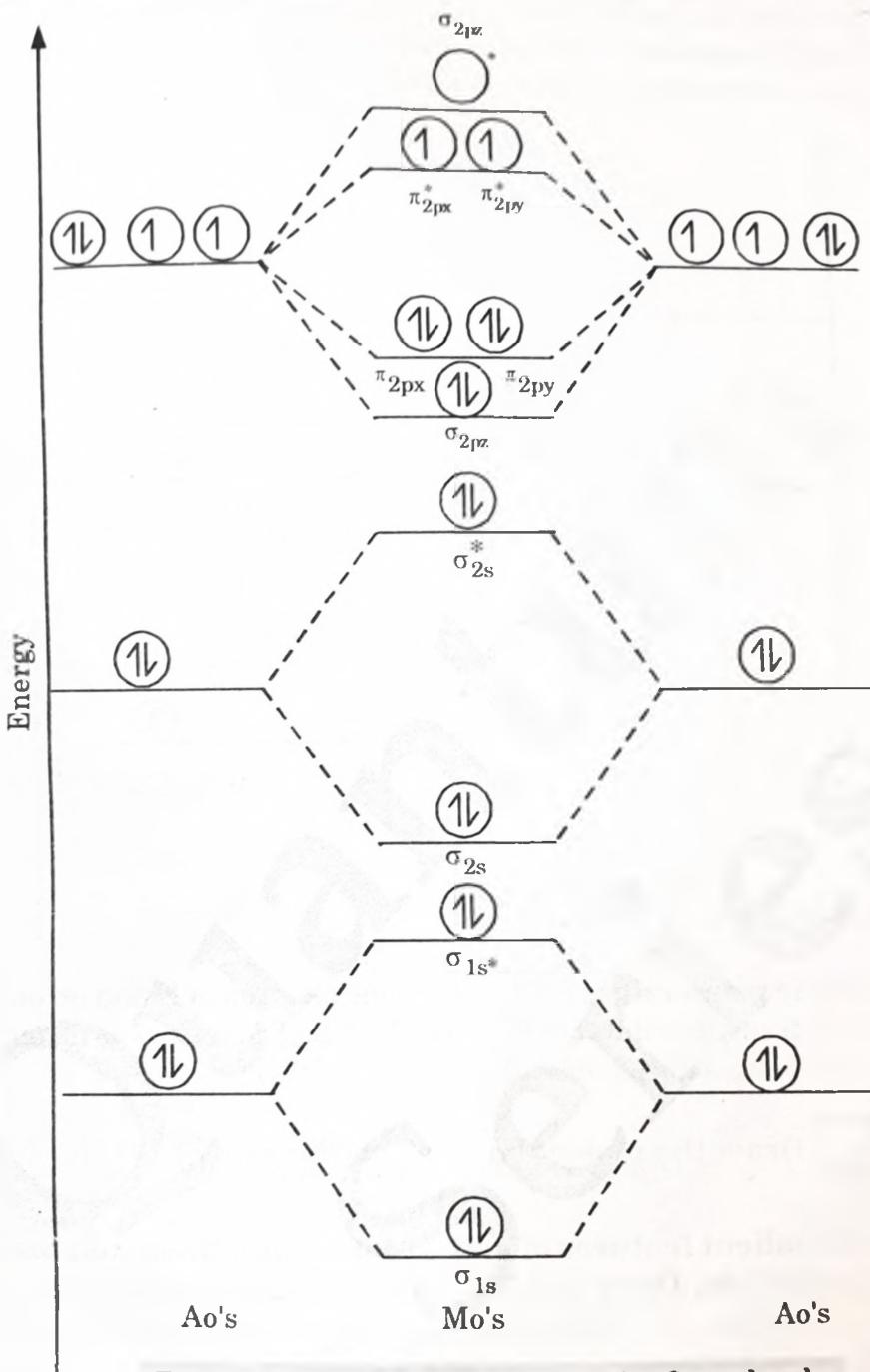


Fig. 1.3.1. Energy level diagram for O_2 molecule.

Que 1.4. Draw molecular orbital diagram of HF. Calculate bond order and determine the magnetic property.

Answer

A. MO (Molecular Orbital) diagram of HF :

1. The structure of HF molecule may be written as :
 $H(1s) + F(1s\ 2s^2\ 2p^5) \rightarrow HF [K(2s)^2 (\sigma_{sp_z})^2 (2p_x)^2 (2p_y)^2]$
2. Out of the three $2p$ orbitals, only $2p_z$ orbital is able to combine with an s-orbital because of symmetry considerations.

3. Therefore, in the formation of HF molecule, the bonding results from the H(1s) electrons and $2p_z$ electrons of F and the other electrons of fluorine remains in atomic orbitals.

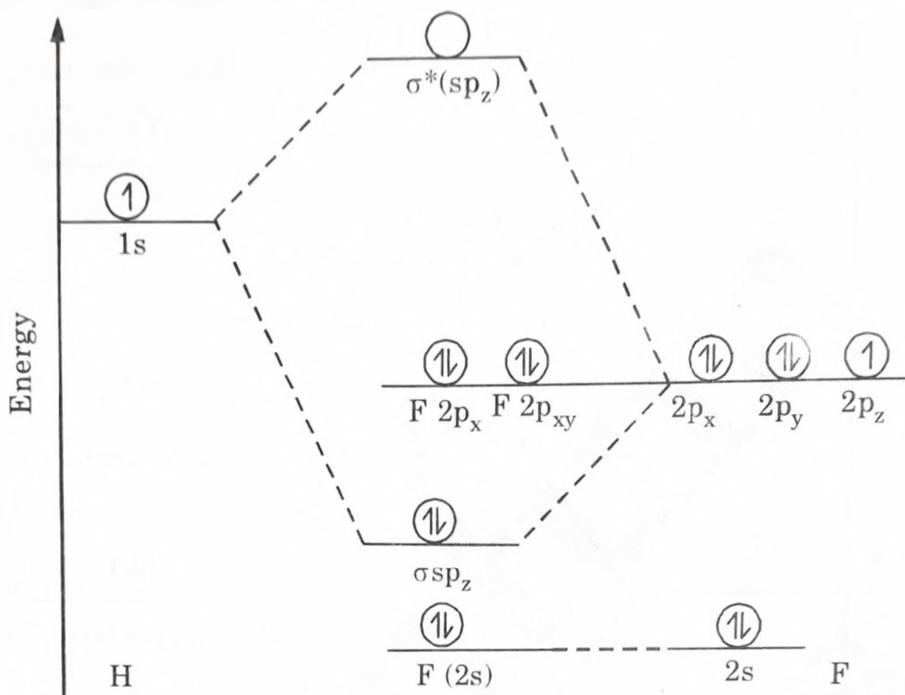


Fig. 1.4.1.

B. Bond order = $\frac{2-0}{2} = 1$

C. Magnetic properties : HF involves one electron of H and an unpaired electron from $2p$ orbital of F. As per MO diagram, there is no unpaired electron in hybridised orbital. Hence it is diamagnetic.

Que 1.5. Draw the molecular orbital diagram of CO.

OR

Outline the salient features of molecular orbital theory on the basis of LCAO principle. Draw the MO energy level diagram for the CO molecule. Calculate its bond order and predict its magnetic behavior.

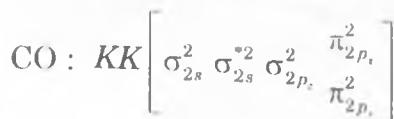
AKTU 2018-19 (Sem-2), Marks 10

Answer

A. Molecular Orbital Theory : Refer Q. 1.1, Page 1-2B, Unit-1.

B.

- There are four electrons in the outermost shell of carbon atom and six electrons in the outermost shell of oxygen. Thus, a total of 10 electrons are to be accommodated in the molecular orbitals of CO molecule.
- The molecular orbital configuration may be written as :



3. Bond order = $\frac{8 - 2}{2} = 3$

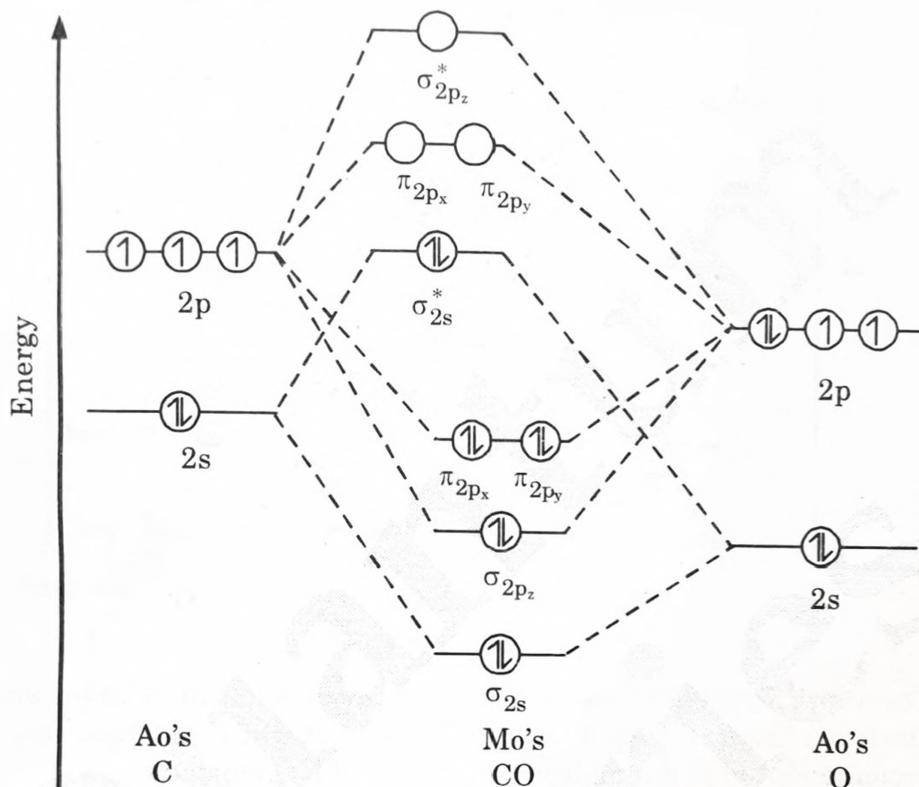


Fig. 1.5.1. Molecular orbital diagram for CO molecule.

Que 1.6. Draw the molecular orbital diagram of CO and NO. Calculate their bond orders.

OR

With the help of molecular orbital diagram, explain why NO molecule is paramagnetic.

OR

Calculate the bond order of N_2^- , CO, NO, and O_2^+ .

OR

With the help of molecular orbital diagram, explain the formation of NO & N_2^- . Calculate their bond order and predict their magnetic behaviour.

AKTU 2021-22 (Sem-1), Marks 10

Answer

- A. Bond Order of N_2^- : Refer Q. 1.2, Page 1-3B, Unit-1.
- B. Bond Order of O_2^+ : Refer Q. 1.3, Page 1-5B, Unit-1.

C. MO Diagram of CO : Refer Q. 1.5, Page 1-8B, Unit-1.

D. MO Diagram of NO :

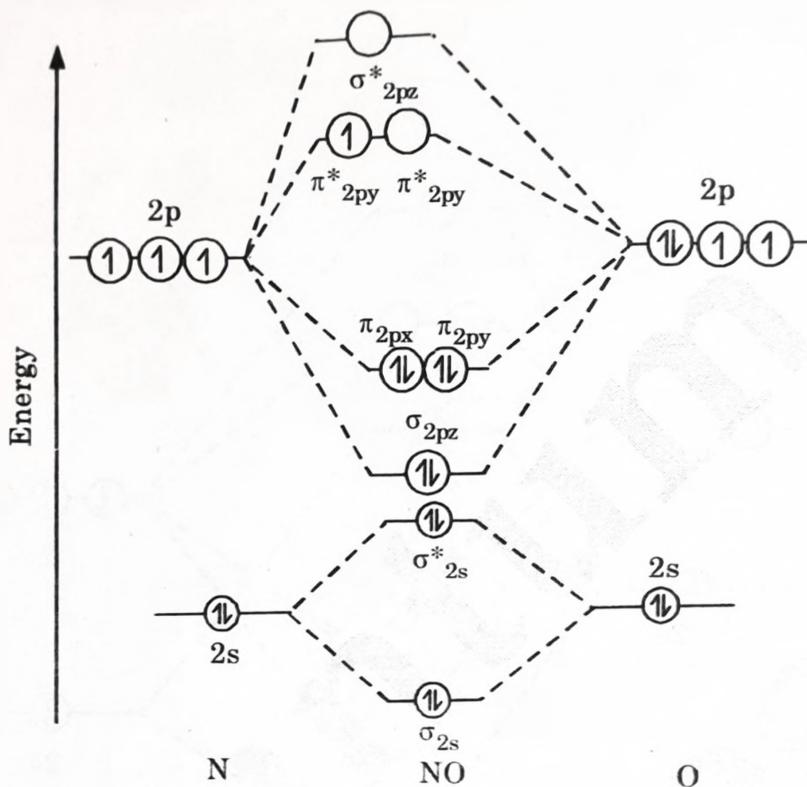


Fig. 1.6.1.

- There are five electrons in the outer most shell of N atom and six electrons in outer shell of O atom. Thus, a total of 11 electrons are to be accommodated in the molecular orbitals of NO molecule.
- The molecular orbital electronic configuration of NO molecule is :

$$\text{NO} = \left[\sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2p_z}^2 \pi_{2p_x}^2 \pi_{2p_y}^2 \pi_{2p_z}^{*2} \right]$$

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

- As there is 1 unpaired electron. So, NO is paramagnetic.

Que 1.7. Explain BMO and ABMO and differentiate between them.

Draw molecular orbital diagram of NO^+ . Calculate its bond order and predict its magnetic properties.

AKTU 2018-19 (Sem-1), Marks 10

Answer

- A. Bonding molecular orbital (BMO) :** Bonding molecular orbital is formed by the addition of overlapping of atomic orbitals. The wave function of the bonding MO may be written as :

$$\Psi_{(MO)} = \Psi_A + \Psi_B$$

B. Anti-bonding molecular orbital (ABMO) : Anti-bonding molecular orbital is formed by the subtraction of overlapping of atomic orbitals. The wave function for the anti-bonding MO may be written as :

$$\Psi^*_{(MO)} = \Psi_A - \Psi_B$$

C. Difference :

S. No.	Bonding MO	Antibonding MO
1.	It is formed by addition overlap of AO's.	It is formed by subtraction overlap of AO's.
2.	Its wave function may be expressed as $\Psi_{AB} = \Psi_A + \Psi_B$.	Its wave function may be expressed as $\Psi^*_{AB} = \Psi_A - \Psi_B$.
3.	Its energy is lower than the energies of AO's participating in overlap.	Its energy is higher than the energies of AO's participating in overlap.
4.	Electron density is higher in between the nuclei.	A node appears in between the nuclei of participating atoms.
5.	Electrons present in BMO contribute to attraction.	Electrons present in ABMO contribute to repulsion.

D. Diagram :

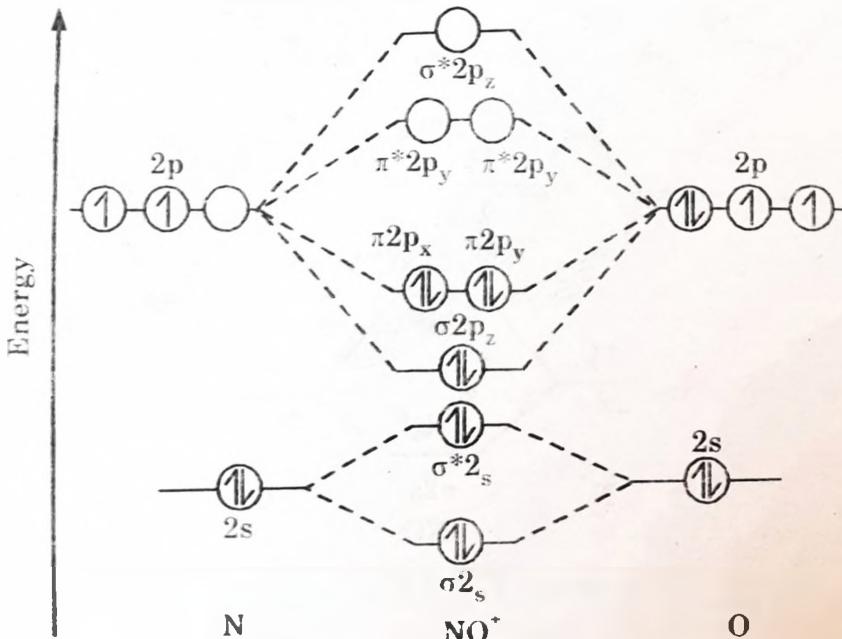


Fig. 1.7.1.

1. Bond order = 3
2. Its magnetic property is diamagnetic.

Que 1.8. Calculate bond order, magnetic behaviour and order of stability of NO , NO^- , NO^+ .

AKTU 2020-21 (Sem-1), Marks 10

Answer

A. For NO : Refer Q. 1.6, Page 1-9B, Unit-1.

B. For NO^+ :

1. There are 7 electrons present in nitrogen and 8 electrons in oxygen.
2. The number of electrons present in molecule = $7 + 8 - 1 = 14$
3. The formula of bond order = $1/2(\text{Number of electrons in bonding orbitals} - \text{Number of electrons in antibonding orbitals})$
 $= 1/2(10 - 4) = 3$
4. The number of unpaired electron in molecule is 0. So, this is diamagnetic. That means more the number of unpaired electrons, more paramagnetism.

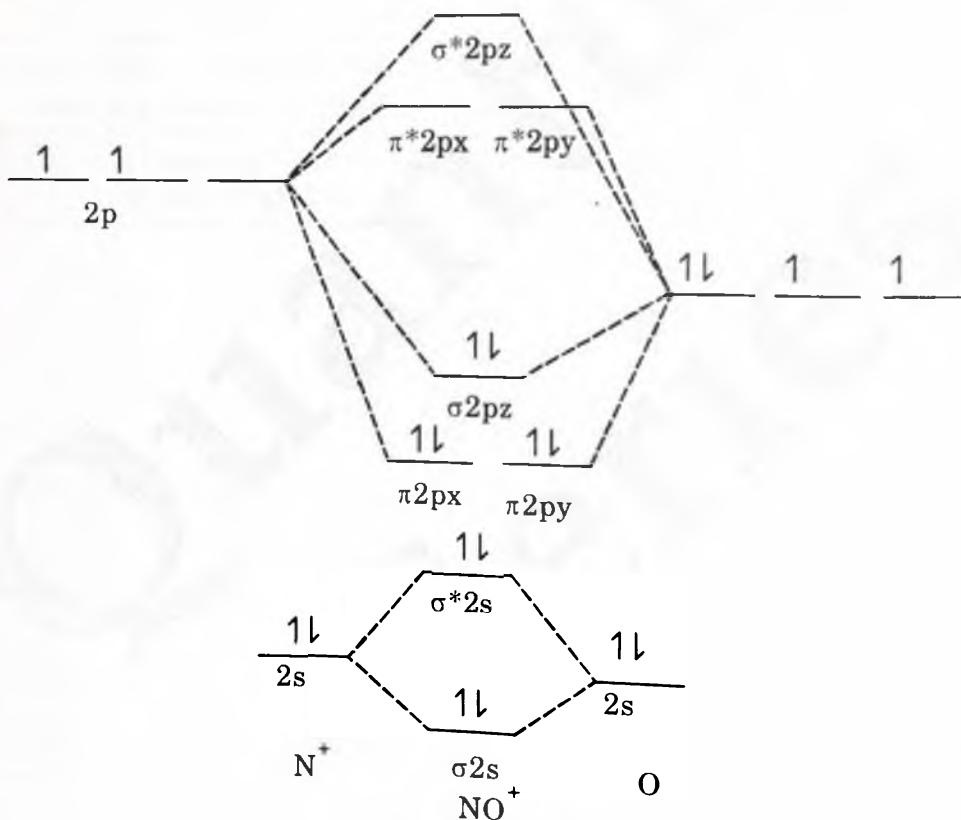


Fig. 1.8.1.

C. for NO^- :

1. The number of electrons present in molecule = $7 + 8 + 1 = 16$
2. The bonding order = $1/2(10 - 6) = 2$
3. The number of unpaired electron in molecule is 0. So, this is diamagnetic.

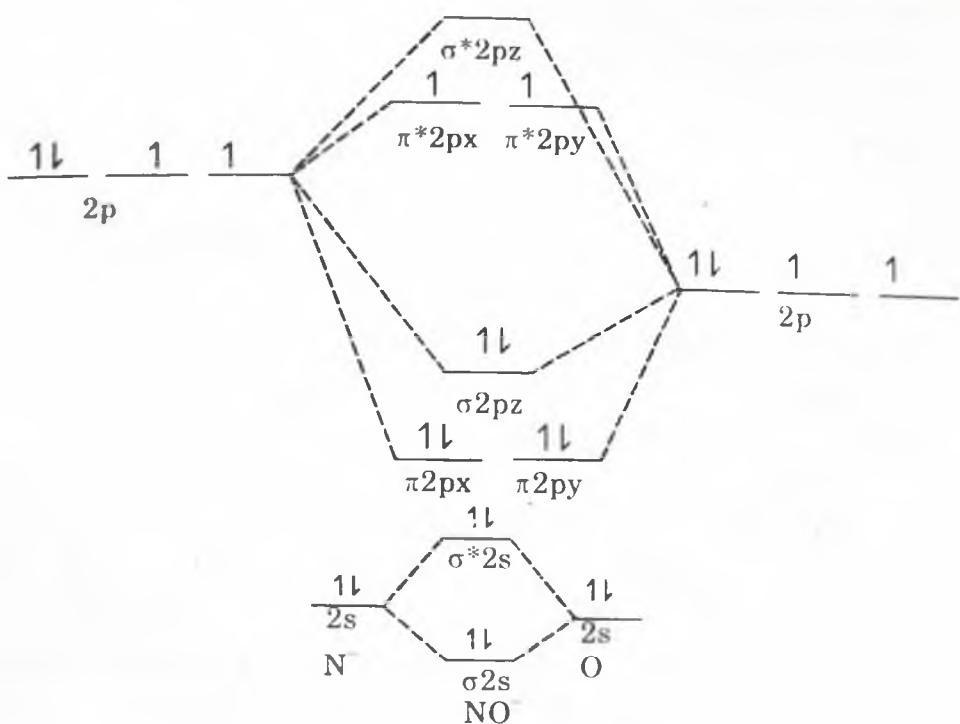


Fig. 1.8.2.

D. Order of Stability : $\text{NO}^- < \text{NO} < \text{NO}^+$

PART-2

Liquid Crystals Introduction.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

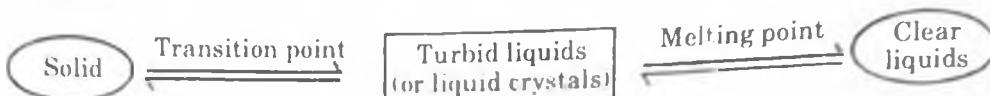
Que 1.9. What is liquid crystal ? Give its principal and working ?

Answer

A. Liquid Crystal :

1. 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.
2. 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.

3. 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.
4. Example : Cholesteryl Benzoate ($C_6H_5COOC_{27}H_{45}$) has two melting point.



B. Principle of Liquid Crystal :

1. The molecules in fluid 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.
2. A liquid crystal display consists of an array of tiny segments called as pixels that can be manipulated to present the information.
3. 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.

C. Working of Liquid Crystal :

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.
3. 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.
4. There is polarizer on outer side of one plate and analyzer on other plate. There is a spacer to control cell gap.
5. Light passing through polarizer has its polarization rotated with the alignment direction of LC.
6. As the light reaches to analyzer, it can be passed or blocked, depending upon extent of rotation.
7. Electric field is controlled with the transparent conductors and the direction of LC molecules.
8. 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.
9. When the electric field is turned off, the molecules relax back to their twisted state and the cell becomes transparent again.

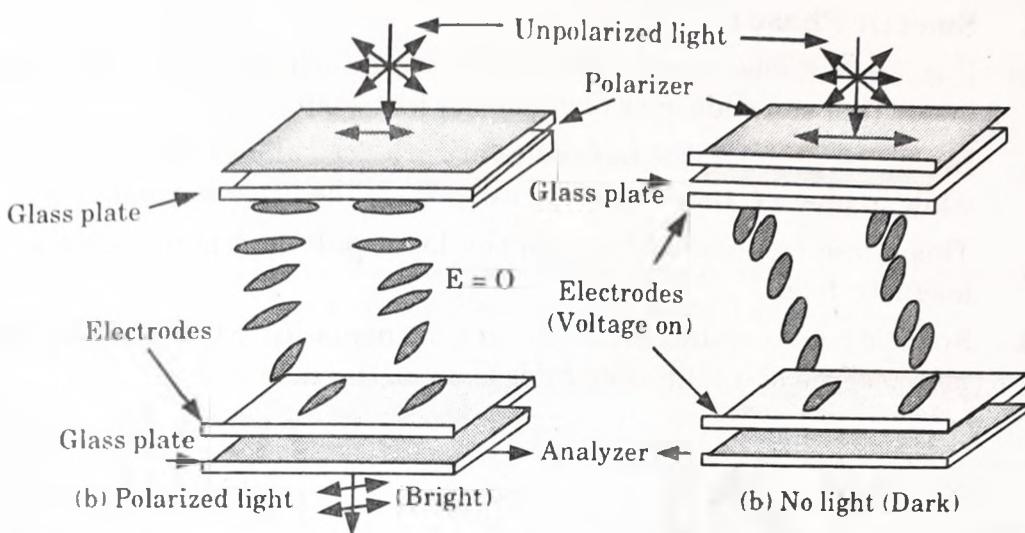


Fig. 1.9.1. Geometry of a working LCD cell. The polarizer and analyzer.

PART-3

Types and Applications of Liquid Crystals.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.10. What is liquid crystal ? Give its classification.

Answer

- Liquid Crystal :** Refer Q. 1.9, Page 1-13B, Unit-1.
- Classification of Liquid Crystals :**
 - Thermotropic liquid crystal
 - Lyotropic liquid crystal.
- Classification of Thermotropic Liquid Crystal :**
 - Nematic Phase :**
 - In Greek, nematic means thread. They are thread like turbid and less anisotropic than smectic.
 - The molecules flow like liquid and their center of mass positions are randomly distributed as in a liquid.
 - Nematics have fluid like structure as isotropic liquids but can easily align by an external magnetic or electric field which has optical properties of uniaxial crystal and makes them extremely useful in LCDs.

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.

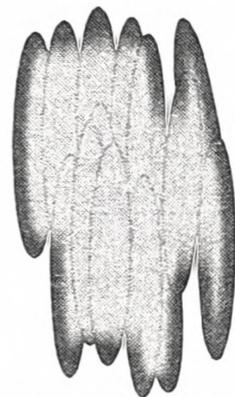


Fig. 1.10.1. Nematic phase.

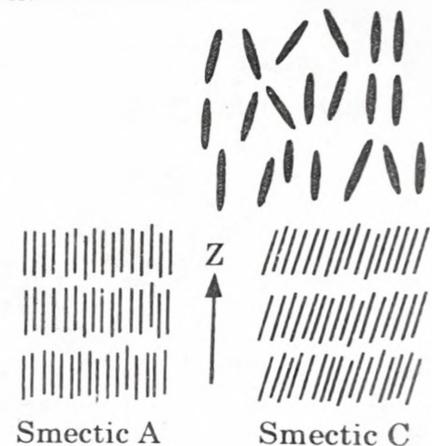


Fig. 1.10.2. Smectic phase.

3. Chiral Nematic / Cholesteric Phase :

- a. Another common phase is cholesteric, also known as chiral nematic.
- b. In this phase, the molecules twist slightly from one layer to the next, resulting in a spiral formation.
- c. This phase shows nematic ordering but the preferred direction rotates throughout the samples. An example of this is shown in Fig. 1.10.3.

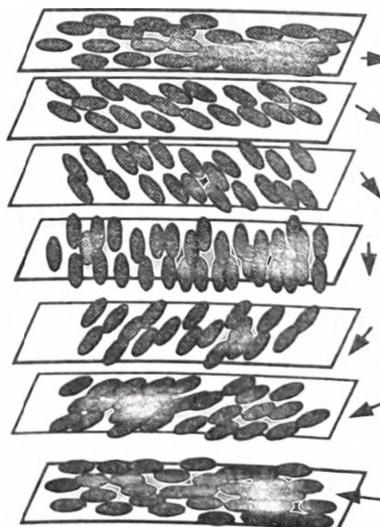


Fig. 1.10.3. Chiral nematic liquid.

Que 1.11. Discuss the principle, working and applications of liquid crystals in LCDs :

- a. Nematic phase
- b. Chiral nematic phase
- c. Smectic phase

OR

What are liquid crystals ? Differentiate between Nematic and smectic liquid crystal ? Write two applications of liquid crystals.

AKTU 2017-18 (Sem-1), Marks 07

AKTU 2018-19 (Sem-1), Marks 10

OR

Write a note on liquid crystal describing classification and applications of liquid crystals.

AKTU 2020-21 (Sem-1), Marks 10

OR

Illustrate the concept of liquid crystals. Classify them on the basis of temperature and mention their important applications.

AKTU 2021-22 (Sem-1), Marks 10

Answer

- A. Liquid Crystal : Refer Q. 1.9, Page 1-13B, Unit-1.
- B. Principle and Working : Refer Q. 1.9, Page 1-13B, Unit-1.
- C. Classification of Liquid Crystals : Refer Q. 1.10, Page 1-15B, Unit-1.
- D. Difference between in Nematic and Smectic Liquid Crystal :

S. No.	Nematic Liquid Crystal	Smectic Liquid Crystal
1.	They are oriented, parallel without periodicity.	They are oriented, parallel with periodicity.
2.	They have more fluidity.	They have less fluidity.
3.	They are found at higher temperature.	They are found at lower temperature.
4.	They have less degree of orientation.	They have more degree of orientation.

E. Applications of Liquid Crystals :

1. Liquid Crystal Displays :

- a. Liquid crystals rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field.
- b. 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.

- c. It is often utilized in battery-powered electronic devices because it uses very small amounts of electric power.
- 2. Liquid Crystal Thermometers :**
- a. Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch.
 - b. Since the pitch is dependent upon temperature, the color reflected is also dependent upon temperature.
 - c. Liquid crystal makes it possible to accurately measure the temperature just by looking at the colour of the thermometer.
- 3. Optical Imaging :**
- a. In this technology, a liquid crystal cell is placed between two layers of photoconductor.
 - b. Light is applied to the photoconductor, which increases the material's conductivity.
 - c. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light.
- 4. Other Liquid Crystal Applications :**
- a. They are used for non-destructive mechanical testing of materials under stress.
 - b. This technique is also used for the visualization of RF (radio frequency) waves in waveguides.
 - c. They are used in medical applications where, for example, transient pressure transmitted by a walking foot on the ground is measured.

Que 1.12. What do you understand by mesomorphic state and illustrate it with the help of vapour pressure temperature curve? Discuss its classification on basis of temperature and give their important applications.

AKTU 2018-19 (Sem-2), Marks 10

Answer

- A. Mesomorphic state :** A state of matter in which the degree of molecular order is between of solid crystal and isotropic liquid or gases.
- B. Curve :**
1. A solid showing the mesomorphic change undergoes following transformations :



Such transformation on vapour pressure-temperature diagram is shown in Fig. 1.12.1.

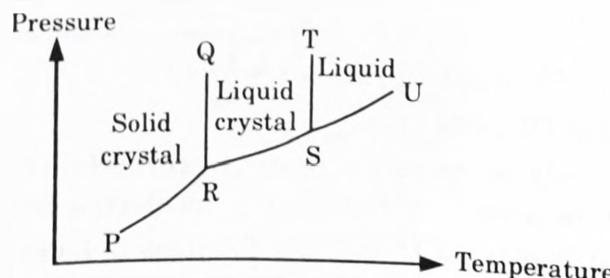


Fig. 1.12.1. Phase diagram of mesomorphic state.

2. Vapour pressure curve of solid (crystalline phase) and liquid crystalline phase are distinctly represented by PR and RS respectively while SU is that of isotropic liquid phase.
3. Here we have two triple points, namely R and S compared to solid, liquid and vapour equilibria phase diagram, where we get only one triple point.
4. At R three phases solid crystals, liquid crystals and vapour phase are co-existing, whereas at S liquid crystal, liquid and vapour phases are co-existing in equilibrium.
- C. Classification on the basis of temperature or classification of thermotropic liquid crystal : Refer Q. 1.10, Page 1-15B, Unit-1.
- D. Application : Refer Q. 1.11, Page 1-17B, Unit-1.

PART-4

Industrially Important Materials used as Liquid Crystals.

Questions-Answers

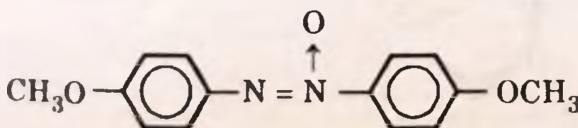
Long Answer Type and Medium Answer Type Questions

Que 1.13. List various materials used as liquid crystals industrially.

Answer

Some Materials that are used as Liquid Crystal Industrially :

1. *p*-azoxyanisole (PAA) :



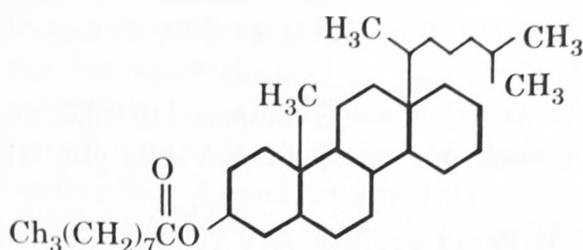
This compound is used in liquid crystal displays. It is solid state compound that convert into powder if heated.

2. *p*-quinquephenyl :



This compound acts as super conductor when it is doped with potassium.

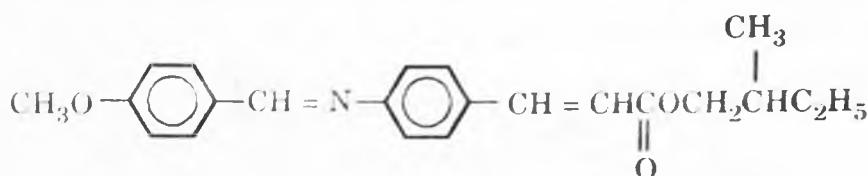
3. cholesteryl nonanoate



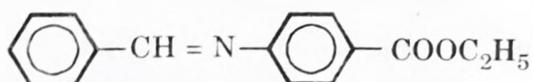
Noncholesteryl, chiral component

This compound used in hair colors, cosmetic products and lotions.

4. (-)-2-methylbutyl-p-(p'-methoxybenzylidene-amino) cinnamate :

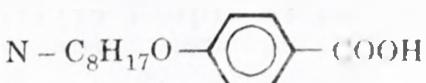


5. ethyl p-(p'-phenylbenzalmino) benzoate :

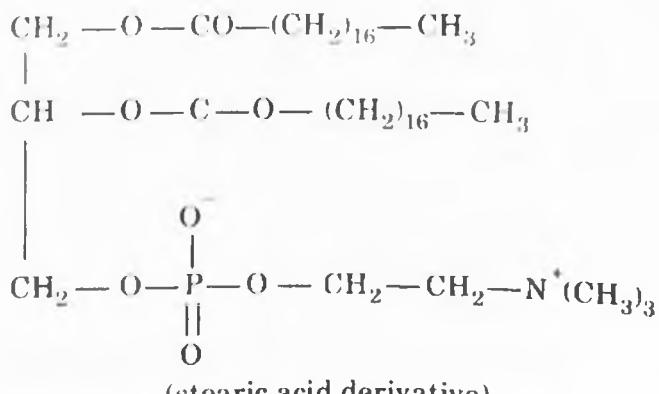


This compound is used in synthesis of hydrogen bonded liquid crystal complexes.

6. p-n-octyloxybenzoic acid :

7. Sodium sterate : $\text{CH}_3(\text{CH}_2)_{16}\text{COO}-\text{Na}^+$

It is used as emulsifier and lubricant in polycarbonates. It also acts as viscosity modifier.

8. α -Lecithin :

This compound used in fertilizer, paint and other industrial applications.

PART-5

Graphite and Fullerene; Introduction, Structure and Applications.

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

Que 1.14. With the help of neat diagram, describe the structure of graphite. Also, give at least five applications of graphite.

OR

Explain the structure, properties and applications of graphite.

AKTU 2017-18 (Sem-1), Marks 07

OR

Explain the applications of graphite and comment upon electrical and lubricant property of graphite.

AKTU 2021-22 (Sem-2), Marks 10

Answer**A. Graphite :**

- Graphite is an allotrope of carbon in which the atoms are arranged in layers.

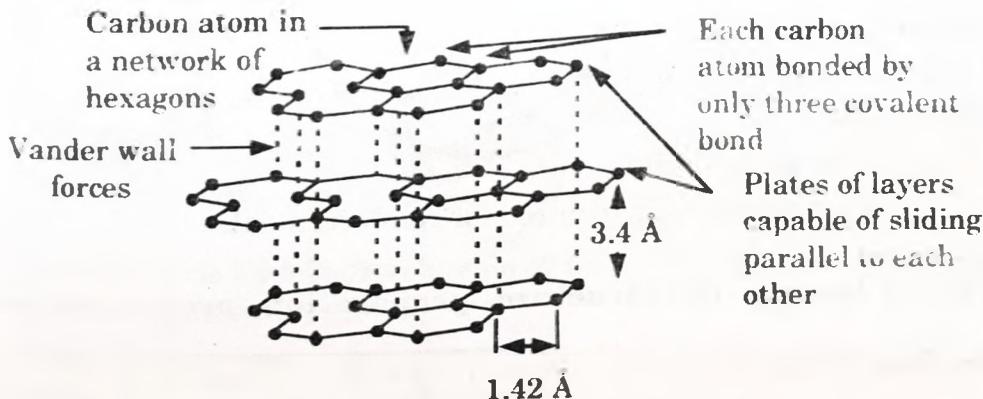


Fig. 1.14.1. Structure of graphite.

- Graphite itself comes in two allotropic forms :
 - Naturally occurring graphite is called beta-graphite and it comes in a hexagonal form.
 - Synthetically produced graphite is called alpha-graphite and it comes in a rhombohedral form.

3. The hexagonal form of graphite has carbon atoms arranged in a hexagon; the hexagons form a plane.
4. Each carbon atom in the hexagon is attached to only three other carbon atoms.
5. The fourth electron of each carbon atom hangs loosely and is not bound.
6. Graphite shows sp^2 hybridization. Within each layer, the carbon atoms are very strongly bonded by sigma σ bonds.
7. The bond angles are 120° with each other. The links between adjacent layers is weak.
8. The resulting network is 2-dimensional, and the resulting flat sheets are stacked and loosely bonded through weak Vander Walls forces.

B. Properties of Graphite :

1. It is very soft because of easy sliding of weakly bonded planes of carbon atoms.
2. It is very good conductor of electricity due to π -electron bonds on both sides of planes of carbon atoms.
3. Graphite sheet-molecules on folding form carbon nano tubes.
4. Graphite has very good adsorption ability because of C-atoms on surface have unsatisfied valences.
5. **Lubrication Properties :** Due to presence of loosely bounded sheets of carbon atoms. Graphite shows slippery texture that makes it effective lubricant.
6. **Electrical Properties :** One to delocalised electrons which can move freely between layers in graphite makes graphite conduct electricity. So, graphite is used in electrodes of batteries and electrolysis.

C. Applications of Graphite :

1. Lead-pencils.
2. For electrodes.
3. As conductor of electricity.
4. For making carbon fibers required for reinforcement.

Que 1.15. | Discuss the structure, preparation, properties and application of fullerene.

AKTU 2018-19 (Sem-1), Marks 10

OR

Give the properties and applications of fullerenes.

AKTU 2017-18 (Sem-2), Marks 07

OR

Give the structure, preparation, properties and applications of an allotrope of carbon having truncated icosahedron's structure.

AKTU 2021-22 (Sem-1), Marks 10

OR

What is fullerene ? Indicating the method of preparation properties and their application ?

AKTU 2021-22 (Sem-2), Marks 10

Answer**A. Fullerene :**

1. Fullerene is an allotrope of carbon (C_{60}) which is popularly known as Buckminster fullerene. It is designed dome structures based on hexagon and pentagons which resemble with C_{60} .
2. Some other discrete molecules with clusters of C atoms like C_{50} , C_{70} , C_{32} have been formed and collectively known as fullerenes.

B. Preparation :

1. Fullerenes are prepared by vapourizing a graphite rod in helium atmosphere.
2. Mixture of fullerenes like C_{60} , C_{70} etc., are formed which are separated by solvent extraction.
3. Pure C_{60} is isolated from this mixture by column chromatography.

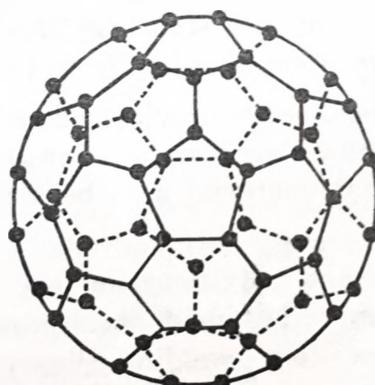
C. Structure :

Fig. 1.15.1. Structure of a buckyball.

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

D. Properties of Fullerene :

1. It is black powdery material.
2. It forms deep magenta solution when dissolved in benzene.
3. It is very tough and thermally stable.
4. It exists as a discrete molecule.

E. Applications of fullerene :

1. It is used in making superconductors.
2. It is used in making soft ferromagnets.
3. It is used in electronic devices.
4. It is used as a lubricant.

PART-6*Introduction to Nanomaterials.***Questions-Answers****Long Answer Type and Medium Answer Type Questions****Que 1.16.** What are nano-materials ?**Answer**

1. Nanomaterial is defined as a material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale (length range approximately from 1 nm to 100 nm).
2. This includes both nano-objects, which are discrete pieces of material, and nanostructured materials, which have internal or surface structure on the nanoscale; a nanomaterial may be a member of both these categories.
3. Nanomaterials that are naturally occurring (e.g., volcanic ash, soot from forest fires) or are generated as incidental (unintentional) by-products of combustion processes (e.g., welding, diesel engines) are usually physically and chemically heterogeneous and often termed 'ultrafine particles'.
4. Engineered nanomaterials, on the other hand, are intentionally produced and designed with physico-chemical properties for a specific purpose or function.

Que 1.17. Discuss various properties of nanomaterials.**Answer****Properties of Nano-materials :****i. Magnetic Properties :**

1. Magnetic nanoparticles are used in a range of applications like imaging, bioprocessing, refrigeration as well as high storage density magnetic memory media.

2. The large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighboring atoms leading to differing magnetic properties.
3. Bulk gold (Au) and platinum are non magnetic but at the nano size they act as magnetic particles. Au nanoparticles become ferromagnetic when they are capped with the appropriate molecules such as thiol.

ii. Optical Properties :

1. In small nano clusters the effect of reduced dimensionality on electronic structure has the most profound effect on the energies of highest occupied molecular orbital (HOMO) which is valence band and the lowest unoccupied molecular orbital (LUMO), essentially the conduction band.
2. The optical emission and adsorption occurs when the transition of the electrons occur between these two states.
3. Semiconductors and many metals show large changes in optical properties such as color, as a function of particle size.
4. Colloidal suspense of gold nano particles have a deep red color which becomes progressively more yellow as the particle size increases. As,
 - i. Gold spheres of 10-20 nm exhibit red color
 - ii. Gold spheres of 2-5 nm exhibit yellow color.
 - iii. Gold spheres of >20 nm exhibit purple color

iii. Electronic Properties :

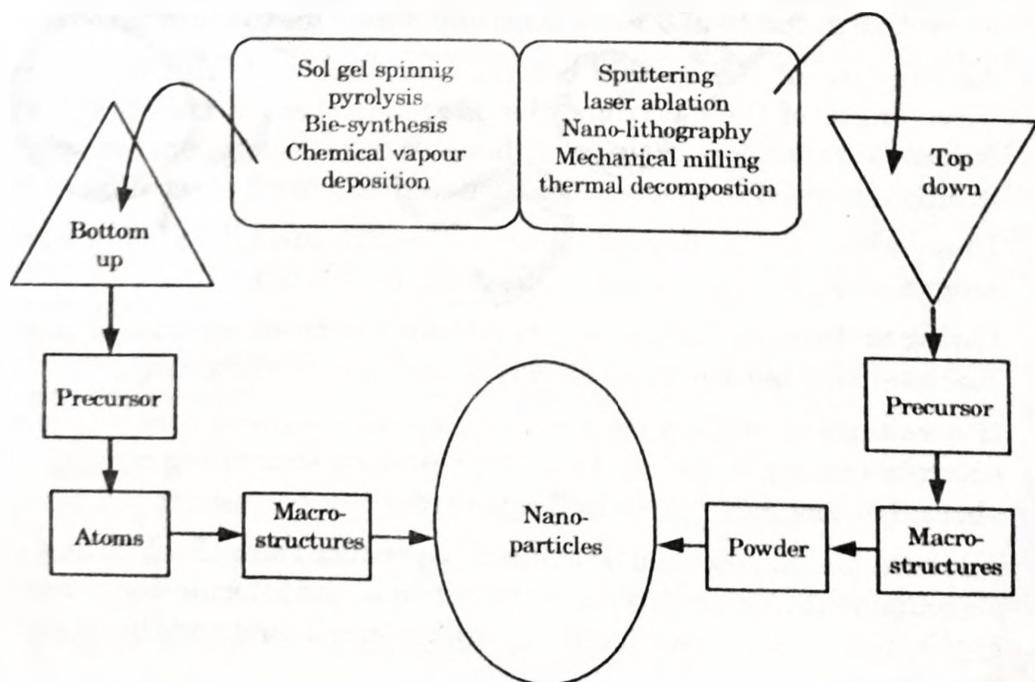
1. The changes which occur in electronic properties as the system length scale is reduced are related mainly to the increasing influence of the wave-like property of the electrons and the scarcity of scattering centres.
2. As the size of the system becomes comparable with the de Broglie wavelength of the electrons, the discrete nature of the energy states becomes apparent once again, although a fully discrete energy spectrum is only observed in systems that are confined in all three dimensions.
3. In certain cases, conducting materials become insulators below a critical length scale, as the energy bands cease to overlap.
4. Owing to their intrinsic wave-like nature, electrons can tunnel quantum mechanically between two closely adjacent nanostructures.
5. If a voltage is applied between two nanostructures which aligns the discrete energy levels in the DOS, resonant tunnelling occurs, which abruptly increases the tunnelling current.
6. All these phenomena can be utilised to produce radically different types of components for electronic, optoelectronic and information processing applications, such as resonant tunnelling transistors and single electron transistors.

PART-7*Preparation of Nanomaterials.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 1.18. Discuss the preparation of nanomaterials.

Answer**Preparation of Nanoparticles :**

1. The nanoparticles can be prepared by various processes i.e., divided into bottom up and top down techniques.
2. Bottom up methods includes the reduction of material components up to the atomic level and then with further self-assembly leading to the formation of nanoparticles.
3. However, during self-assembly, the physical forces functioning at nano-scale are used to connect basic units into macro structures.
4. Pyrolysis, bio-synthesis, sole gel, spinning and chemical vapor deposition are most extensively used methods fall in bottom up approach.

**Fig. 1.18.1.**

5. Top-down approach involves the breaking down of the bulk material into nanosized structures or particles. It starts with a pattern produced on a higher scale, then compacted to nanoscale.
6. This technique includes sputtering, laser ablation, nano-lithography, mechanical milling and thermal decomposition.

Que 1.19. Explain different types of Bottom-up techniques for preparation of nanomaterials.

Answer

Bottom up Technique :

1. Sol Gel :

- i. Sol gel is one of the simplest and, most commonly used methods for the synthesis of nano-particles.
- ii. It is a chemical method which comprises of a solution working as a precursor for an assimilated system of distinct particles.
- iii. In this method, metal oxides, metal chlorides and alkoxysilanes are most commonly used as precursors.
- iv. The precursor is mixed by means of stirring and then spread in second liquid which form a solid-liquid phase.
- v. Sedimentation, filtration and centrifugation are the typical methods used for phase separation to get nano-particles and then the sample is dried to remove moisture.
- vi. The main advantage of this process is that we attain uniform nano-structures even at a very low temperature, having controlled chemical composition and purity.

2. Chemical-Vapor Deposition (CVD) :

- i. In this method of preparation, substrate is coated with a thin film of gaseous reactants.
- ii. The gas molecules are combined at ambient temperature in a reaction chamber to carry out deposition.
- iii. Upon heating substrate comes in vicinity of combined gas where a chemical reaction occurs and a thin film is formed on the surface of substrate.
- iv. This thin film can be recovered and reused for different applications.
- v. The basic influencing factor in this method is the temperature of the substrate.
- vi. The nanoparticles achieved through this method are highly pure, uniform in size, strong and have high mechanical stability. The disadvantages of CVD include the use of special equipment as well as the high toxicity of the gaseous by-products.

3. Biosynthesis :

- i. Biosynthesis is one of the inexpensive, green, safe, decomposable and environment friendly methods used for the synthesis of nano-particles.
- ii. In this method bacterium, fungi and plant extracts are used in conjunction with precursor for bio-reduction and capping functions rather than conventional chemicals.
- iii. This method has its distinctive and enriched properties that find its approaches in medical applications.

4. Pyrolysis :

- i. Pyrolysis is the method used in industries to prepare nano-particles on large scale.
- ii. In this method, precursor used can be liquid or vapor. A furnace is used in order to burn the precursor.
- iii. Precursor is added to the furnace through a small opening where flame is applied to burn it.
- iv. Nano-particles are collected by the gases produced as by product.
- v. Pyrolysis is an effective method for nano-particle preparation due to its simplicity, high product yield and sensitiveness.

Que 1.20. | Explain various Top-down techniques for preparation of nanomaterials.

Answer**Top down Techniques :****1. Mechanical Milling :**

- i. One of the most widely used top down techniques to produce nano-particles is mechanical milling.
- ii. In this method various elements are milled under an inert atmosphere and during this process particles are milled and then turned into thin film.
- iii. The influencing factor in this method is plastic distortion which ends up with particle size, breakage that ends up in particle size, and cold-soldering that ends up to increased particle size.

2. Nano-lithography :

- i. Nanolithography is the investigation of manufacturing nano-scale structures of one dimension at least, with size ranging from 1 to 100 nm.
- ii. There are different nano-lithographic forms, for example optical, electron-pillar, multiphoton, nanoimprint and filtering test lithography.
- iii. Mostly lithography is the way towards printing a required shape or structure of a light sensitive material, which specifically evacuates a bit of material to make the ideal shape and structure.

- iv. The primary advantage of nanolithography is to create a bunch from a solitary nano-particle with desired shape and size.

3. Laser-Ablation :

- i. Laser-ablation is a typical method for the preparation of nano-particles from various solvents in solution.
- ii. A metal immersed in a liquid solution is irradiated by the laser beam, resulting in the formation of plasma crest that yields into nano-particles.
- iii. In this process, a chemical reduction of metals occurs to produce inorganic (metal based) nano-particles.
- iv. As laser ablation gives a steady synthesis of nano-particles in natural solvents and water that does not require any balancing agent or synthetic substance.

4. Thermal Decomposition :

- i. In this method heat is applied to decompose the chemical bonds of the compound.
- ii. It is an endothermic chemical process where the nano-particles are synthesized by roasting a metal at a precise temperature called as decomposition temperature.
- iii. As a result of this decomposition secondary products are also produced.
- iv. This method is useful for the preparation of metal oxide and carbon based nano-particles.

PART-8

Characteristics of Nanomaterials.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.21. | Discuss different characteristics of nanomaterials.

Answer

Characteristics of Nanomaterials :

1. Nanomaterials have structure sizes smaller than 100 nm in at least two dimensions.
2. Nanomaterials can have various shapes and structures such as spherical, needle-like, tubes, platelets, etc.
3. Chemical composition is another important parameter for the characterization of nanomaterials, which comprise nearly all substance

classes e.g. metals/ metal oxides, polymers, compounds as well as biomolecules.

4. Under ambient conditions nanoparticles tend to stick together and form aggregates and agglomerates.
5. These aggregates and agglomerates have various forms, from branched structure to chain or spherical structures with sizes normally in the micrometer range.
6. The properties of nanomaterials can be significantly altered by surface modification.
7. Physical state of nanomaterials depends on medium in which they are dispersed e.g., in gaseous, liquid or solid phase.

PART-9

Applications of Nanomaterials.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.22. Give general application of nano-materials.

OR

Give the applications of nano-materials in electronics and medicine.

AKTU 2017-18 (Sem-2), Marks 07

Answer

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. **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.
- d. Nano-materials 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 terabyte per square inch.
 3. Very high speed transistors from single atom thick graphene film.

PART-10

Carbon Nano Tubes.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.23. Explain carbon nano tubes (CNTs) and its types. Also discuss properties and application of CNTs.

Answer

A. CNTs :

1. Carbon nano tubes (CNTs) are a type of carbon with a diameter of nanometers and a length of micrometres (where the length to diameter ratio exceeds 1000).
2. CNT is made up of enrolled cylindrical graphitic sheets (named graphene) wrapped up into a seamless cylinder with a nanometer-sized diameter.

3. There are two types of Carbon Nanotubes :

- i. **Single-walled Carbon Nanotubes :** Single-walled Carbon nanotubes is represented as SWCNT. The Single-walled Carbon nanotubes exist in a 1-d structure.
- ii. **Multi-walled Carbon Nanotubes :** Multi-walled Carbon nanotubes is represented as MWCNT. It is composed of several nested carbon nanotubes. This type of nanotubes has two diameters, one is known as outer diameter and another one is known as inner diameter.

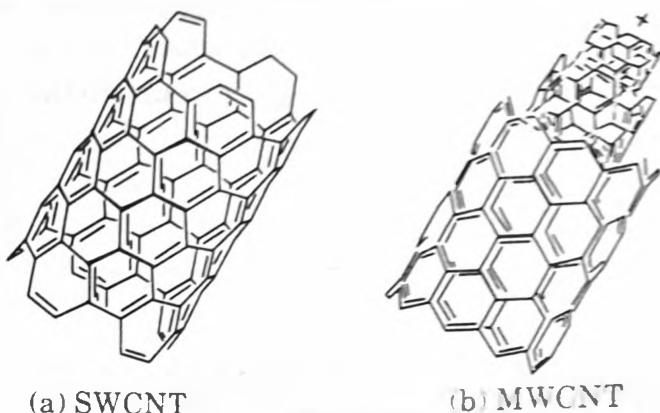


Fig. 1.23.1.

B. Properties of Carbon Nanotube :

1. Carbon nanotubes are stiff in nature.
2. The gravitational weight of the nanotube is very low.
3. The density of the carbon nanotubes is one-fourth of that of steel.
4. Carbon nanotubes are stronger than steel.
5. Carbon nanotubes have a high thermal capacity. Therefore carbon nanotubes uses in making bridges and aircrafts material.
6. In carbon nanotubes, each carbon atom is surrounded by three other carbon atoms through covalent bonds. These carbon-carbon covalent bonds form lattices in the shape of hexagons.
7. The crystalline structure of carbon nanotubes exists in the form of regular hexagons.
8. Carbon nanotubes are elastic.
9. Carbon nanotubes are good conductors of heat and electricity.
10. Carbon nanotubes are chemically neutral. Therefore, carbon nanotubes resist corrosion.

C. Applications of Carbon Nanotubes :

1. **Cancer Tumor Destruction :** CNTs are used to destroy cancer tumors. The antibody along with nanotubes is attracted to the proteins by cancer cells in the body and nanotubes absorb the laser beam killing the bacteria of the tumor.
2. **Windmill Blades :** CNTs are also used in the windmill blades because of their low weight. It increases the efficiency of the windmill and helps to produce more electricity at a faster rate.
3. **Filtration :** CNTs can be used to separate particles of size greater than the diameter of carbon nanotubes during filtration through them. They can also be used to trap smaller sized ions from a solution.
4. **Absorb Infrared Lights :** CNTs absorb infrared light and have applications in the IR optics industry.

5. **Aircraft Stress Reduction :** CNTs are also used in space and aircraft to reduce the weight and stress of the various components working together.
6. **Other uses of Carbon Nanotubes :** CNTs are used as catalysts in some reactions. They are also used in drug delivery systems and in applications related to conductivity in electronics.

PART-11

Green Chemistry.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.24. Define green chemistry and discuss its benefits.

Answer

A. Green Chemistry :

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

B. Benefits of Green Chemistry Includes :

1. **Cleaner Air :** Less release of hazardous chemicals to air leading to less damage to lungs.
2. **Cleaner Water :** Less release of hazardous chemical wastes to water leading to cleaner drinking and recreational water.
3. **Increased Safety :** Less use of toxic materials, so that, less personal protective equipment required and less potential for accidents in chemical industries.
4. **Safer food :** Elimination of persistent toxic chemicals that can enter the food chain, safer pesticides that are toxic only to specific pests and degrade rapidly after use.

PART-12

Principles and Importance of Green Synthesis.

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

Que 1.25. Discuss 12 principles of green chemistry.

Answer

Principles that Demonstrate the Breadth of the Concept of Green Chemistry :

1. **Prevent Waste** : It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Maximize Atom Economy** : Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Design Less Hazardous Chemical Syntheses** : Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Design Safer Chemicals and Products** : Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Use Safer Solvents and Reaction Conditions** : The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Increase Energy Efficiency** : Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use Renewable Feedstocks** : A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Avoid Chemical Derivatives** : Unnecessary derivatization (use of blocking groups, protection / deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Use Catalysts, not Stoichiometric Reagents** : Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. Example: Synthetic reagents, organometallics and building blocks.
10. **Design Chemicals and Products to Degrade after use** : Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Analyze in Real Time to Prevent Pollution :** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Minimize the Potential for Accidents :** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Que 1.26. What is the importance of green synthesis ?

Answer

Importance of Green Synthesis Includes :

1. Green synthesis prevents pollution at the molecular level.
2. Green chemistry is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry.
3. It applies innovative scientific solutions to real-world environmental problems.
4. It results in source reduction because it prevents the generation of pollution.
5. It reduces the negative impacts of chemical products and processes on human health and the environment.
6. It lessens and sometimes eliminates hazard from existing products and processes.
7. It designs chemical products and processes to reduce their intrinsic hazards.

PART- 13

Green Chemicals.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 1.27. Define green chemicals and discuss examples of green chemicals.

Answer

- A. **Green Chemicals :** Green chemicals are one that provides higher performance and functionality while being more environmental friendly throughout its entire life-cycle.

B. Examples of Green Chemicals :

1. **Green Solvents** : Traditional solvents are often toxic or chlorinated. Green solvents, on the other hand, are generally less harmful to the environment. Ideally, solvents derived from renewable resources and naturally occurring product like water and supercritical CO₂.
2. **Carbon Dioxide as Blowing Agent** : Polystyrene foam is a common material used in packing and food transportation. Supercritical carbon dioxide works equally as well as a blowing agent like polystyrene without any emission of CFCs (Ozone depleting gases).
3. **Bio-succinic Acid** : Succinic acid is a platform chemical that is an important starting material in the formulations of everyday products. Bio-succinic acids made from the fermentation of renewable feedstock in place of petroleum products, at a lower cost and lower energy expenditure than the petroleum equivalent.
4. **Bio-Diesel** : Bio-Diesel is a type of biofuel made by process of alcoholysis in place of petroleum products. It involves reacting vegetable oils or animal fats catalytically with short chain alcohols like methanol or ethanol.
5. **Green Hydrazine** : Hydrazine is traditionally produced by the Olin Raschig process from sodium hypochlorite (the active ingredient in many bleaches) and ammonia which is hazardous in nature. So, the peroxide process for producing hydrazine without cogenerating salt account as green chemical.
6. **1,3-Propanediol** : Green route to 1,3-propanediol, which is traditionally generated from petrochemical precursors. It can be produced from renewable precursors via the bio-separation of 1,3-propanediol. This is used to make new polyesters for the manufacture of carpets.
7. **Lactide** : Lactic acid is produced by fermenting corn and converted to lactide a cyclic dimer ester of lactic acid. Which converted into crystallize polymer, which has some applications including textiles and apparel, cutlery, and food packaging.

PART - 14

Synthesis of typical Organic Compounds by Conventional and Green Route (Adipic Acid and Paracetamol).

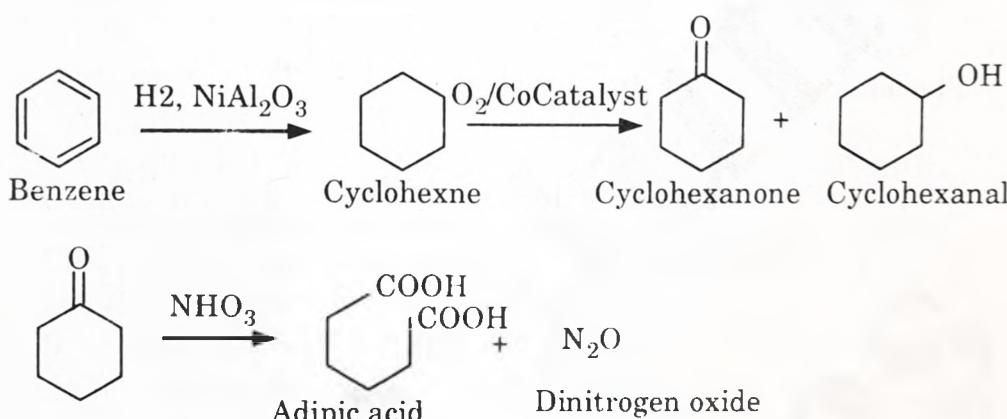
Questions-Answers

Long Answer Type and Medium Answer Type Questions

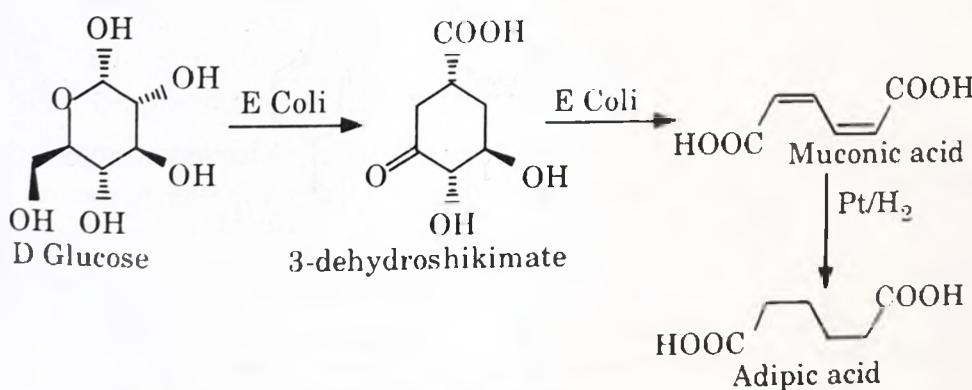
Que 1.28. Explain conventional and green synthesis of adipic acid.

Answer**A. Synthesis of Adipic acid - Conventional synthesis from Benzene :**

1. Adipic acid is the essential feedstock for making synthetic fibres such as nylon.
2. Reduction of benzene in presence of Raney Nickel gives cyclohexane.
3. Cyclohexane on oxidation in presence of Cobalt catalyst gives cyclohexanone and cyclohexanal.
4. The final product adipic acid is obtained by the oxidation of cyclohexanone in the presence of nitric acid.

**Fig. 1.28.1.****B. Synthesis of Adipic acid - Green Synthesis from Glucose :**

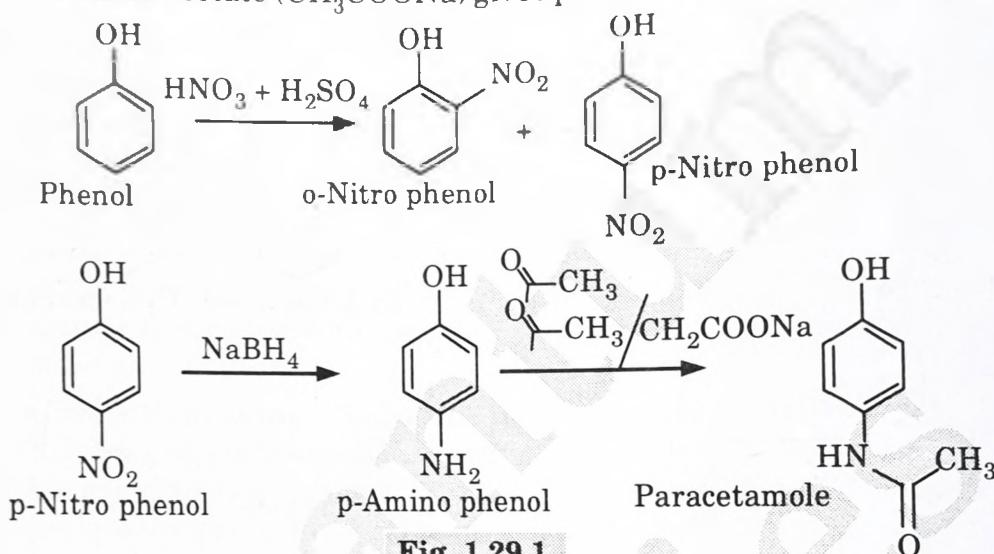
1. Glucose is treated with Escherichia coli (E.coli) bacteria to produce 3-dehydroshikimate. 3-dehydroshikimate is further reacted with E.coli to produce Cis-Cis muconic acid.
2. The formed product on reduction in presence of Pt/H₂, produces adipic acid.

**Fig. 1.28.2.**

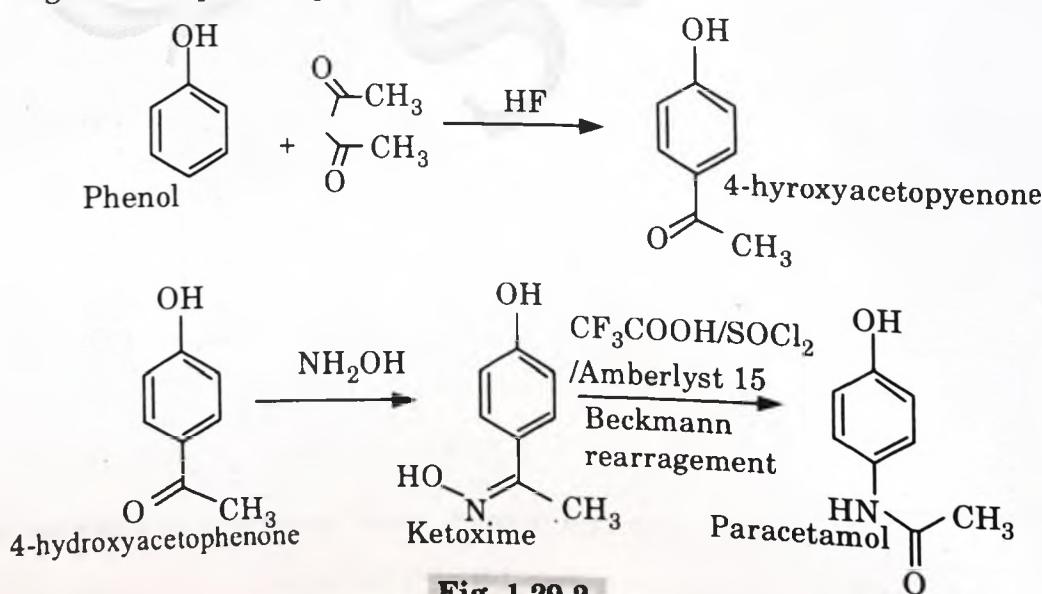
Que 1.29. Explain conventional and green synthesis of paracetamol.

Answer**Paracetamol-Conventional Synthesis from Phenol :**

- When Phenol is treated with nitrating mixture P-nitro phenol and o-nitro phenol are formed.
- In the presence of sodium boro hydride (or hydruxylamine (NH_2OH), or Raney Ni/ H_2). p-nitrophenol gets reduced to p-aminophenol.
- On acetylation of p-aminophenol with acetic anhydride in the presence of sodium acetate (CH_3COONa) gives paracetamol.

**Paracetamol- Green Synthesis from Phenol :**

- Phenol undergo acylation reaction with acetic anhydride in presence of hydrogen fluoride gives ketone.
- Which on reaction with hydroxylamine gives ketoxime.
- Ketoxime undergoes Beckmann's rearrangement reaction in the presence of trifluoroacetic acid, thionyl chloride and Amberlyst 15 catalyst gives final product paracetamol.



PART - 15*Environmental Impact of Green Chemistry on Society.***Questions-Answers****Long Answer Type and Medium Answer Type Questions****Que 1.30. | Discuss impact of green chemistry on society.****Answer**

Green chemistry impact society positively in various aspects such as :

A. Human Health :

1. **Cleaner Air :** Less release of hazardous chemicals to air leading to less damage to lungs.
2. **Cleaner water :** Less release of hazardous chemical wastes to water leading to cleaner drinking and recreational water.
3. **Increased Safety :** Less use of toxic materials, so that, less personal protective equipment required and less potential for accidents in chemical industries.
4. **Safer Food :** Elimination of persistent toxic chemicals that can enter the food chain, safer pesticides that are toxic only to specific pests and degrade rapidly after use.
5. **Hazardous Safety :** Less exposure to toxic chemicals which may act as endocrine disruptors.
6. **Safer Products :** Safer products such as medicines, sanitization products and pesticides available in the market for consumer use.

B. Environment :

1. Many chemicals end up in the environment during use or during disposal. In case green chemicals, they either degrade to innocuous products or recovered for further use.
2. Reduced plants and animals sufferation from harmful and toxic chemicals in the environment.
3. Lower potential for global warming, ozone depletion, and smog formation.
4. Less chemical disruption of ecosystems.
5. Less use of landfills, especially hazardous waste landfills.

C. Economy and Business :

1. Fewer synthetic steps allow faster manufacturing of products, increasing plant capacity and save energy.
2. Reduced waste, eliminating costly remediation, hazardous waste disposal, and end-of-the-pipe treatments.
3. Reduced use of petroleum products and avoiding their hazards and price fluctuations.
4. Reduced manufacturing plant size or footprint.
5. Higher yields for end product, by consuming smaller amounts of raw materials.

VERY IMPORTANT QUESTIONS

Following questions are very important. These questions may be asked in your SESSIONALS as well as UNIVERSITY EXAMINATION.

Q. 1. Draw the molecular orbital diagrams of N₂ and O₂. Calculate their bond orders.

Ans. Refer Q. 1.3, Unit-1.

Q. 2. Discuss the principle, working and applications of liquid crystals in LCDs :

- a. Nematic phase
- b. Chiral nematic phase
- c. Smectic phase

Ans. Refer Q. 1.11, Unit-1.

Q. 3. With the help of neat diagram, describe the structure of graphite. Also, give at least five applications of graphite.

Ans. Refer Q. 1.14, Unit-1.

Q. 4. Discuss the structure, preparation, properties and application of fullerene.

Ans. Refer Q. 1.15, Unit-1.

Q. 5. Discuss 12 principles of green chemistry.

Ans. Refer Q. 1.25, Unit-1.

Q. 6. Explain conventional and green synthesis of adipic acid.

Ans. Refer Q. 1.28, Unit-1.





Atomic and Molecular Structure (2 Marks Questions)

1.1. Graphite is good conductor of electricity. Why ?

AKTU 2017-18 (Sem-2), Marks 02

Ans. It is a very good conductor of electricity due to π -electron clouds on both sides of planes of carbon atoms.

1.2. Write any two applications of nanotechnology.

AKTU 2017-18 (Sem-1), Marks 02

AKTU 2018-19 (Sem-1), Marks 02

Ans.

- i. In automobiles
- ii. In space of defence
- iii. In medical field
- iv. In textile

1.3. What is Valence band ?

Ans. The band formed by a series of energy levels containing the valence electrons is called the valence band.

1.4. What is Forbidden band ?

Ans. The energy gap between the valence band and conduction band is called the Forbidden Energy Gap or the Forbidden Band.

1.5. On the basis of MO theory explain why hydrogen forms diatomic molecule while helium remains monoatomic.

Ans.

- A. **Hydrogen :** As per MO theory, the electronic configuration of H_2 is σ_{1s}^2 which is a stable form. So hydrogen exists in diatomic form.
- B. **Helium :** As per MO theory, the electronic configuration of He_2 is $\sigma_{1s}^2, \sigma_{1s}^{*2}$. Thus, the stabilizing effect of bonding orbitals is cancelled out by the destabilizing effect of antibonding orbitals hence the molecule does not exist. This is why helium remains monoatomic.

1.6. Arrange the following in the increasing order of their bond energy O_2, O_2^{2+}, O_2^{2-} .

AKTU 2017-18 (Sem-1), Marks 02

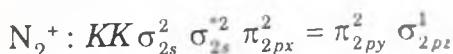
Ans. $O_2^{2+} > O_2 > O_2^{2-}$

- 1.7. Calculate the bond order of N_2^+ .

AKTU 2017-18 (Sem-2), Marks 02

Ans.

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



$$3. \quad \text{Bond order} = \frac{1}{2} (7 - 2) = 2 \frac{1}{2}$$

- 1.8. Arrange the following molecules/ions in order of their increasing bond length : N_2 , N_2^- and N_2^{2-} .

AKTU 2018-19 (Sem-1), Marks 02

Ans. $N_2 < N_2^- < N_2^{2-}$

- 1.9. Give the approaches used for the preparation of nanomaterials.

AKTU 2018-19 (Sem-2), Marks 02

Ans.

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

- 1.10. Why O_2 is paramagnetic and N_2 is diamagnetic ?

AKTU 2020-21 (Sem-1), Marks 02

Ans. O_2 is paramagnetic because it contains unpaired electrons while N_2 is diamagnetic due to no presence of unpaired electrons.

- 1.11. Why graphite used as lubricant ?

AKTU 2018-19 (Sem-2), Marks 02

Ans. Due to presence of loosely bounded sheets of carbon atoms graphite shows slippery texture that makes it effective lubricant.

- 1.12. Arrange the following molecules or ions in increasing order of bond length. O_2 , O_2^+ & O_2^-

AKTU 2021-22 (Sem-1), Marks 02

Ans. Increasing order of bond length



Because bond order $\propto \frac{1}{\text{Bond length}}$

1.13. What are nano-materials ? How are they different from bulk materials ?

AKTU 2021-22 (Sem-1), Marks 02

Ans.

- A. Nanomaterial is defined as a material with any external dimension is **not** scale or having internal structure or surface structure in nanoscale.
- B. Nanomaterials are invisible to naked eyes but bulk material's particle can be seen.

1.14. Explain why helium is monatomic and hydrogen is diatomic ?

AKTU 2021-22 (Sem-2), Marks 02

Ans. As per molecular orbital theory, the electronic configuration of helium molecule is $(\sigma 1s^2)(\sigma^* 1s^2)$ and hence the bond order is 0. Thus zero value indicates that Helium He_2 molecule does not exist.

Hydrogen exist in diatomic molecules as per molecular orbital theory, the electronic configuration of Hydrogen molecule is $(\sigma 1s^2)(\sigma^* 1s^0)$ and hence the bond order is 1. Thus 1 bond order indicates that H_2 molecule exists.

1.15. Arrange the following molecules or ions in increasing order of bond stability. N_2^{2-} , N_2^- and N_2

AKTU 2021-22 (Sem-2), Marks 02

Ans. Bond stability \propto Bond order

$$\text{B.O. of } \text{N}_2^{2-} = 2$$

$$\text{B.O. of } \text{N}_2^- = 2.5$$

$$\text{B.O. of } \text{N}_2 = 3$$

Increasing order of Bond stability as

$$\text{N}_2^{2-} < \text{N}_2^- < \text{N}_2$$

Increasing order of Bond stability

1.16. What is green chemistry ?

Ans. Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.

1.17. List the benefits of green chemistry ?

Ans. Benefits of green chemistry include :

- i. Cleaner air
- ii. Cleaner water
- iii. Safer food.



2

UNIT

Spectroscopic Techniques and Applications

CONTENTS

Part-1 :	Elementary Idea and Simple	2-2B to 2-24B
	Applications of UV, IR and NMR	
Part-2 :	Stereo Chemistry	2-24B to 2-25B
Part-3 :	Optical Isomerism in Compounds	2-25B to 2-26B
	without Chiral Carbon	
Part-4 :	Geometrical Isomerism	2-26B to 2-28B
Part-5 :	Chiral Drugs	2-28B to 2-30B

PART - 1*Elementary Idea and Simple Applications of UV, IR and NMR.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 2.1. | **What is spectroscopy ? Discuss various types of spectroscopy.**

Answer**A. Spectroscopy :**

1. The study of the emission and absorption of light and other electromagnetic radiations by matter is known as spectroscopy.
2. This technique employ light tends to interact with matter and exhibit some features of a sample to know much about its consistency or structure.
3. The nature of the interactions in spectroscopy techniques between radiation and matter may includes- absorption, emission or scattering.
4. Spectroscopy also deals with the study of the interactions between particles like protons, electrons, and ions.
5. They are measured by examining the absorbed or emitted radiant energy by the sample or object.
6. Here, the beam of electromagnetic radiation like infrared rays, UV rays, etc., are passed on the sample and the response of the sample is measured through the wavelength of the electromagnetic spectrum applied from the external energy source.

B. Types of Spectroscopy :

1. **Absorption Spectroscopy :** Absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample.
2. **Emission Spectroscopy :** Emission spectroscopy is a spectroscopic technique which examines the wavelengths of photons emitted by atoms or molecules during their transition from an excited state to a lower energy state.
3. **Scattering Spectroscopy :** Scattering spectroscopy tests the amount of light at specific wavelengths, incident angles, and polarization angles that a material scatter. Raman spectroscopy is one of the most beneficial applications of light scattering spectroscopy.

Que 2.2. Explain principle of absorption spectroscopy (Beer-Lambert's Law).

Answer

Principles of Absorption Spectroscopy :

1. Absorption spectroscopy is based on law known as Beer-Lambert law.
2. When electromagnetic radiations pass or fall onto homogeneous medium, some amount of light is reflected, some amount is absorbed and remained is transmitted.
3. Absorption spectroscopy is governed by two laws i.e., Lambert's law and Beer's law, in the combined form it is known as Beer-Lambert law.
4. **Lambert's Law :** It states that when monochromatic light passes through a transparent medium, the intensity of transmitted light decreases exponentially as the thickness of absorbing material increases.
5. **Beer's Law :** It states that the intensity of transmitted monochromatic light decreases exponentially as the concentration of the absorbing substances increases.
6. Beer-Lambert's law mathematically expressed as,

$$A = \log I_o / I e.c.l$$

Where,

A = Absorbance

I_o = Intensity of incident light

I = Intensity of light through the sample.

e = Extinction coefficient or absorption coefficient.

c = Concentration

l = Path length (cm)

Que 2.3. Give various application of spectroscopy.

Answer

Application of Spectroscopy :

1. Spectroscopy is mainly used for studying the structure of molecules and atoms.
2. Spectroscopy can also be used for finding the unknown chemical composition of materials.
3. The study of the spectral emission lines will help astronomers to study distant galaxies.
4. Spectroscopy used for monitoring of composites using optical fibers.
5. It is most commonly used for estimating weathered wood exposure using infrared spectroscopy.
6. Absorption spectroscopy is usually used both visible and infrared spectrum for Measurement of different compounds in food samples.
7. Spectroscopy is also used for the measurement of toxic compounds in blood samples.

8. Non-destructive elemental analysis by X-ray fluorescence used in the electronic structure research by using various types of spectroscopy.

Que 2.4. Explain UV-Visible spectroscopy and electronic transition on absorption of UV visible light.

Answer

A. UV-Visible spectroscopy :

- 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.
- According to this, positions and velocities of nuclei do not change during the electronic transitions which occur more quickly than the period of vibration of the nuclei as they are heavier compared to electron.
- This spectroscopy is usually applied to molecules or inorganic complexes in solution. The UV-Visible spectra have broad features that are of limited use for sample identification but are very useful for quantitative measurements.
- UV-Visible spectroscopy is useful to characterize the absorption, transmission and reflectivity of a variety of technologically important materials, such as pigments, coatings, windows, and filters.
- This more qualitative application usually requires recording at least a portion of the UV-Visible spectrum for characterization of the optical or electronic properties of materials.

B. Classifications of electronic transitions :

- ($\sigma - \sigma^*$) Transition :** As (σ) electrons are held more firmly in the molecule, this transition takes place in UV or far UV region.
- ($\pi \rightarrow \pi^*$) Transition :** This transition takes place in the near UV and visible regions.
- ($n - \pi^*$) Transition :** This transition is generally of weak intensities and lie in the visible region.

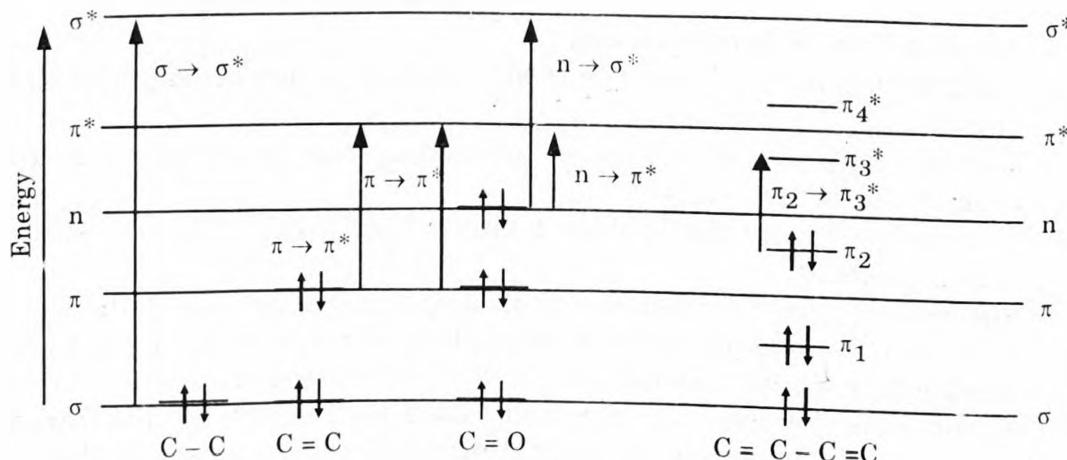


Fig. 2.4.1. Electronic transitions and relative energies of molecule orbitals.

Que 2.5. Define the term chromophore and auxochrome in UV spectroscopy.

OR

Write notes on chromophore and auxochrome. Explain transition in UV spectra.

AKTU 2020-21(Sem-1), Marks 10

Answer

A. **Transition in UV Spectra :** Refer Q. 2.4, Page 2-4B, Unit-2.

B. **Chromophore :**

1. A chromophore was considered any system (atom or group) which is responsible for imparting colour to the compound. It is a Greek word, i.e., Chromophorus which means colour carrier.
2. For example, in nitro compounds the yellow colour is carried by $-NO_2$ group and hence NO_2 group is a chromophore.
3. The term has been extended these days and chromophore is defined as a covalently bonded unsaturated group that shows a characteristic absorption in UV or visible region.
4. The absorption occurs irrespective of the fact whether the colour is produced or not. Typical examples are $C = C$, $C \equiv C$, $C = N$, $C \equiv N$, $C = O$ etc.
5. Chromophores can further be classified into two types :
 - i. Chromophores which contain π electrons and they undergo $\pi - \pi^*$ transitions. Examples are $C = C$, $C \equiv C$ etc.
 - ii. Chromophores which contain both π electrons as well as non-bonding electrons and undergo $\pi - \pi^*$ and $n - \pi^*$ transitions. Examples are $C = O$, $C \equiv N$ etc.

C. **Auxochrome :**

1. Auxochrome can be defined as any group whose presence brings about a shift of the absorption band towards the longer wavelength. Actually auxochrome is the colour enhancing group.
2. The effect of auxochrome is due to its ability to extend the conjugation of a chromophore by the sharing of non-bonding electrons.
3. Thus, a new chromophore which has different value of absorption results maximum.
4. The examples of auxochrome groups include $-OR$, $-NH_2$, $-NR_2$ etc. Benzene shows an absorption maximum at 255 nm whereas aniline at 280 nm. Hence, amino group ($-NH_2$) is an auxochrome.

Que 2.6. Give the applications of UV-Visible spectroscopy.

OR

Discuss the instrumentation of UV-Visible spectrophotometry.

Answer

A. Instrumentation : Name of the various parts of the UV-Visible spectrophotometer are :

1. Source of radiation
2. Monochromator
3. Slits
4. Sample holder
5. Detectors.

B. Applications :

1. **Qualitative analysis :** The UV spectrum of an unknown compound is taken and it is compared with the spectra of known compound, to identify the unknown.
2. **Detection of impurities :** UV absorption method is one of the best methods of determining impurities. Due to impurities the bands are very intense. Further impurity of an unsaturated compound in saturated, is very easy to detect as saturated compounds have negligible UV absorption.
3. It can be used for Quantitative analysis
4. **Chemical kinetics :** Since absorbance is directly proportional to concentration of the species (reactant or product), it is possible to study progress of a reaction by UV spectrophotometer.
5. **Tautomeric equilibrium :** UV spectroscopy can be used to determine percentages of various keto and enol forms in tautomeric equilibria.
6. **Structural information :** The fact that $n \rightarrow \pi^*$ transition has particular λ_{max} , it is possible to identify the nature of the chromophore present in a molecule and whether the chromophore - auxochrome are adjacent or apart.
7. Dissociation constants of weak acids / weak bases.

Que 2.7. Predict the electronic transition in CH_3CHO .

Answer

Electronic transition in CH_3CHO :

The possible transition are :

1. $\sigma - \sigma^*$: Due to sigma bond but not allowed (below 190 nm).
2. $n - \pi^*$ and $n - \sigma^*$: Non-bonding electrons are available which can jump over next higher energy level π^* and σ^* . So, the transitions are allowed and can be recorded (from 200 – 480 nm).
3. $\pi - \pi^*$: C = O in this bond π electrons are available but not in conjugation.

Que 2.8. What is Beer-Lambert law in UV-Visible 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 400.

Can ultra-violet spectral data be useful to distinguish the following compounds ? Give reasons.

- Ethyl benzene and styrene.
- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ and $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$

AKTU 2018-19(Sem-1), Marks 10

Answer

A. Beer-Lambert law : Refer Q. 2.2, Page 2-3B, Unit-2.

B. Numerical :

Given : Length = 1 cm, $C = 10^{-3}$ g/L, Mol. Wt = 400, $A = 0.2$

To Find : K and ϵ .

- $$A = K \times x \times C$$

$$0.2 = K \times 1 \times 10^{-3}$$

 Absorptivity, $K = 200$
- Moles $= \text{Wt in gm} / \text{Mol wt} = 10^{-3} / 400 = 25 \times 10^{-5}$ moles
- $$A = \epsilon \times x \times C$$

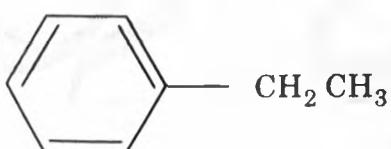
$$0.2 = \epsilon \times 1 \times 25 \times 10^{-5}$$

Molar absorptivity,

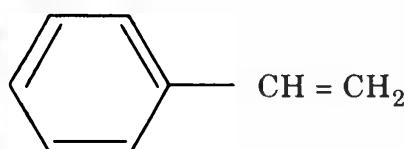
$$\epsilon = 800$$

C.

i.



Ethy benzene



Styrene

Ethyl benzene has 3 conjugated double bonds and styrene has four conjugated double bonds. Hence these two compounds can be differentiated by observing the λ_{\max} value. Styrene will absorb at higher wavelength compared to ethyl benzene

- $\text{CH}_2=\text{CH}-\text{CH}-\text{CH}=\text{CH}_2$ $\text{CH}_3-\text{CH}=\text{CH}=\text{CH}_3$
 1, 4 pentadiene 1, 3 pentadiene

1, 3 pentadiene has two conjugated double bonds. It absorbs UV radiations. 1, 4 pentadiene does not have a conjugated double bond. Therefore it does not show absorption maxima in UV range.

Que 2.9. What type of electronic transitions is involved in UV-visible spectroscopy? Explain the absorption and intensity shift in the UV spectroscopy and support with examples. Illustrate, the effect of polar and non polar solvent on $\pi-\pi^*$ transition in acetone?

AKTU 2018-19(Sem-2), Marks 10

OR

Explain the different types of electronic transitions involved in UV-VIS spectroscopy. Also explain the different types of absorption and intensity shifts taking place in UV-VIS spectroscopy.

AKTU 2021-22(Sem-1), Marks 10

Answer

- A. **Types :** Refer Q. 2.4, Page 2-4B, Unit-2.
- B. **Absorption and Intensity Shift :** There are four types of absorption and intensity shifts observed in the UV spectroscopy :

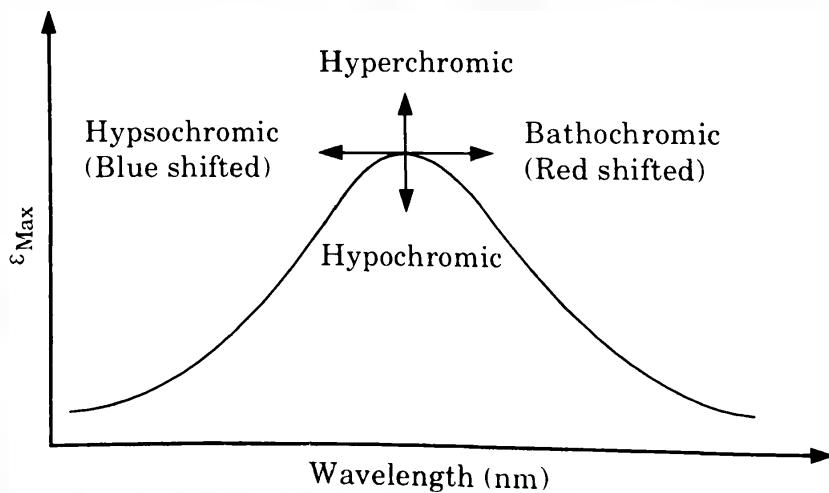


Fig. 2.9.1. Absorption and intensity shifts.

a. Bathochromic Effect :

1. This type of shift is also known as red shift. Bathochromic shift is an effect by virtue of which the absorption maximum is shifted towards the longer wavelength due to the presence of an auxochrome or change in solvents.
2. The nonbonding to pie transition of carbonyl compounds observes bathochromic or red shift.

b. Hypsochromic Shift :

1. This effect is also known as blue shift. Hypsochromic shift is an effect by virtue of which absorption maximum is shifted towards the shorter wavelength.

2. Generally it is caused due to the removal of conjugation or by changing the polarity of the solvents.
- c. **Hyperchromic Effect :** Hyperchromic shift is an effect by virtue of which absorption maximum increases. The introduction of an auxochrome in the compound generally results in the hyperchromic effect.
- d. **Hypochromic Effect :** Hypochromic effect is defined as the effect by virtue of intensity of absorption maximum decreases. Hypochromic effect occurs due to the distortion of the geometry of the molecule with an introduction of new group.

C. Effect :

1. The extent of hydrogen bonding or dipole-dipole interactions in the ground state will be more as compared to that in the excited state.
2. Therefore, the ground state energy of the compound containing the group will tend to decrease as the energy is released during the interactions.
3. Thus, in such groups absorption shifts to shorter wavelength because energy difference ΔE_2 is more than ΔE_1 .
4. For example, λ_{\max} for acetone is 279 nm in hexane solvent (non-polar in nature) but it drops to 264 nm in water (polar solvent).

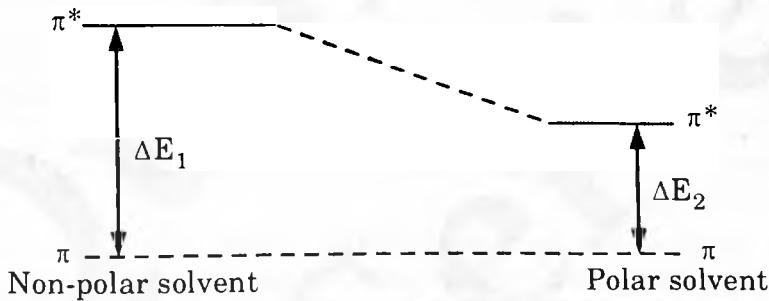


Fig. 2.9.2. Effect of solvent in solvent in $\pi \rightarrow \pi^*$ transition electronic transition.

Que 2.10. | Discuss vibrational spectroscopy.

OR

Write a short note on infrared spectroscopy.

OR

Discuss about various regions of IR spectroscopy.

Answer

A. Vibrational Spectroscopy :

1. Vibrational spectroscopy involves the transitions between the vibrational energy levels of a molecule on the absorption of radiations falling in the spectral range of $400 \text{ cm}^{-1} - 4000 \text{ cm}^{-1}$ (infrared region).

2. A single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appear as vibrational-rotational bands.
3. IR spectroscopy is an invaluable tool in organic structure determination and verification. It uses infrared (IR) radiation with frequencies between 400 cm^{-1} – 4000 cm^{-1} (wave numbers).
4. IR radiations can be utilized in organic structure determination by making use of the fact that it is absorbed by interatomic bonds in organic compounds.
5. Chemical bonds in different environments will absorb varying intensities and at varying frequencies.
6. Thus, IR spectroscopy involves collecting absorption information and analyzing it in the form of a spectrum.
7. The frequencies at which there are absorptions of IR radiation can be correlated directly to bonds within the compound under investigation.
8. As a general rule, the most important factors determining where a chemical bond will absorb are the bond order and the types of atoms joined by the bond.

B. IR spectra are commonly divided into following three regions :

1. Functional Group Region :

- i. It is the high frequency region, between 4000 cm^{-1} – 1300 cm^{-1} (or $2 \mu\text{m}$ – $7.7 \mu\text{m}$).
- ii. This is because the characteristic stretching frequencies for important functional groups such as C = O, OH, and NH occur in this region.

2. Finger Print Region :

- i. It is the middle frequency region, between 1300 cm^{-1} – 900 cm^{-1} (or 7 – $11 \mu\text{m}$).
- ii. In this region, complex absorptions occur due to combinations of interacting vibrational modes, providing a unique finger print for every molecule.
- iii. In this region, numerous peaks are observed and the pattern is complex, due to interacting vibrational modes.
- iv. A peak to peak match of an unknown spectrum with the spectrum of suspected compound in this region helps to assign its structure.

v. 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.

3. Low Frequency Region :

- i. It is the region between 10 cm^{-1} – 650 cm^{-1} (or $11 \mu\text{m}$ – $15 \mu\text{m}$).
- ii. It provides general classification of molecules from the pattern of absorption, such as substitution patterns on a benzene ring.
- iii. The absence of absorptions in this region can provide a good evidence for the absence of an aromatic compound.

- iv. Obtaining a broad, moderately intense absorption in this region indicates the presence of carboxylic dimers, amines, or amides.

Que 2.11. What is finger print region ? Two isomers A and B of the molecular formula C_3H_6O gives an IR absorption at 1650 cm^{-1} and 1710 cm^{-1} respectively. Assign structural formula to A and B isomers.

OR

What is finger print region and functional group region in IR spectroscopy ? Two isomers A and B of the molecular formula C_6H_6O gives IR absorption at 1650 cm^{-1} and 1710 cm^{-1} respectively. Assign structural formula to A and B isomers.

AKTU 2018-19(Sem-1), Marks 10

OR

Explain the different types of molecular vibrations taking place in IR Spectroscopy. Differentiate between Functional group region and finger print region.

AKTU 2021-22(Sem-1), Marks 10

Answer

- A. IR Spectroscopy and Finger Print Region : Refer Q. 2.10, Page 2-9B, Unit-2.
 B. Types of Molecular Vibrations (Normal Modes in XY_2 Groups) :

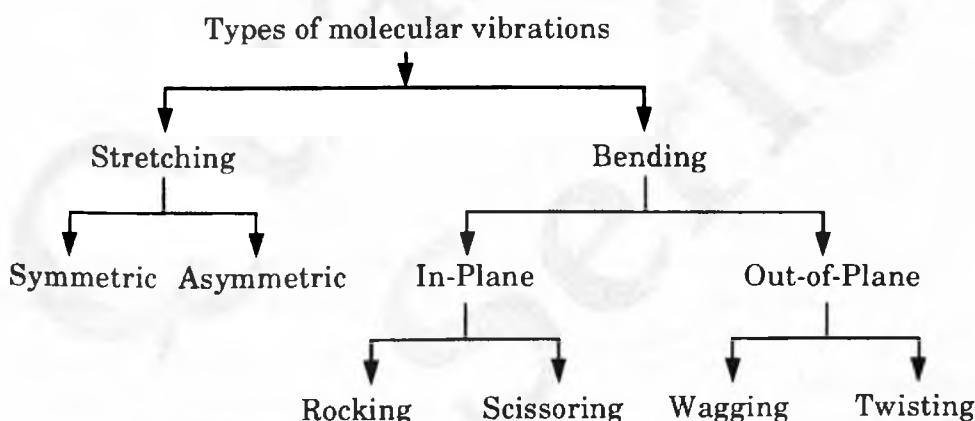
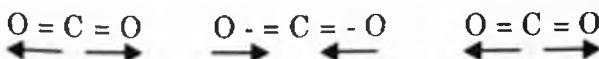


Fig. 2.11.1. Molecular vibration types.

1. **Stretching Vibrations** : In this, bond angle remains constant but the bond length changes. It is of following two types :
 - a. **Symmetric Stretching Vibrations** : It involves alternate stretching and compression of bonds in symmetrical manner.
 For example, in case of CO_2 molecule, the two oxygen atoms move away from or towards the central carbon atom without change in the bond angle.



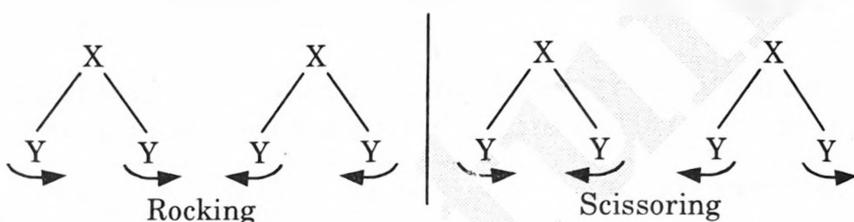
- b. **Asymmetric stretching vibrations :** In this one bond is stretched and the other is compressed and vice-versa. This is illustrated below for CO_2 molecule :



2. **Bending Vibrations :** In this bond angle changes but bond length remains constant. Bending vibrations can either take place within the same plane or out of plane. It is of two types :

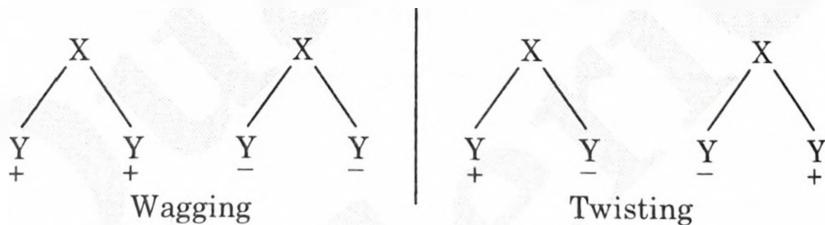
a. **In-Plane Bending Vibrations :**

- i. Rocking, involves the movement of atoms in same direction.
- ii. Scissoring, in it two atoms joined to a central atom move toward and away from each other with the change in bond angle.



b. **Out-of-Plane Bending Vibrations :**

- i. Wagging, in it both the atoms move up and below the plane with respect to the central atom.
- ii. Twisting involves the movement of one atom up and the other atom down the plane w.r.t. the central atom.

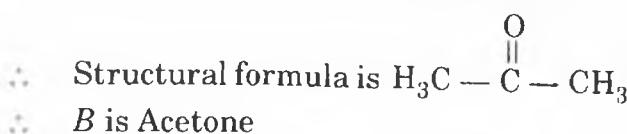


In out-of-plane bending vibrations, the plus sign indicates motion from the page towards the reader, and the minus sign indicates motion away from the reader.

C. Numerical :

Two isomers A and B of Molecular Formula $\text{C}_3\text{H}_6\text{O}$:

1. The peak at 1650 cm^{-1} corresponds to $-\text{OH}$ (alcohol group)
 - ∴ Structural formula is $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{OH}$
 - ∴ A is allyl alcohol
2. The peak at 1710 cm^{-1} corresponds to $\text{C} = \text{O}$ (ketone group)



D. Examples of XY_2 Groups :

1. Methylene groups ($-\text{CH}_2-$)

2. $-\text{NO}_2$ group
3. $-\text{NH}_2$ group.

Que 2.12. Discuss instrumentation of IR spectroscopy.

Answer

1. **Source of Radiation :** IR instruments require a source of radiant energy which emits IR radiation which must have sufficient intensity and should be continuous and stable.
2. **Sampling :**
 - a. **For Gas Sample :** The spectrum of a gas can be obtained by permitting the sample to expand into an evacuated cell, also called a cuvette. Gas cell has NaCl windows at the end.
 - b. **For Solution Sample :** Infrared solution cells consist of two windows of pressed salt sealed. Samples that are liquid at room temperature are usually analyzed in pure form or in solution.

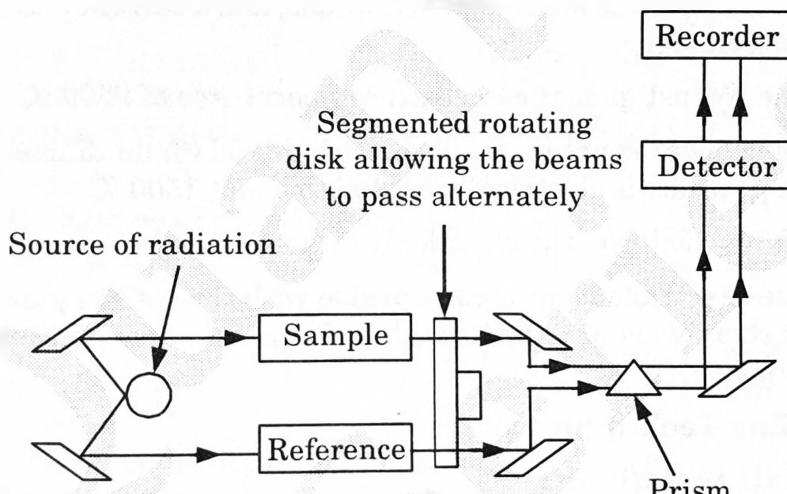


Fig. 2.13.1.

- c. **For Solid Sample :** Solids reduced to small particles (less than 2 micron) can be examined as a thin paste or mull. The mull is formed by grinding 2-5 milligrams of the sample in the presence of one or two drops of a hydrocarbon oil. The resulting mull is then examined as a film between flat salt plates
3. **Monochromator :**
 - a. It splits the polychromatic radiation to component wavelengths with the use of prisms or grating.
 - b. Resolution depends on slit width and quality of mirrors.
4. **Detector :**
 - a. It reacts to infrared radiation.
 - b. It receives infrared frequencies and converts infrared thermal energy into electrical energy.

5. Recorder :

- a. The amplified signal is recorded by a Pen Recorder.
- b. This instrument optically balances out differences between two beams.
- c. In these instruments the intensities of both sample and reference beams are measured.

Que 2.13. | Explain the following in IR spectroscopy

- i. **Radiation sources and**
- ii. **Sampling techniques.**

Answer**i. Radiation Sources :**

- 1. An inert solid is electrically heated to a temperature in the range 1500-2000 K. The heated material will then emit infrared radiation.
- 2. The Nernst glower is a cylinder (1-2 mm diameter, approximately 20 mm long) of rare earth oxides.
- 3. Platinum wires are sealed to the ends, and a current passed through the cylinder.
- 4. The Nernst glower can reach temperatures of 2200 K.
- 5. The glower source is a silicon carbide rod (5mm diameter, 50 mm long) which is electrically heated to about 1500 K.
- 6. Water cooling of the electrical contacts is needed to prevent arcing.
- 7. The spectral output is comparable with the Nernst glower, except at short wavelengths (less than 5 nm) where its output becomes larger.

ii. Sampling Techniques :**1. Mull Technique :**

- a. In this technique, the finely crushed sample is mixed with Nujol (mulling agent) in a marble or agate mortar, with a pestle to make a thick paste.
- b. A thin film is applied onto the salt plates.
- c. This is then mounted in a path of IR beam and the spectrum is recorded.

2. Solid Run in Solution :

- a. In this technique, solid sample may be dissolved in a non-aqueous solvent provided that there is no chemical interaction with the solvent and the solvent is not absorbed in the range to be studied.
- b. A drop of solution is placed on the surface of alkali metal disc and solvent is evaporated to dryness leaving a thin film of the solute.

3. **Case Film Technique :** If the solid is amorphous in nature then the sample is deposited on the surface of a KBr or NaCl cell by evaporation of a solution of the solid and ensured that the film is not too thick to pass the radiation.
4. **Pressed pellet technique :**
 - a. In this technique, a small amount of finely ground solid sample is mixed with 100 times its weight of potassium bromide and compressed into a thin transparent pellet using a hydraulic press.
 - b. These pellets are transparent to IR radiation and it is used for analysis.

Que 2.14. | Give the applications for IR or vibrational spectroscopy.

OR

Define infrared spectroscopy. Describe the various molecular vibrations in the technique and write the application of infrared spectroscopy.

AKTU 2021-22(Sem-2), Marks 10

Answer

- A. **Infrared Spectroscopy :** Refer Q. 2.10, Page 2-9B, Unit-2.
- B. **Molecular Vibrations :** Refer Q. 2.11, Page 2-11B, Unit-2.
- C.
 1. **Identification of functions groups :** As various functional groups have characteristic absorption in IR region, therefore, they can be identified in the organic compound.
 2. **Strength of bonds :** As stronger bonds absorb IR at greater wave number, the relative strength of various bands in the molecule can be understood.
 3. **Identification of organic compound :** From the matching of IR spectra of an unknown sample and a known organic compound, it is possible to identify the unknown organic compound.
 4. **Isomers :** Since IR absorption of a trans isomer is very weak and of cis is stronger, it can be concluded whether the organic compound is having cis or trans structure.
 5. **Structural information :** Since molecules having symmetrical structure about a bond, have negligible absorption in the symmetrical mode of stretching therefore, structure of molecule can be assigned.
 6. **Purity of samples :** Whenever a compound is impure, its IR spectrum is blurred (no sharp peaks).
 7. **Quantitative estimation :** Determining concentration of solution in terms of certain functional group, on the basis of extent of absorption by the group is useful as quantitative estimation technique.
 8. **Study of hydrogen bonding :** Hydrogen bonding decreases the frequency of absorption. Stronger the hydrogen bonding, greater is the shift in frequency of IR absorption.

9. **Monitoring environmental pollution :** A polluted air can be taken in a 20 cm long tube for identification and finding quantity of the pollutant by IR spectroscopy. Water pollutants can also be analyzed by this technique.
10. **Study of reactions :** The kinetics of the organic reactions can be studied by IR spectroscopy. The tautomeric conversions, isomeric conversions, other equilibrium reactions can also be studied with spectroscopy.

Que 2.15. Write the criteria for a molecule to show Raman, IR, rotational and UV spectra. Give the possible electronic transitions (UV spectra) in $\text{CH}_3\text{CH}_2\text{CH}_3$, $\text{CH}_3\text{CH}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{O}$ and $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$. How many fundamental vibrational degrees of freedom are expected for the following molecules : CO_2 , H_2O and C_2H_2 ?

AKTU 2020-21(Sem-1), Marks 10

Answer

A. Criteria :

S. No.	Spectra	Transition	Region of Electromagnetic Spectrum	Criteria
1.	Rotational	Between rotational energy levels	Microwave ($1 - 100$) cm^{-1}	Molecule must possess permanent dipole moment e.g. HCl , H_2O etc.
2.	IR	Between vibrational energy levels	Infrared ($500 - 4000$) cm^{-1}	Dipole moment of molecule must change during vibrations.
3.	UV	Between electronic energy levels	Visible ($12500 - 25000$) cm^{-1} and UV ($25000 - 70000$) cm^{-1}	Presence of chromophore in a molecule.
4.	Raman	Between vibrational and rotational energy levels	Far and near infrared regions	Periodic change in polarizability due to vibrational and rotational transitions.

B. Electronic Transition :

S. No.	Compound	Electronic Transition
1.	$\text{CH}_3\text{CH}_2\text{CH}_3$	$\sigma \rightarrow \sigma^*$
2.	$\text{CH}_3\text{CH}=\text{CH}_2$	$\pi \rightarrow \pi^*$
3.	$\text{CH}_3\text{CH}=\text{O}$	$n \rightarrow \sigma^*$
4.	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	$\pi \rightarrow \pi^*$

C. Vibrational Degree of Freedom :

S. No.	Compound	Degree of Freedom
1.	CO_2	4
2.	H_2O	3
3.	C_2H_2	7

Que 2.16. How will you distinguish between the following pairs of compounds of the basis of infrared spectroscopy ?

- i. CH_3COOH and $\text{CH}_3\text{COOC}_2\text{H}_5$
- ii. $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$

Answer

- i. CH_3COOH shows strong absorption at $2500-3500 \text{ cm}^{-1}$ because of O-H bond while $\text{CH}_3\text{COOC}_2\text{H}_5$ does not show.
- ii. $\text{C}_2\text{H}_5\text{OH}$ shows strong absorption at $3200-3500 \text{ cm}^{-1}$ because of O-H bond while $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ does not show.

Que 2.17. An organic compound having molecular formula $\text{C}_7\text{H}_6\text{O}$ shows absorption peaks at $3010, 2700, 1600, 1580, 1520, 1480$, and 1270 cm^{-1} in its IR spectrum. Suggest its structure.

Answer

1. The compound must be : $\text{C}_6\text{H}_5\text{CHO}$
2. Functional group may be OH or $>\text{C}=\text{O}$.
3. The peak at 1720 cm^{-1} corresponds to $>\text{C}=\text{O}$.
4. The peak at 2700 cm^{-1} corresponds to $>\text{C}=\text{O}$.
5. The peak at 3010 cm^{-1} corresponds to benzene ring.
6. The peak at $1600, 1580, 1520, 1480 \text{ cm}^{-1}$.
7. Corresponds to C = C in ring.
8. The proposed structure is shown in Fig. 2.17.1.



Fig. 2.17.1.

Que 2.18. Among H_2 , HCl , CO_2 , H_2O molecules identify which will be IR active and why?

Explain different mode of vibrations observed in CO_2 molecule. Out of the following pairs which one is expected to absorb at higher frequency for stretching vibrations? Also state reason.

- HCHO , CH_3CH
- $\text{C} \equiv \text{C}$, $\text{C} = \text{C}$

- O-H , C-C

AKTU 2018-19(Sem-2), Marks 10

Answer

A.

- Homonuclear diatomic does not show IR spectra, so H_2 is not IR active.
- HCl is IR active because of net dipole moment.
- CO_2 is not IR active because of symmetrical stretching vibration.
- H_2O is IR active because of net dipole moment.

B. Modes of vibration : Refer Q. 2.11, Page 2-11B, Unit-2.

C.

- HCHO absorbs at higher frequency because its stretching frequency increased due to increase in bond order.
- $\text{C} \equiv \text{C}$ absorbs at higher frequency because it gives higher stretching bonds.
- O-H absorbs at higher frequency because of lower value of reduced mass.

Que 2.19. Explain NMR spectroscopy with its instrumentation and working.

Answer

A. NMR Spectroscopy :

- NMR-spectroscopy is a type of spectroscopy by which we can determine the quality and purity of a sample and the molecular structure of a compound.
- It provides information on the structure of the molecule and determines the content and purity of the sample.

3. The protons present in the molecule will behave differently depending on the surrounding chemical environment, making it possible to depict their structure.
4. The principle behind NMR is that many nuclei have spin and all nuclei are electrically charged.
5. If an external magnetic field is applied, an energy transfer is possible between the base energy to a higher energy level (generally a single energy gap).
6. The energy transfer takes place at a wavelength that corresponds to radio frequencies and when the spin returns to its base level, energy is emitted at the same frequency.
7. The signal that matches this transfer is measured and processed in order to obtain an NMR spectrum for the concerned nucleus.

B. NMR Spectroscopy Instrumentation :

1. **Sample Holder :** It is a glass tube which is 8.5 cm long and 0.3 cm in diameter.
2. **Magnetic Coils :** Magnetic coil generates magnetic field whenever current flows through it
3. **Permanent Magnet :** It helps in providing a homogenous magnetic field at 60 - 100 MHZ
4. **Sweep Generator :** Modifies the strength of the magnetic field which is already applied.
5. **Radiofrequency Transmitter :** It produces a powerful but short pulse of the radio waves.
6. **Radiofrequency :** It helps in detecting receiver radio frequencies.
7. **RF Detector :** It helps in determining unabsorbed radio frequencies.
8. **Recorder :** It records the NMR signals which are received by the RF detector.
9. **Readout System :** A computer that records the data.

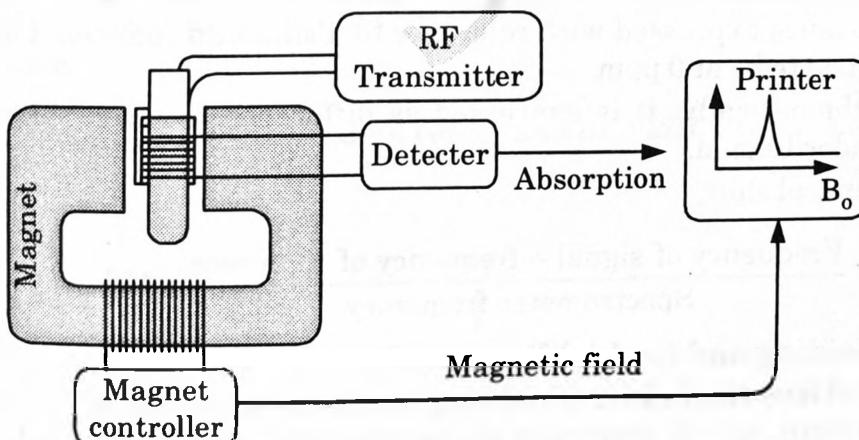


Fig. 2.19.1. NMR Spectroscopy instrumentation.

C. NMR Spectroscopy Working :

1. Place the sample in a magnetic field.
2. Excite the nuclei sample into nuclear magnetic resonance with the help of radio waves to produce NMR signals.
3. These NMR signals are detected with sensitive radio receivers.
4. The resonance frequency of an atom in a molecule is changed by the intramolecular magnetic field surrounding it.
5. This gives details of a molecule's individual functional groups and its electronic structure.
6. Nuclear magnetic resonance spectroscopy is a conclusive method of identifying monomolecular organic compounds.
7. This method provides details of the reaction state, structure, chemical environment and dynamics of a molecule.

Que 2.20. Explain chemical shift in NMR spectroscopy. Also discuss phenomena of shielding and deshielding.

Answer**A. Chemical Shift in NMR Spectroscopy :**

1. Nuclear magnetic resonance chemical change is one of the most important properties used for molecular structure determination.
2. Chemical shift is defined as the difference between the resonant frequency of the spinning protons and the signal of the reference molecule.
3. It is not possible to measure in absolute term the pre existed frequency for a group of nuclei.
4. So, chemical shift is measured with respect to some standard frequency compound (tetramethylsilane).
5. The chemical shift in absolute terms is defined by the frequency of the resonance expressed with reference to a standard compound which is defined to be at 0 ppm.
6. Mathematically, it is expressed as difference between sample and standard signal.

Chemical shift,

$$\delta = \frac{\text{Frequency of signal} - \text{frequency of reference}}{\text{Spectrometer frequency}} \times 10^6$$

B. Shielding and Deshielding :

1. **Shielding (Upfield) :** Shielding is a barrier made of inner-shell electrons and it decreases the nucleus pull on the outer electrons. Shielding is defined as a nucleus whose chemical shift has been decreased due to addition of electron density, magnetic induction, or other effects.

- 2. Deshielding (Downfield) :** When we say that an atom is deshielded, we mean that a nucleus whose chemical shift has been increased due to removal of electron density, magnetic induction, or other effects.

The phenomena of shielding and deshielding with respect to chemical shift could be better understood by the diagram below.

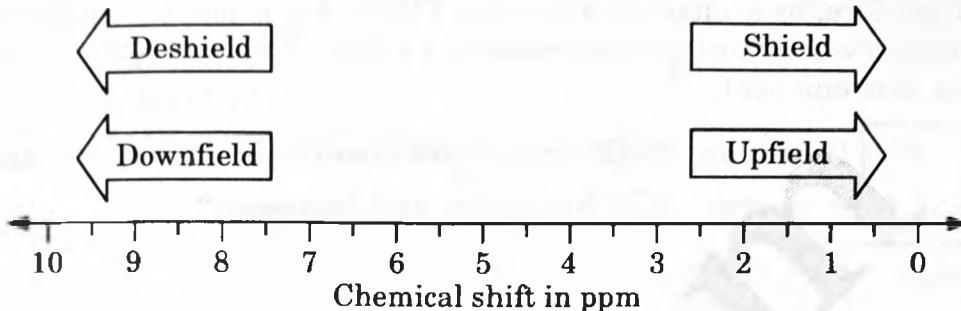


Fig. 2.20.1.

Que 2.21. Give various applications of NMR spectroscopy.

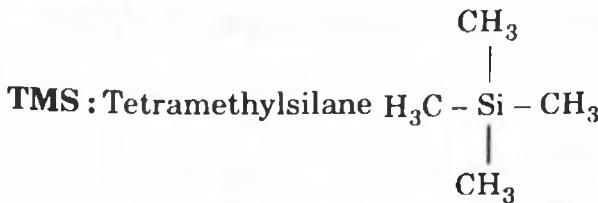
Answer

NMR Spectroscopy Applications :

1. NMR spectroscopy used by chemists and biochemists to investigate the properties of organic molecules.
2. It is used for quantitative analysis of mixtures of compounds.
3. It is a type of spectroscopy used for quality control.
4. It is also used to determine the molecular structure of compounds.
5. It is used to check the purity of samples.
6. It is also used in food science.
7. It is used in the study of drugs in medical sciences.
8. NMR spectroscopy is used in the study of bio-fluids, cells and nucleic acids.

Que 2.22. Why TMS used as reference in NMR spectroscopy.

Answer



TMS is generally employed as a reference in NMR spectrum because of the following facts :

- i. It gives a single sharp line from twelve magnetically equivalent protons.

- ii. It is chemically inert and miscible with a large range of solvents.
 - iii. It being highly volatile can easily be removed if the sample has to be recovered.
 - iv. It does not involve in intermolecular association with the sample.
 - v. It has the added advantage that its resonance position is far removed from the absorptions due to protons in most organic molecules. Therefore, by arbitrarily assigning TMS = 0, it is possible to devise a scale in which most proton resonances will be of the same sign (positive for convenience).

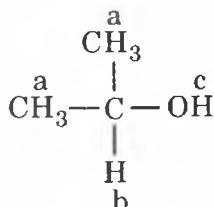
Que 2.23. How many NMR signals are observed in the spectrum of ethanol, isopropyl alcohol, butanone and benzene ?

Answer

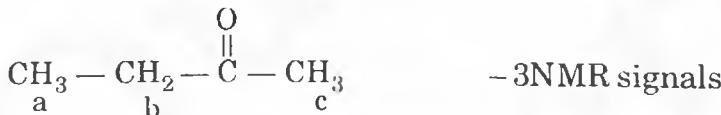
- i. Ethanol : – 3 NMR signals



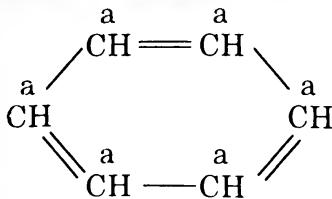
- ii. Isopropyl alcohol : - 3 NMR signals



- ### iii. Butanone :



- #### iv. Benzene:



– single NMR signal

Que 2.24. At what frequency shift from TMS should a group of nuclei with $\delta = 1.00$ resonate in a spectrometer operating at 500 MHz?

Answer

$$\delta = \frac{v_s - v_0}{v} \times 10^6 \text{ or } v_s - v_0 = \delta v \cdot 10^{-6}$$

$$v_s - v_0 = 1.00 \times 500 \text{ MHz} \times 10^6$$

$$= 1.00 \times 500 \times 10^6 \text{ Hz} \times 10^{-6} = 500 \text{ Hz}$$

Que 2.25.

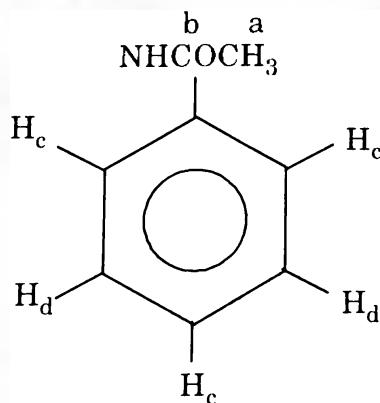
- Explain shielding and deshielding in NMR spectroscopy.
- An aromatic compound (Molecular mass = 135) give the following signal in NMR spectrum.
 - Singlet (2.09δ), 3H
 - A distorted singlet (3.09δ), 1H
 - A multiplet (7.27δ), 3H
 - A multiplet (7.75δ), 2H.

Predict the structure of the compound.

AKTU 2017-18(Sem-1), Marks 10

Answer

- A. Shielding and Deshielding :** Refer Q. 2.20, Page 2-20B, Unit-2.
- B. Molecular Mass of Aromatic Compound is 135 g/mol :**
- singlet 3H $\rightarrow 2.09 \delta$
This appearance of singlet at 2.09δ for three protons shows the presence of the methyl group.
 - A distorted singlet (3.09δ) H.
This distorted singlet at 3.09δ for one proton is due to amide proton
The others are due to benzene ring protons so the predicted structure of compound is,



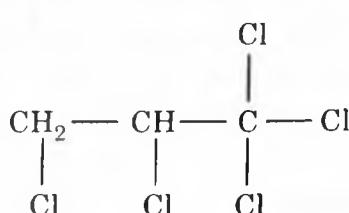
- Que 2.26.** Explain the term chemical shift along with shielding and deshielding. An organic compound with molecular formula $C_3H_3Cl_5$ gave the following proton NMR data :
- A triplet 4.52δ 1H
 - A doublet 6.07δ 2H

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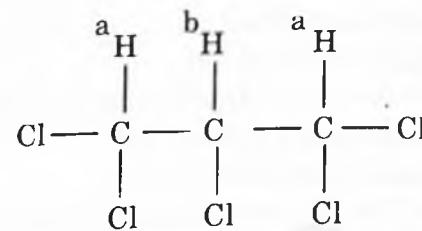
Answer

- A. Chemical Shift, Sheilding and Deshielding :** Refer Q. 2.20, Page 2-20B, Unit-2.

- B.** The formation of a triplet and a doublet suggest that there are two kinds of protons. A doublet due to 2H appearing at low field is clearly more deshielded by greater number of chlorine atoms. The possible structures of the compound may be written as :



(i)



(ii)

Structure (ii) looks more probable. Deshielding due to four chlorine atoms bring the two proton absorption at 607δ . Thus, the given data is consistent with structure (ii).

PART - Z

Stereochemistry.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 2.27. What is stereochemistry ? Explain different types of stereoisomers.

Answer

A. Stereochemistry :

1. Stereochemistry is defined as the branch of chemistry which involves "the study of various spatial arrangements of atoms present in molecules".
2. Using stereochemistry, any chemist can work out the relationships between different molecules that are made up of the same category of atoms.
3. It also studies the effect on the physical or biological properties of molecules.
4. An important part of stereochemistry is the study of chiral molecules.
5. Another branch of 3-D chemistry, known as dynamic stereochemistry, involves the study of the effects of different spatial arrangements of atoms in a molecule on the rate of a chemical reaction.

B. Different types of Stereo Isomerism :

1. **Atropisomerism :** Atropisomerism is the property of any molecule or an object of being non-superimposable on its mirror image.
2. **Cis-trans isomerism :** Cis-trans isomerism shares the same atoms which are joined to one another in the same way but have a different configuration.

3. **Conformational isomerism :** Conformational isomerism is a type of stereoisomerism in which isomers can only be converted by formally single bond rotations.
4. **Diastereomers :** Diastereomers are more optically active in the isomers, which are not enantiomers.
5. **Enantiomers :** An enantiomer is given as one of a pair of optical isomers, which are the structures that are not superimposable on their mirror images.

Que 2.28. Explain the terms :

- i. **Optical Isomerism,**
- ii. **Chirality**

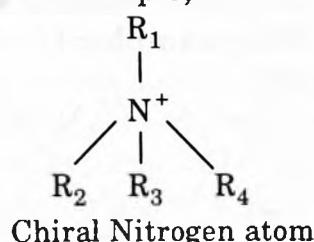
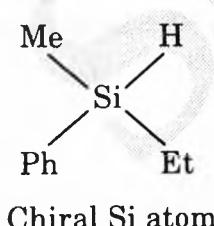
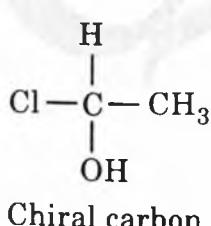
Answer

Optical Isomerism :

1. Compounds having similar chemical and physical properties but differing only in the behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomerism.
2. The optically active isomer which rotates the plane polarised light to the right is known as dextrorotatory (Dexter-right).
3. It is represented by (*d*) or (+) and the one which rotates the plane polarised light towards left is called laevo-rotatory and represented by *l* or (-).

Chirality :

1. Chirality Word comes from Greek and means hand.
2. A chiral molecule is a stereoisomer whose mirror image is non superimposable and which has a chiral centre bounded tetrahedrally to four different atoms or groups.
3. It is usually a carbon atom but may be other element like nitrogen, sulphur, phosphorous which show chirality. For example,



PART-3

Optical Isomerism in Compound without Chiral Carbon.

Questions-Answers

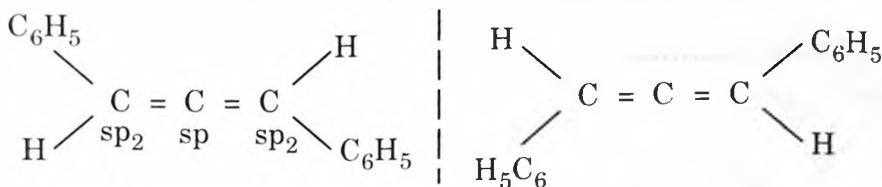
Long Answer Type and Medium Answer Type Questions

Que 2.29. Explain optically active compounds that do not have chiral centre.

Answer

Some compounds are optically active without the presence of chiral carbon atom examples are :

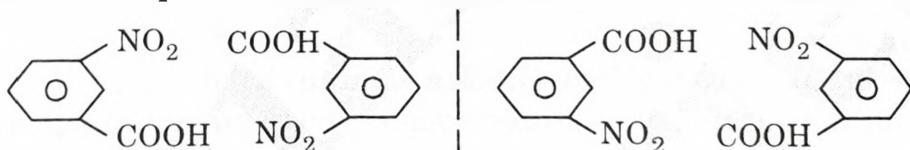
1. **Allenes** : The derivatives of allenes like 1, 3-diphenyl propadiene in which various atoms are hybridised as follows :



Central carbon atom has two mutually perpendicular p orbitals. The substituent at one end are in a plane which is perpendicular to the substituent at other end and compound exist in two non-superimposable mirror images hence it is optically active.

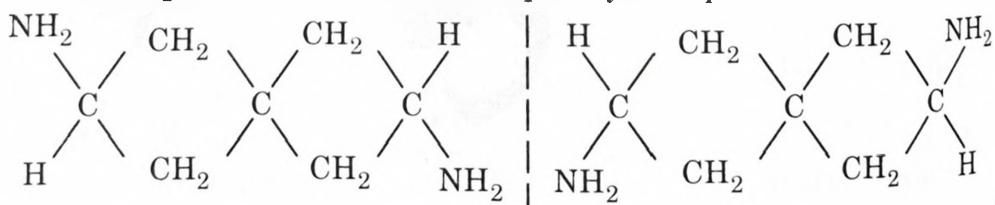
2. **Derivatives of Biphenyls** : When the substituent in second position are large enough to prevent rotation about the bond joining two benzene rings. This restricted rotation prevents two rings from acquiring coplanarity hence optically active.

For example : 2,2-dinitro-6,6-diphenic acid.



3. **Spiranes** : Bicyclic or polycyclic systems have a C atom common to two rings. Spiranes are the compound in which a carbon atom is bonded to four other carbon atoms in such a way that each belongs to a ring. Due to restricted rotation spiranes exhibit optical activity.

For example : 1,7-diamino-(3,3)-spiro cycloheptane



PART-4

Geometrical Isomerism.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 2.30. Explain geometrical isomerism.

Answer

Geometrical Isomerism :

1. The isomerism which results from a restriction in rotation about double bonds in acyclic or about single bond in cyclic molecules is known as geometrical isomerism.
2. A geometric isomer describes the orientation of a functional group in a compound.
3. Generally in a geometric isomer, the atoms are bonded by a double bond that does not rotate but it can also happen because of the ring structure.
4. Based on the position of the functional group the isomers are named as *cis* and *trans*.
5. When a similar group is placed at an adjacent position the compound is named with the prefix *cis*.
6. When a similar group is placed at the opposite position the compound is named with the prefix *trans*.

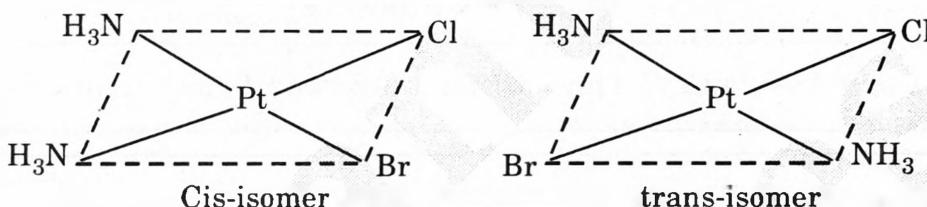


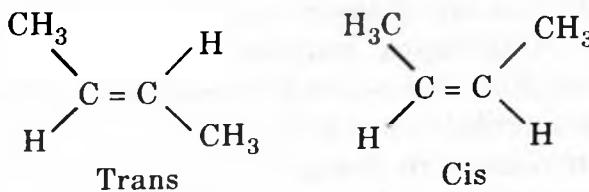
Fig. 2.30.1.

Que 2.31. Explain Geometrical isomerism in simple acyclic and cyclic molecules.

Answer

Geometrical Isomerism in Acyclic Molecules :

In Simple acyclic molecules the isomer in which two similar groups are on the same side of the double bond is termed as *cis* and the isomer in which two similar groups are on opposite side is termed as *trans*. This isomerism is possible when each double bonded carbon atom is attached to two different atom or groups.



Geometrical Isomerism in Cyclic Molecules :

This isomerism is possible in cyclic molecules because there is no rotation about single Carbon-Carbon bonds as they form a ring and rotation will break the ring.

When two R(alkyl) groups are on same side of the ring *cis* isomer is formed, and when are on different side of the ring *trans* is formed. The two alkyl groups must be on different ring carbon atoms.

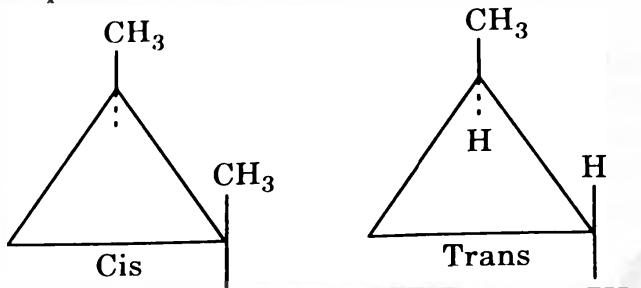


Fig. 2.31.1.

PART-5*Chiral Drugs.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 2.32. Explain chiral drugs and role of enantiomers.

Answer**A. Chiral Drugs :**

1. Chiral stereoisomerism results in different physical and chemical properties of the compound.
2. If this compound happens to be drug then it results in different pharmacokinetic and pharmacodynamic properties.
3. The importance of chiral drugs in the drug development space should not be understated.
4. In pharmaceutical industries, more than half of the drugs currently in use are chiral molecules and most of them are racemic mixtures, consisting of an equimolar mixture of two enantiomers.
5. These two different enantiomers are recognized as two very different substances by our biological systems.
6. And our biological system reacts differently with different enantiomers which may be harmful to our body.

B. Role of enantiomers in drugs :

1. The enantiomers of chiral drugs have the same chemical connectivity of atoms; they exhibit marked differences in their pharmacology, toxicology, pharmacokinetics, metabolism etc.

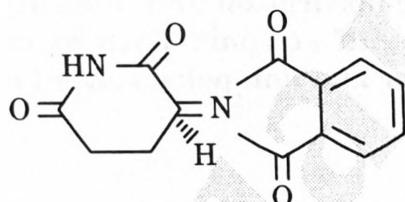
2. Therefore, when chiral drugs are synthesized, the rigorous separation of the two enantiomers is done for safety purposes.
3. This ensures that only the biologically active enantiomer is present in the final drug preparation.
4. The enantiomers of a chiral drug differ in their interactions with enzymes, proteins, receptors and other chiral molecules too including chiral catalysts.
5. These differences in interactions, in turn, lead to differences in the biological activities of the two enantiomers, such as their pharmacology, pharmacokinetics, metabolism, toxicity, immune response etc.

Que 2.33. List drugs whose enantiomers have different properties.

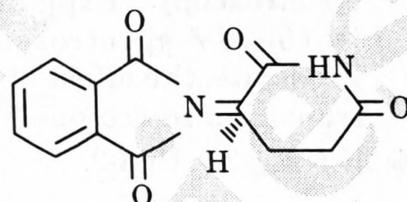
Answer

Few examples of chiral drugs, whose enantiomers vary drastically in their properties :

1. **Thalidomide** : The R-enantiomer is an effective sedative, which has a soothing effect that relieves anxiety and makes the patient drowsy, while, the S-enantiomer is known to cause teratogenic birth defects.

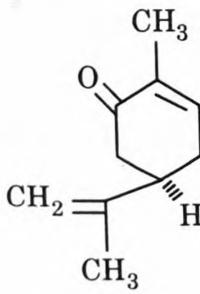


S-Thalidomide

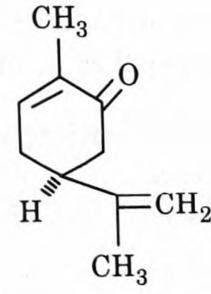


R-Thalidomide

2. **Carvone** : Human olfactory sensory organs are chiral, so the following pair of enantiomers smell very differently to us. R-isomer of carvone smells like spearmint leaves, while S-isomer of carvone smells like caraway seeds.

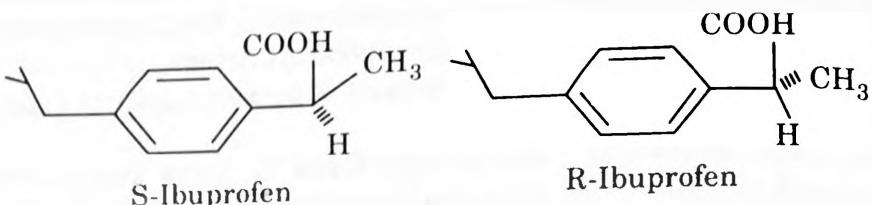


R-Carvone spearmint oil



S-Carvone caraway oil

3. **Ibuprofen** : In the case of the well-known painkiller, ibuprofen, the (S)-enantiomer has the desired pharmacological activity while the (R)-enantiomer is totally inactive.



VERY IMPORTANT QUESTIONS

Following questions are very important. These questions may be asked in your SESSIONALS as well as UNIVERSITY EXAMINATION.

Q. 1. Define the term chromophore and auxochrome in UV spectroscopy.

Ans. Refer Q. 2.5, Unit-2.

Q. 2. What type of electronic transitions is involved in UV-visible spectroscopy ? Explain the absorption and intensity shift in the UV spectroscopy and support with examples. Illustrate, the effect of polar and non polar solvent on $\pi-\pi^*$ transition in acetone ?

Ans. Refer Q. 2.9, Unit-2.

Q. 3. What is finger print region ? Two isomers A and B of the molecular formula C_3H_6O gives an IR absorption at 1650 cm^{-1} and 1710 cm^{-1} respectively. Assign structural formula to A and B isomers.

Ans. Refer Q. 2.11, Unit-2.

Q. 4. Explain chemical shift in NMR spectroscopy. Also discuss phenomena of shielding and deshielding.

Ans. Refer Q. 2.20, Unit-2.

Q. 5. Explain optically active compounds that do not have chiral centre.

Ans. Refer Q. 2.29, Unit-2.





Spectroscopic Techniques and Applications (2 Marks Questions)

2.1. Give the principle of UV-Visible spectrophotometry.

Ans. Energy required for the electronic transitions from BMO (bonding molecular orbital) to ABMO (antibonding molecular orbital) occurs from UV-Visible region and the absorption takes place as per Beer's law.

2.2. Write applications of UV-Visible spectroscopy.

Ans.

- i. Qualitative analysis
- ii. Detection of impurities
- iii. Chemical kinetics
- iv. Structural information.

2.3. Give principle of IR spectroscopy.

Ans. When a molecule absorbs certain wavelength from IR region, the energy in the photons of the wavelength, is utilized for stretching, or bending the two covalent bond depends upon the strength of the bond and masses of the atoms forming the covalent bond.

**2.4. IR spectra is often characterized as molecular fingerprints.
Comment on it.**

Ans. Peaks for various molecules in the region ($1400\text{--}400\text{ cm}^{-1}$) of IR spectra are unique for every molecule. No two molecules have similar peaks in this region so it is known as fingerprint.

2.5. Explain stretching vibration.

Ans. In this mode of vibration, the atoms move along the bond axis so that bond length increases or decreases periodically. This type of vibration corresponds to one dimensional motion.

2.6. Explain bending vibration.

Ans. In this mode, changes occur in bond angles between bonds with a common atom or movement of a group of atoms with respect to remainder of molecule without movement of atoms in the group.

2.7. Write the Beer-Lambert's law

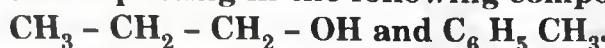
Ans. Beer-Lambert law can be stated as absorption of a light by solution is directly proportional to the concentration of solution and the path length.

$$A = \epsilon \times C$$

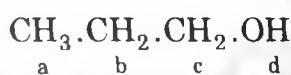
where,
 ϵ = Molar extinction coefficient
 x = Path length
 C = Concentration of sample.

2.8. 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.

2.9. 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

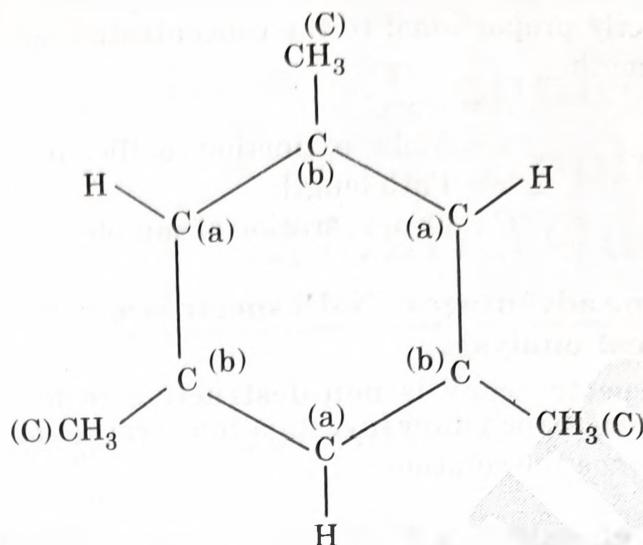
**2.10. How many NMR signals are found in $\text{CH}_3\text{CHOHCH}_2\text{CH}_3$?**

Ans. NMR signals in CH_3 CH OH CH_2 CH_3
 a b c d e

Total signals : Five

2.11. How many NMR signal will be obtained from mesitylene ?

AKTU 2017-18 (Sem-1), Marks 02

Ans.

- 2.12. Which of the following molecules will show rotational spectrum : H₂, HCl, CH₄, CH₃Cl, CH₂Cl₂, H₂O and SF₆ ?

AKTU 2018-19 (Sem-1), Marks 02

Ans. HCl, CH₃Cl and H₂O.

- 2.13. What is the selection rule for the molecule to show rotational spectrum ?

AKTU 2018-19 (Sem-2), Marks 02**Ans.**

1. A molecule must have a transitional dipole moment that is in resonance with an electromagnetic field for rotational spectroscopy to be used.
2. The conservation of the angular momentum is fundamental for the selection rules that allow or prohibit transitions of a linear molecule.

- 2.14. Explain, which one will exhibit higher value λ_{\max} in UV/Visible spectra of CH₃COCH₃ and CH₂ = CHCOCH₃.

AKTU 2018-19 (Sem-2), Marks 02

Ans. CH₂ = CH—C—CH₃ has higher value of λ_{\max} because of presence of conjugation which is not present in CH₃—C—CH₃.



- 2.15. What is selection rule ?

AKTU 2020-21 (Sem-1), Marks 02

Ans. A selection rule describes how the probability of transitioning from one level to another cannot be zero. It has two sub-pieces: a gross selection rule and a specific selection rule.

2.16. On the basis of IR spectra distinguish between intermolecular and intramolecular hydrogen bonding.

AKTU 2020-21 (Sem-1), Marks 02

Ans.

S. No.	Intermolecular Hydrogen Bonding	Intramolecular Hydrogen Bonding
1.	It has free OH group.	It has hydrogen bonded OH group.
2.	Its absorption frequency is 3600 cm^{-1} .	Its absorption frequency ranges from 3200 to 3400 cm^{-1} .

2.17. Explain why CO_2 is IR active and N_2 is IR inactive molecule.

AKTU 2021-22 (Sem-1), Marks 02

Ans. Since CO_2 is linear it has $3n - 5 = 4$
Where n = Number of atoms

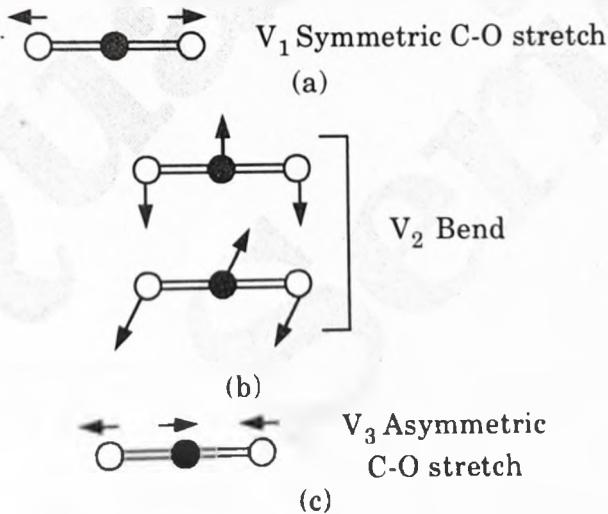


Fig. 1. Vibrational modes of CO_2 .

1. The symmetric stretch does not result in a change (of the initially zero dipole moment), so it is IR active. (See Fig. 1(a))
2. The asymmetric stretch does result in a change in dipole moment so it is IR-active (See Fig. 1(c))
3. The bend also results in a change in dipole moment so it too is IR active (See Fig. 1(b))
4. As N_2 has symmetric molecules and it has only vibrational modes that can exist are stretching of the only bond, which because it is symmetric, does not lead to a dipole change, thus it is not IR active.

2.18. Define stereoisomersim.

Ans. Stereoisomerism is a form of isomerism in which molecules have the same molecular formula and sequence of bonded atoms, but differ in three-dimensional orientation of their atoms.

2.19. Name different types of stereoisomerism.

Ans. Following are the different types of stereoisomerism :

- i. Atropisomerism
- ii. Diasteromers
- iii. Enantiomers

2.20. Define optical isomerism.

Ans. Compound having similar chemical and physical properties but only differing behaviour towards plane polarised lights are called optical isomerism.



3

UNIT

Electrochemistry

CONTENTS

- Part-1 : Basic Concept of Electrochemistry 3-2B to 3-3B**
- Part-2 : Classification and Application of 3-3B to 3-9B**
Primary (Dry Cells) and Secondary
Cells (Lead Acid Battery)
- Part-3 : Introduction to Corrosion 3-9B to 3-10B**
- Part-4 : Types of Corrosion 3-10B to 3-13B**
- Part-5 : Cause of Corrosion 3-13B to 3-14B**
- Part-6 : Corrosion Prevention and 3-14B to 3-20B**
Control
- Part-7 : Corrosion Issues in Specific 3-20B to 3-22B**
Power Generation, Chemical
Processing Industry, Oil and Gas
Industry, Pulp and Paper Industries
- Part-8 : Cement Constituents 3-22B to 3-24B**
- Part-9 : Cement Manufacturing 3-24B to 3-26B**
- Part-10 : Cement Hardening and Setting 3-26B to 3-28B**
- Part-11 : Deterioration of Cement 3-28B to 3-31B**
- Part-12 : Plaster of Paris 3-31B to 3-32B**

PART- 1*Basic Concept of Electrochemistry.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 3.1. Define electrochemistry. What are the two types of cells used in electrochemical process ? Give its importance in practical life.

Answer**A. Electrochemistry :**

1. Electrochemistry 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. This phenomenon is called electrolysis.
3. The reverse is also true i.e., we can generate electric current by the use of a chemical reaction.

B. 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.

C. Importance of Electrochemistry :

1. A number of metals such as Na, Mg, Ca and Al and a number of chemicals such as NaOH, Cl₂, F₂ 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.

PART-2

Classification and Applications of Primary Cells (Dry Cells) and Secondary Cells (Lead Acid Battery).

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.2. Explain primary cells and its types. Also give its applications.

Answer

A. Primary Cell :

1. A primary cell or battery is non-rechargeable, and cannot be reused once its electrolyte is all consumed. Once these batteries get discharged, they serve no more purposes and must be disposed.
2. Primary cells have high density and get discharged slowly.
3. Since there is no fluid inside these cells they are also known as dry cells.
4. The internal resistance is high and the chemical reaction is irreversible. Its initial cost is cheap and also primary cells are easy to use.

B. Types Primary Cell :

1. Zinc-Carbon Cell :

A dry cell consists of a metal container in which a low moisture electrolyte paste covers the graphite rod or a metal electrode. Generally, the metal container will be zinc whose base acts as a negative electrode (anode) and a carbon road acts as a positive electrode (cathode). Zinc-carbon cell is the most common dry cell and is also called Leclanche cell.

2. **Alkaline Battery :** The alkaline battery will have almost same half-cell reactions as zinc-carbon cell, where KOH or NaOH replaces the ammonium chloride.
3. **Mercury Cell :** In the mercury cell, HgO serves as a cathode and zinc metal serves as an anode.
4. **Silver Oxide Cell :** In the basic medium, silver metal acts as inert support in the reduction of silver oxide (Ag_2O) and in the oxidation of zinc.

3-4 B (Sem-1 & 2)

C. Applications of Primary Cells : Primary batteries are found in many common consumer products such as remotes, wall clocks, watches, and mini electronic gadgets.

Que 3.3. Explain secondary cells and its types. Also give its applications.

Answer**A. Secondary Cells :**

1. A secondary cell or battery is the one that is rechargeable and serves multiple purposes for a longer span.
2. By passing current opposite to the direction of discharge, one can effectively recharge the cell again to its original state.
3. Secondary cells have low energy density and are made of molten salts and wet cells.
4. The internal resistance is low and the chemical reaction is reversible. Its initial cost is high and is a little complicated to use when compared to the primary cell.

B. Types of Secondary Cells :**1. Lead Storage Cell :**

In this cell number of voltaic cells is connected in series. The anode is grid of lead and cathode is a grid of lead packed with PbO₂. The electrolyte is an aqueous solution of sulphuric acid.

2. Nickel-cadmium cell :

The Nickel-cadmium cell comprises cadmium as an anode and Nickel plate as a cathode and a separator acts as an insulator between the anode plate and cathode plate. Sodium hydroxide or potassium hydroxide acts as an electrolyte.

3. Lithium-ion cell :

These are popular batteries used nowadays on laptops, iPods, cellphones. The electrodes of the cell are made up of lightweight carbon and lithium. They are less harmful even after disposing and self-discharge is less than half of the NiCd cell.

4. Nickel-metal hydride cell :

In the Nickel-metal hydride cell, NIMH acts as anode and hydrogen-absorbing alloy acts as a cathode.

C. Applications of Secondary cells :

Secondary batteries, often called rechargeable batteries, can be used, discharged, and then restored to their original condition by reversing the current flow (charging). These batteries are commonly used to power Cars, UPS, robotics, cordless phones, solar lights, drones, etc.

Que 3.4. Differentiate between primary and secondary cells.**Answer**

Difference between primary and secondary cells :

S. No.	Primary Cell	Secondary Cell
1.	These cannot be recharged again after getting discharged once.	These can be recharged easily.
2.	These are cheap or low cost.	These are expensive compare to Primary Cell.
3.	These are easy to use.	These are difficult to use in comparison to Primary Cell.
4.	These can be used only once.	These can be used more than once.
5.	In these Cells irreversible reactions occur.	In these Cells reversible reaction occurs.
6.	These have a lower self-discharge rate.	These have a higher self-discharge rate.
7.	These are used in torch and other portable devices as they produce electric current immediately.	These are used in inverters and automobiles.
8.	These Cells don't require regular maintenance and can be disposed of easily after use.	These Cells require regular maintenance.
9.	They have a low or small lifetime.	They have a high lifetime.
10.	Examples of these Cells are dry Cells, Daniel Cells, etc.	Examples of these Cells are lead-acid Cell, nickel - iron Cell etc.

Que 3.5. What is dry cell ? Explain its structure and working.**Answer****A. Dry Cell :**

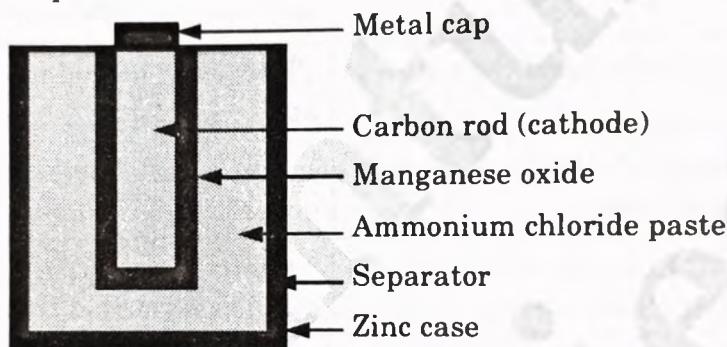
- It is a portable cell contain semi solid electrolyte. This is why; it is called dry cell as it does not contain any liquid.

3-6 B (Sem-1 & 2)

2. Basically, a dry cell could be categorized as a type of electric battery that can be commonly used for portable electrical devices.
3. A commonly used dry cell is the zinc carbon cell or the dry Leclanche cell.
4. As it is portable and easy to use it is used in our day to day life in torch, clock, toys, remotes etc.

B. Structure of Dry Cell :

1. The basic structure of a dry cell consists of a zinc anode and a carbon cathode.
2. It uses ammonium chloride as electrolyte in the form of paste.
3. There is also a second paste present in the cell which is a mixture of ammonium chloride and manganese dioxide where manganese dioxide acts as a depolarizer.

**Fig. 3.5.1.****C. Working of Dry Cell :**

1. The working of this cell is based on the chemical reactions that take place in dry cell.
2. As the result of these reaction electrons are being built up at the anode which further results in potential difference between the cathode and the anode.
3. And due to this potential difference the electrons are able to flow through the circuit.

D. Chemical Reactions :

The reactions taking place in the cell is shown below. First is the oxidation reaction.

1. $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$
In this, the zinc cathode is oxidized to positively charged zinc ions releasing two ions. These electrons are collected by the anode.
2. $2\text{MnO}_2(\text{s}) + \text{H}_2\text{O(l)} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3(\text{s}) + 2\text{OH}^-$

The reduction reaction at the anode is shown above. This reaction produces an electric current. It releases oxide ions with magnesium oxide. This reaction forms when magnesium is combined with the electrolyte.

3. $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(1)$
 $\text{NH}_3 + \text{Zn}^{2+}(\text{aq}) + \text{Cl}^- \rightarrow [\text{Zn}(\text{NH}_3)_2]\text{Cl}_2(\text{s})$
4. The other two reactions represent an acid-base reaction and precipitation reaction taking place in the dry cell. In the acid-base reaction, NH is combined with OH to produce NH₃ along with water. The outcomes are NH₃ and water base.

Que 3.3. What is lead storage battery? Give its construction and working.

OR

What are secondary batteries? Discuss the various reactions involved during the charging and discharging of lead storage battery.

AKTU 2018-19 (Sem-2), Marks 10

OR

Define the term batteries. Explain the construction of Lead acid battery. Write all the chemical reactions taking place during charging and discharging of lead acid battery.

AKTU 2021-22 (Sem-1), Marks 10

OR

What is secondary storage battery? Write charging and discharging reaction of Lead acid battery with application of lead acid battery.

AKTU 2021-22 (Sem-2), Marks 10

Answer

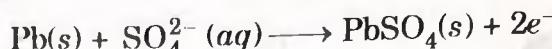
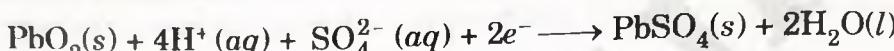
- A. Secondary Batteries :** Refer Q. 3.3, Page 3-4B, Unit-3.
- B. Batteries :** Batteries can be defined as a device consisting of one or more electrochemical cells which can be charged with an electric current and discharged after use.
- C. Lead Storage Battery :**
- Lead storage battery (or lead acid battery) is the oldest type of rechargeable battery and one of the common energy storage devices.
 - In these batteries electrodes and electrolytes are altered by chemical action that takes place when cell delivers the current which can be restored by forcing current through them.
 - The batteries used in automobiles, for example, in cars, buses, trucks etc are lead storage batteries.
- D. Construction :**
- The cell consists of a lead grid filled with a spongy lead as anode and a lead grid packed with lead oxide as cathode.
 - A solution of H₂SO₄ (38 % by mass) is used as an electrolyte.

3-8 B (Sem-1 & 2)

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.

E. Working :**i. Discharging :**

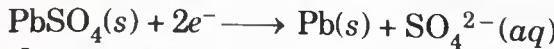
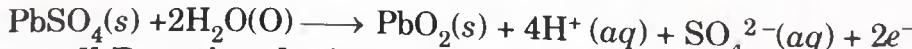
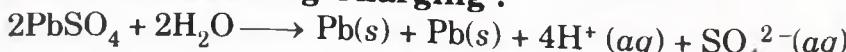
1. When the battery is discharging, i.e., when it is supplying a current, the reactions are :

At the Anode :**At the Cathode :****The Overall Reaction during discharge :**

2. 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 leads 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.

ii. Charging :

1. When the battery is being charged, electrons are supplied to the anode of the battery and this converts the lead sulphate to lead.
2. At the same time, the lead sulphate at the anode is converted to lead dioxide.
3. That is, the cell reactions are reversed and the cell operates like an electrolyte cell.
4. The reactions are :

At Cathode :**At Anode :****Overall Reaction during Charging :**

5. The concentration of H_2SO_4 decreases during discharging whereas it increases during charging.
6. The lead storage cell is both a voltaic cell and an electrolytic cell.
7. When electricity is being drawn from the cell to start the car, it acts as voltaic cell.

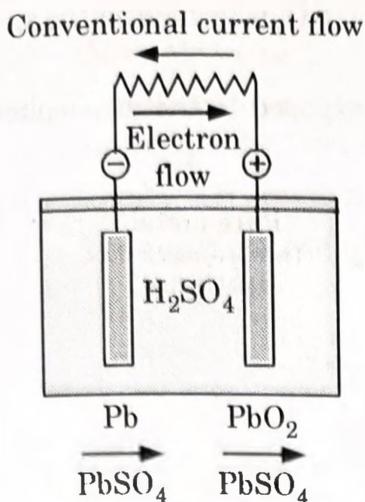


Fig. 3.6.1. Discharging.

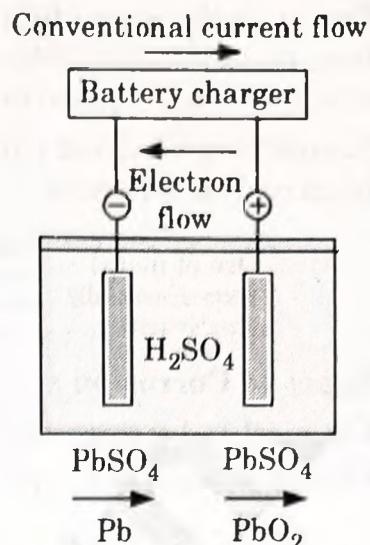


Fig. 3.6.2. Charging.

PART-3*Introduction to Corrosion.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 3.7. | What is corrosion ? What are the types of corrosion ?

Answer**A. Corrosion :**

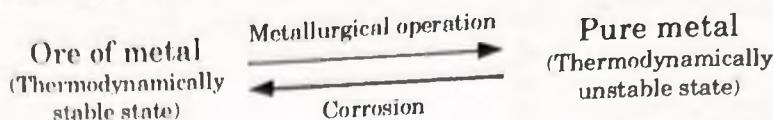
1. Corrosion can be defined as degradation or deterioration of a metal by chemical or electrochemical reaction with its environment (gaseous or liquid medium).
2. Degradation or deterioration means reduction in the useful properties of the material which include :
 - a. Weakening of the material due to loss of cross-sectional area.
 - b. Loss of properties such as malleability, ductility.
 - c. Decaying of surfaces of metals.
 - d. Cracking of a polymer due to sunlight.

3. Example of Corrosion in Metals :

- a. **Rusting of iron :** When exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe₃O₄ is formed on the surface.

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- b. **Formation of green film on the surface of copper :** A green layer of basic carbonate consisting of $\text{CuCO}_3 + \text{Cu}(\text{OH})_2$ is formed on the surface of copper when exposed to moist air.
- c. **Tarnishing of silver :** When silver is exposed to the atmosphere, a black coating is formed.

**B. Types of Corrosion :**

- Chemical or dry corrosion.
- Electrochemical or wet corrosion.

PART-4*Types of Corrosion.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 3.8. Write a short note on chemical or dry corrosion.

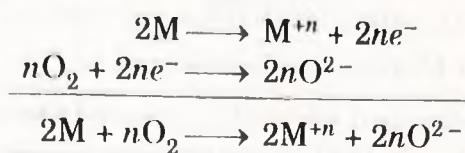
OR

Explain the corrosion phenomenon involving oxide film growth law.

Answer

- A. **Chemical or Dry Corrosion :** Chemical or dry corrosion is the simplest case of corrosion, where corrosion takes place by direct chemical attack. This type of corrosion occurs mainly when metal surface come in direct contact with the atmospheric gases such as oxygen, halogens etc.
- B. **Dry or Chemical Corrosion is generally of three main types :**
1. Corrosion by gases.
 2. Liquid metal corrosion.
 3. **Oxidation Corrosion :** Oxidative corrosion takes place by direct action of oxygen on metals, at low or high temperature, forming oxides of the metal. It generally takes place in absence of moisture.
- i. **Mechanisms of Dry Corrosion :** The growth of the oxide film on metal takes place at the surface as :
- a. The oxygen is adsorbed at the surface of the metal by physical adsorption.

- b. When the temperature rises the physical adsorption turns into chemisorption, wherein metal gets oxidized to metal ions ($M \rightarrow M^{n+} + ne^-$).
- c. The electrons are taken up by oxygen which gets reduced to oxide ion ($nO_2 + 2ne^- \rightarrow 2nO^{2-}$).
- d. The $M^{n+}O^{2-}$ combine to form metal oxide (M_2O_n).
- e. The reactions can be written as :



- f. The metal oxide scale so formed forms a barrier between the metal and the oxygen and restricts further oxidation or corrosion of the metal.
- g. As the metal cation is much smaller in size, the outward diffusion of metal ion is much more rapid than inward diffusion of oxide ion. Hence corrosion continues by rapid diffusion of highly mobile cations.

ii. The Nature of the Film :

- a. **Stable Film :** The stable oxide film is fine grained in structure and adheres tightly to the metal surface. This can be impervious in nature, thereby preventing the penetration of oxygen to the underlying metal.
- b. **Unstable Film :** The oxide film formed on the surface of metal decomposes back into metal and oxygen and hence the film is called unstable film.
Hence in such cases corrosion is not possible.
- c. **Volatile Film :** The metal-oxide film volatizes from the surface as soon as it is formed. Hence the underlying metal is exposed to the further attack by oxygen leading to rapid and continuous corrosion.
- d. **Porous Film :** Sometimes the oxide film so formed is porous or has cracks. Hence the diffusion of oxygen takes place through these pores leading to further oxidation or corrosion.

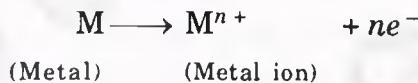
Que 3.9. What is electrochemical corrosion ? Write down the mechanism involved in electrochemical corrosion.

Answer

A. Electrochemical or Wet 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 example :
- a. Formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron, also known as "rusting of iron".

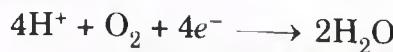
- b. Formation of a layer of black coating on the surface of silver, when it is exposed to atmosphere. It is known as tarnishing of silver.
- B. Mechanism of Electrochemical or Wet corrosion :** The corrosion of metals in aqueous medium seems to be the electrochemical in nature. This type of corrosion is also known as immersed corrosion and generally takes place when :
- A metal is in contact with the moist air or any liquid medium or
 - When two different metals or an alloy is in contact with a solution.
- 1. Electrochemical Corrosion involves :**
- Separate 'anodic' and 'cathodic' areas between which current flows through the conducting medium.
 - Non-metallic ions like OH^- or O_2^- are formed at cathodic areas.
 - Occurrence of oxidation (corrosion) at anodic areas which generates metallic ions.
 - Diffusion of metallic and non-metallic ions towards each other through conducting medium results in the formation of corrosion product somewhere between anodic and cathodic areas.
- 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.
 - The corrosion takes place as discussed below :
- Anodic Reactions :** At anodic area, oxidation reaction takes place where metal atoms lose their electrons to the environment and pass into the solution.



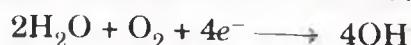
Thus metal is destroyed by dissolving or changing into metallic ions. Hence, corrosion takes place at anodic areas or metal, which forms the anode, is corroded.

- Cathodic Reactions :** The electrons released in the anodic reactions are consumed in the reactions at the cathode or cathodic reactions. Depending upon the nature of the corrosive environment, cathodic reactions may result in :

- Oxygen Absorption :** In presence of dissolved oxygen
 - In acidic medium :



- In neutral or weak alkaline medium :



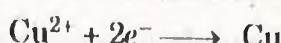
- Hydrogen Evolution :** In absence of O_2
 - In acidic medium :



ii. In neutral or alkaline medium :



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



PART-5

Cause of Corrosion.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.10. What are the causes of corrosion ?

Answer

1. The main causes of corrosion are chemical reactions, weather conditions, friction and a lack of durability.
2. Rust is a chemical reaction in which iron exposed to the atmospheric conditions.
3. Environmental elements like water, wind, and moisture oxidize the metal surface and corrode it.
4. Friction can cause stress cracking, fretting, intergranular corrosion and erosion.
5. Two pieces of metal that rub on each other cause fretting and lead to corrosion.

Que 3.11. State the factors influencing corrosion.

Answer

1. **Nature of the Metal :**
 - a. **Physical state of the metal :**
 - i. Physical state of the metal means orientation of crystal, grain size, stress etc.
 - ii. The larger the grain-size of the metal/alloy, the smaller will be its solubility and hence, lesser will be its corrosion.
 - b. **Nature of the oxide film :**

The smaller the specific volume ratio = $\frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$, greater

is the oxidation corrosion because oxide film formed will be porous, through which oxygen can diffuse and bring about further corrosion.

c. 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, Rate of corrosion of anodic region $\propto \frac{\text{Cathodic area}}{\text{Anodic area}}$

d. Volatility of corrosion products :

- Excessive (rapid and continuous) corrosion of metal takes place if corrosion product is volatile.
- 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 :

- The rate of corrosion increases with rise in temperature.
- 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 :

- The greater is humidity, the greater is the rate and extent of corrosion.
- 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.

c. Presence of impurities in atmosphere :

- Corrosion of metals is more in areas near the industry and sea.
- 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 : Due to differential aeration, oxygen concentration cell sets up and anodic part which has less oxygen concentration suffers corrosion.

PART-6

Corrosion Prevention and Control.

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

Que 3.12. Discuss the electrochemical theory of corrosion along with equations. Explain why sheets of Zinc metal are hung around the ship hull of ocean going ships.

AKTU 2017-18 (Sem-2), Marks 07**OR**

Define the term corrosion. Describe the mechanism of electrochemical corrosion with the help of hydrogen evolution and oxygen absorption reactions. How it can be prevented using sacrificial anodic protection ?

AKTU 2021-22 (Sem-1), Marks 10**OR**

Explain the mechanism of electrochemical theory of corrosion with the help of hydrogen evolution and oxygen absorption reactions. Describe cathodic protection in detail.

AKTU 2021-22 (Sem-2), Marks 10**OR**

Describe the mechanism of electrochemical or wet corrosion with help of reactions. Explain the cathodic protection method of prevention of corrosion.

AKTU 2018-19 (Sem-1), Marks 10**OR**

Discuss rusting of iron by Hydrogen evolution and Oxygen absorption mechanism. Briefly explain sacrificial cathodic protection and impressed current cathodic protection.

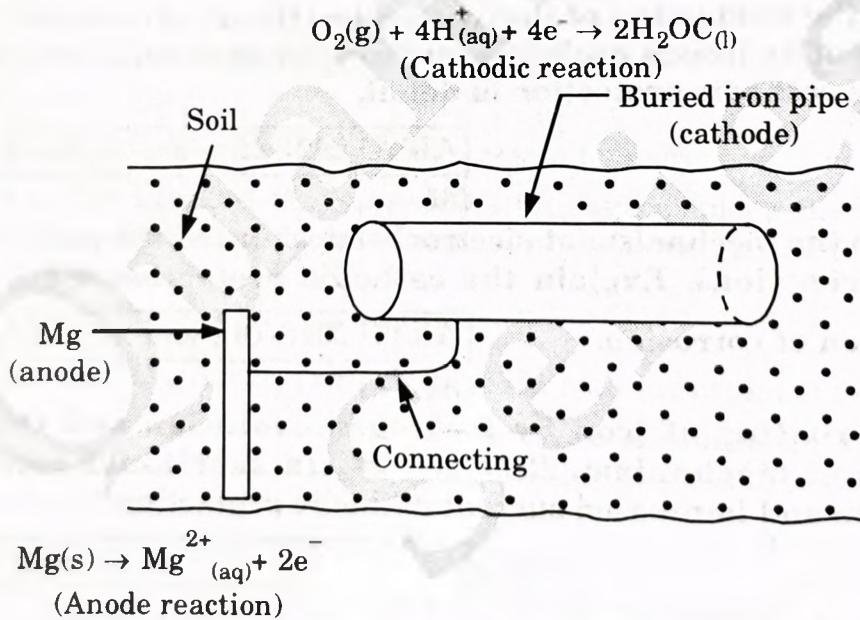
AKTU 2018-19 (Sem-2), Marks 10**Answer**

- A. **Hydrogen Evolution and Oxygen Absorption :** Refer Q. 3.9, Page 3-11B, Unit-3.
- B. **Corrosion :** Refer Q. 3.7, Page 3-9B, Unit-3.
- C. **Electrochemical Theory of Corrosion :** Refer Q. 3.9, Page 3-11B, Unit-3.
- D.
 1. **Cathodic Protection or Electrochemical Protection :** 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 :

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a. Galvanic or Sacrificial Anodic Protection :

- In galvanic protection or 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.
- Example (Zinc metal in ship) :** In ship, a sacrificial anode (sheets of zinc metal) is a anode, electrically linked to the ship metal (cathode) to be protected, that is more reactive to the surrounding corrosive environment. In this way, the sacrificial anode corrodes and protects the metal of the ship.

**Fig. 3.12.1. Galvanic protection using sacrificial anode.****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 impressed current cathodic protection has been applied to protect:

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

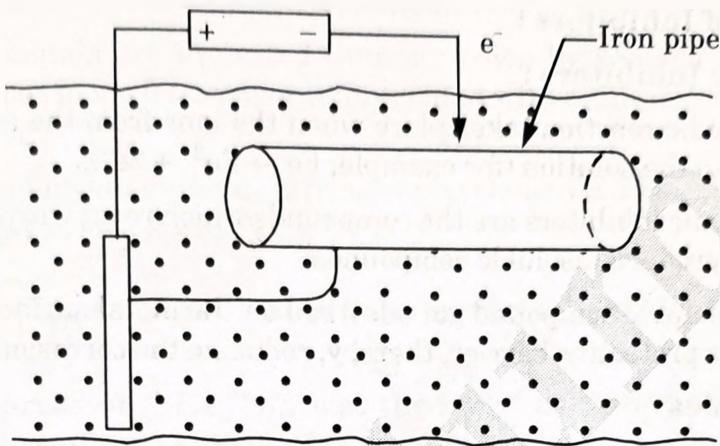


Fig. 3.12.2. Impressed current cathodic protection.

2. Anodic Protection :

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

Que 3.13. What are corrosion inhibitors ? Explain the mechanism of their action.

OR

What are corrosion inhibitors ? Explain with examples how anodic and cathodic inhibitor provides protection against corrosion.

Answer

A. Corrosion Inhibitors :

1. Corrosion inhibitors are the substances which when added in small quantities to the corrosive environments decrease the corrosion rate.

3-18 B (Sem-1 & 2)

2. Inhibitors are organic as well as inorganic substances that dissolve in the corroding medium.
3. Inhibitors are generally classified on the basis of electrode at which their action is predominant.

B. Type of Inhibitors :**1. Anodic Inhibitors :**

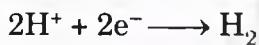
- i. The anodic reaction takes place when the ions from the anodic metal pass into the solution (for example, $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$).
- ii. The anodic inhibitors are the compounds which react with these metal ions to produce insoluble compounds.
- iii. This insoluble compound get adsorbed on the metal surface forming a film or a protective barrier, thereby, reducing the corrosion rate.

iv. Examples :

- a. Molybdates, phosphates and chromates of alkali and transition elements.
- b. Substances like Na_2CrO_4 , NaNO_2 act as anodic inhibitors by forming less soluble compounds with the anodic metal ions.
- c. The organic compounds can also act as anodic inhibitors and example include sodium benzoate.

2. Cathodic Inhibitors :

- i. The cathodic reaction in acidic medium is represented by :



- ii. Thus, corrosion can be controlled by slowing down the diffusion of H^+ ions to the cathode.
- iii. The diffusion of H^+ ions is considerably reduced by organic inhibitors such as amines, mercaptans, heavy metal soaps, substituted ureas and thioureas.
- iv. These substances are capable of being adsorbed at the metal surfaces and thus restrict the diffusion of H^+ ions.
- v. 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.
- vi. Compared to anodic inhibitors, cathodic inhibitors are quite safe.
- vii. 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 :

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

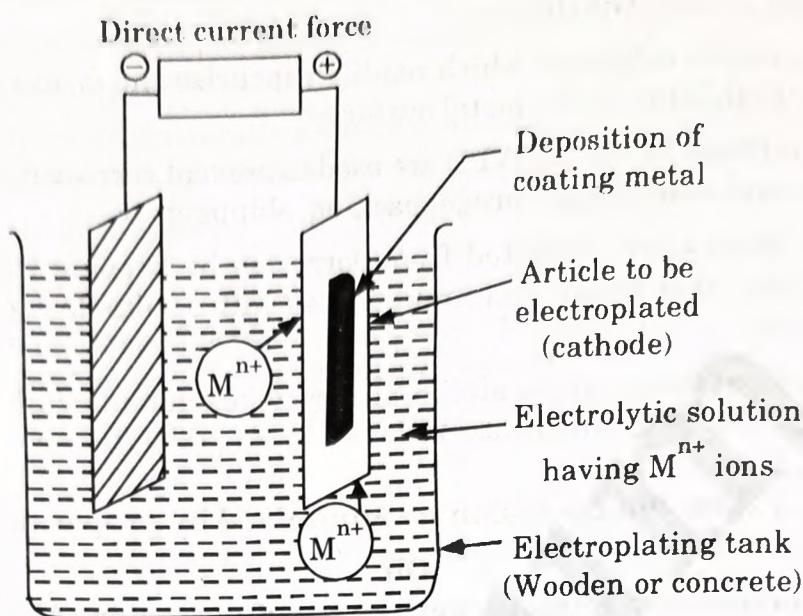
Que 3.14. | How can corrosion be minimized by proper design ?

OR

What is corrosion ? Explain wet theory of corrosion. Also discuss the methods of prevention of corrosion.

Answer

- A. **Corrosion :** Refer Q. 3.7, Page 3-9B, Unit-3.
- B. **Wet Theory of Corrosions :** Refer Q. 3.9, Page 3-11B, Unit-3.
- C. **Methods of Prevention of Corrosion :**
 1. **Anodic and Cathodic Protection Method :** Refer Q. 3.12, Page 3-15B, Unit-3.
 2. **Corrosion Inhibitors :** Refer Q. 3.13, Page 3-17B, Unit-3.
 3. **Metal Cladding :**
 - i. Metal cladding is the process of coating of base metal by a dense, homogeneous layer of cladding materials.
 - ii. Cladding materials 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).
 - iii. Generally, a base metal is sandwiched between two layers of cladding materials which are then passed through rollers, under the action of heat and pressure to form clad sheeting which is very widely used in the air-craft industry.
 4. **Electroplating :**
 - i. 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.
 - ii. Apart from increasing the resistance of metal to corrosion and chemical attack, electroplating also improves physical appearance, hardness, surface properties and aesthetics.

**Fig. 3.14.1. Electroplating.****5. Proper Design :**

- The contact between different metals and alloys should not be made, especially if they are far apart in the galvanic series. If this is not followed then the more active metal will get corroded causing local corrosion.
- The rate of corrosion also depends upon the relative sizes of the anode and the cathode. As far as possible, if two dissimilar metals are in contact, the combination of small anode and large cathode should be avoided.
- The presence of crevices between adjacent parts of structure, even in the case of the same metal, should be avoided.
- As moisture is the main factor governing corrosion, the design should be such that retention of moisture should be as low as possible.

PART-7

Corrosion Issues in Specific Industries, Power Generation, Chemical Processing Industry, Oil and Gas Industry, Pulp and Paper Industries.

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

Que 3.15. Discuss corrosion issues in

- Power generation plant
- Chemical processing industry
- Oil and gas industry
- Pulp and paper industries

Answer**A Power Generation Plant :**

1. Power plant has several different parts like turbines, boilers, engines, pipes, valves and tubes which face different types of corrosive activities which lead to the failure in those parts.
2. Common types of corrosion occur at power plants are oxidation, galvanic corrosion, hot corrosion and erosion.
3. Hot, or dry, corrosion is a type of oxidation that occurs in the absence of moisture when a surface has a thin film of salt in an oxidizing gas coating it. This type of corrosion affects gas turbines, incinerators, boilers, and internal combustion engines of power plant.
4. In a plant, a humid area with steel pipes and copper fittings could experience galvanic corrosion, as one metal would become an anode and the other a cathode, accelerating oxidation.
5. Erosion is a type of corrosion which cause serious problem within turbines, pipelines, valves, heat exchanger tubes, and combustion systems of power plant.

B Chemical processing industry :

1. Within chemical processing plants, corrosion in metals and metal alloys can cause major failures in the equipments and parts of machineries.
2. Cracking due to corrosion in the walls of a pressure vessel resulted in an explosion at a crystal chemical processing plants.
3. Heat recovery steam generators, steam turbines, mixing tanks, heat exchangers, storage tanks, and transfer pipelines are all pieces of chemical processing equipment subject to corrosion and potential failure.
4. Low pH vapors present in chemical facilities are acidic in nature and can penetrate organic coating materials that can cause various types of corrosion, including pitting.
5. A fire can occur when combustible material come in contact with steam or self-igniting chemical leaks due to corroded valves and piping.

C Oil and Gas Industry :

1. Corrosion is a common problem encountered in the oil and gas industry. Oil and gas pipelines, refineries and petrochemical plants have serious corrosion problems.
2. Internal corrosion in oil and gas industry is generally caused by water, carbon dioxide (CO_2) and hydrogen sulfide (H_2S), and also can be aggravated by microbiological activity.
3. The flow regimes of multiphase fluids greatly influence the corrosion rate. For example, at high flow rates, erosion-corrosion may occur, whereas at low flow rates pitting corrosion is more common.

4. Corrosion is also related to the amount and nature of the sediments. High-velocity flow tends to sweep sediments out of the pipeline, whereas low velocity allows sediments to settle at the bottom, providing sites for pitting corrosion.

D. Pulp and Paper Industries :

- Materials in the pulp and paper industry (CPPI) are exposed to corrosive environments in almost all applications.
- While producing pulp and paper, there are many production steps in which materials are exposed to extreme corrosive environments, such as in digesters, evaporators, recovery boilers, bleaching, paper making machines and chemical storage tanks.
- Corrosion problem in pulp and paper industry is more serious as wide variety of corrosive chemicals like chlorine, Sulphuric acid, hydrochloric acid are used that generate several corrosive substances and reaction products at various stages.
- The severity of corrosion has increased considerably during the recent years due increased recycling of back-water and use of other nonconventional raw materials like rice and wheat straw.

PART-8

Cement Constituents.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.16. 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 limestone at high temperature and then pulversing 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 calcerous raw materials.	Important and reliable use in making strong structures.

Que 3.17. Write the chemical composition of Portland cement.

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 :

Chemical composition

Oxide	Percentage
Lime (CaO)	60 – 67
Silica (SiO_2)	17 – 25
Alumina (Al_2O_3)	3 – 8
Iron oxide (Fe_2O_3)	0.5 – 6
Magnesia (Mg O)	0.1 – 4
Sulphur trioxide (SO_3)	1 – 3
Soda and Potash ($\text{Na}_2\text{O} + \text{K}_2\text{O}$)	0.5 – 1.5

PART-9*Cement Manufacturing.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 3.18. Describe the process of manufacturing of Portland cement with the help of schematic diagram.

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.

- c. The kiln is heated by coal powder or fuel oil introduced from other end.
- d. Hot flame of the fuel is forced inside the kiln.
- e. Due to slope and rotation, the material flows towards the hottest end slowly.

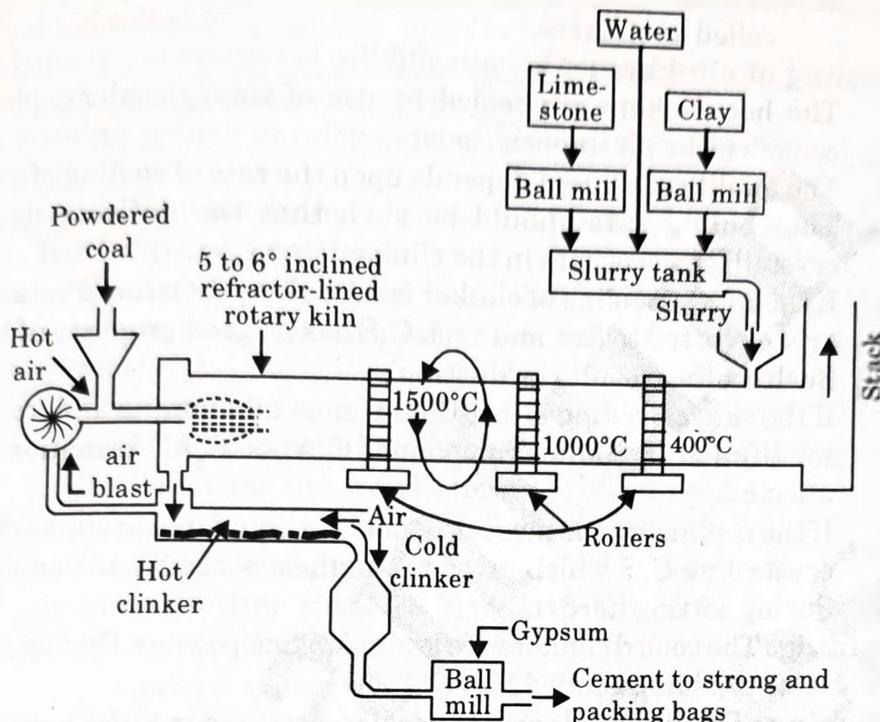
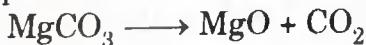


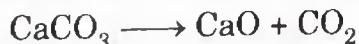
Fig. 3.18.1. Rotary cement kiln.

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

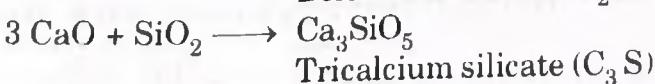
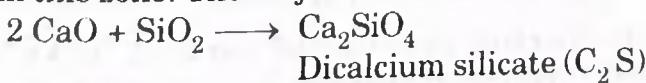
- i. **Drying zone** : Upper part of the kiln is the drying zone where temperature is 300-400°C. In the zone, most of the water in the slurry gets evaporated.
- ii. **Pre-heating zone** : The upper central part having temperature of about 400-700°C. In this zone, clay and magnesium carbonate decomposes.

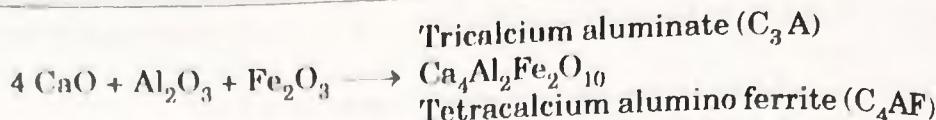


- iii. **Calcination zone** : It is the central part of the kiln where temperature is 700-1000°C. Limestone decomposes here.



- 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 :





- g. The C_2S , C_3S , C_3A , C_4AF , formed are in molten form.
- h. When cooled by air, there is formation of small hard, greyish stones called as clinkers.

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.
 - 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. **Griding** : 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.

PART- 1 □

Cement Hardening and Setting.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.19. | What is Portland cement ? Give the chemical reactions involved during setting and hardening of cement.

AKTU 2017-18 (Sem-1), Marks 07

OR

Explain manufacturing process of cement. Give the chemical composition of Portland cement along with its setting and hardening.

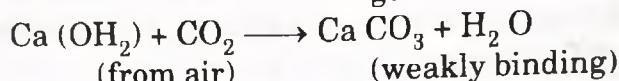
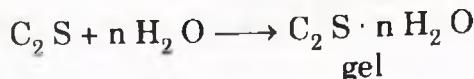
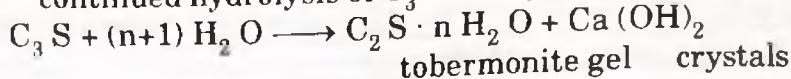
AKTU 2017-18 (Sem-2), Marks 07

Answer

- A. Manufacturing :** Refer Q. 3.18, Page 3-24B, Unit-3.
- B. Composition :** Refer Q. 3.17, Page 3-23B, Unit-3.
- C. Portland Cement :**
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.
$$C_3A + 6 H_2O \longrightarrow C_3A \cdot 6 H_2O + 880 \text{ kJ/kg}$$
 - 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.
$$C_4AF + 7 H_2O \longrightarrow C_3A \cdot 6 H_2O + CF \cdot H_2O + 420 \text{ kJ/kg}$$
 - 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.
$$C_3S + (n+1) H_2O \longrightarrow C_2S \cdot n H_2O + Ca(OH)_2 \\ (\text{gel})$$
- iv. The tobermorite gel formed is strongly binding in character.

c. Final hardening :

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



Que 3.20. What is the role of gypsum in cement ?

Answer

Role of gypsum :

- 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.
 - 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 sulphaaluminate and this reaction is not high heat liberating.

$C_3A + x CaSO_4 + 7 H_2O \longrightarrow C_3A \cdot x CaSO_4 \cdot 7 H_2O$

 - 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.

PART-11

Deterioration of Cement

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 3.21. Explain different cause of deterioration in the cement and how to prevent it.

Answer**A. Alkali-silica Reaction (Alkali Aggregate Reaction) :**

1. Portland cement contains very alkaline ingredients such as Na^+ and K^+ which in presence of water create a high alkali environment.
2. If the aggregates contain reactive silicates, these silicates react with the alkali and produce ASR gel.
3. ASR gel in presence of moisture can swell and cause tensile stress throughout the concrete core, which results in cracks and deterioration.

Prevention :

1. Incorporation of non-reactive aggregates, low alkali Portland cement, and supplementary cementitious materials (SCMs) are the three effective solutions to prevent ASR in concrete structures.

B. Alkali Carbonate Reaction (ACR) :

1. ACR occurs when certain types of dolomitic limestone aggregates are used in concrete in the presence of high alkali Portland cement. The products of this reaction are also expansive like ASR gel and cause deterioration of concrete.

Prevention :

1. To protect structures from carbonation distress, all the exposed concrete surfaces need to be coated to reduce the rate of CO_2 penetration.
2. In addition, incorporation of supplementary cementitious materials such as fly ash, slag and silica fume enhances the density and quality of the concrete and prevents CO_2 penetration in new concrete.

C. Corrosion :

1. In the presence of high alkali ions in concrete's solution results in high pH of the concrete, the steel reinforcement inside the concrete passivates itself by forming a passive layer at the steel reinforcement.
2. This passive layer protects the reinforcement from chloride attack and corrosion. Once the pH of the concrete decreases, the concrete matrix is no longer in the alkali condition, and the passive layer at the reinforcement is destroyed.
3. The existing reinforcement is now exposed to aggressive chemicals such as chloride ions. As soon as the chloride content at the level of reinforcement steel exceeds the threshold, the corrosion of the reinforcement is propagated, and deteriorates concrete.

Prevention :

1. To protect concrete structures from chloride attack, the top surface of the concrete slabs needs to be coated properly to decrease the penetration of chloride ions.

D. Sulfate Attack :

1. One of the components of the hydrated Portland cement is calcium sulfo-aluminate.
2. The source for formation of this component is gypsum which is usually added to the Portland cement to control the setting time of the concrete.
3. The formation of this compound is an expansive process and occupies more space which causes internal tensile pressure.

4. Sulfates from external sources like water or soil penetrate the concrete and react with monosulfate which is one of the cement's hydration products and form calcium sulfo-aluminate which expands and cause damages.

Prevention :

1. The most effective ways to prevent sulfate attack in new structures are using high quality concrete (with low water-to-cement ratio and/or SCM content).

E. Delayed ettringite formation (DEF) :

1. The other common form of sulfate attack is called delayed ettringite formation (DEF) which is more common in precast concrete manufacturing.
2. Unlike the sulfate attack mentioned above where the source of the reaction is external (sulfate from soil or water).
3. The sulfate source for DEF is internal, and no external source of sulfate is required to trigger the reaction.
4. At high exposure temperature the sulfate ions form the existing ettringite are released into the concrete matrix.
5. These released sulfates which react with the hydration products of Portland cement and form secondary ettringite.
6. As mentioned above, when the concrete is hard, any formation of ettringite causes internal pressure and distresses.

Prevention :

1. The effective ways to prevent DEF damages in precast elements are limiting the exposure temperature during the curing process to prevent ettringite's decomposition as well as using an air entraining agent in concrete to create voids for secondary ettringite to accumulate.

F. Acid attack :

1. Two main components of Portland cement are calcium silicate hydrate (C-S-H gel) and calcium hydroxide (Ca(OH)_2).
2. C-S-H gel occupied most of the paste matrix and is responsible for concrete's mechanical and durability properties.
3. Calcium hydroxide occupies approximately 25% of the concrete paste volume and is not as effective as C-S-H to provide strength for concrete.
4. The alkali ions from Portland cement along with the calcium hydroxide are the reasons for high pH of the concrete materials.
5. External concentrated acids penetrate the concrete, react with calcium hydroxide, and form salt and water which can leach out from the surface of the concrete and negatively affect both the mechanical and durability properties of concrete.

Prevention :

1. Incorporation of SCMs enhances the quality of concrete and consequently prevents the acid attack.

G. Salt Attack :

1. Salt attack occurs when the exterior surface of the concrete structure is exposed to water that contains salt. Once the water evaporates, salt remains on the surface of the concrete and causes pressure and damage.

Prevention :

1. Applying sealer to the face of the concrete and using high quality concrete can mitigate salt attack.

PART- 12

Plaster of Paris.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

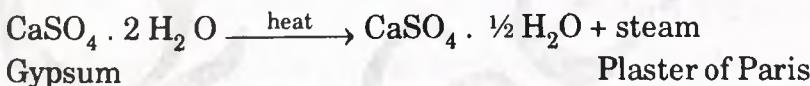
Que 3.22. | What is Plaster of Paris ? How it is prepared ?

Answer

Plaster of Paris is the material having formula $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ 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.

1. 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.
 2. 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°C.



Que 3.23. What are the properties of POP ? Also, give the applications.

Answer

Properties of POP :

1. Setting and hardening with water is the most important property of Plaster of Paris.
 2. 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.
 3. Chemically, on mixing with water, Plaster of Paris expands slightly and regains the closely-packed crystalline structure of gypsum.
 4. 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.

5. It is a white coloured powder and light in weight.
6. The set material is not strong.
7. It is easy to work and setting time is also conveniently small.

Applications of POP :

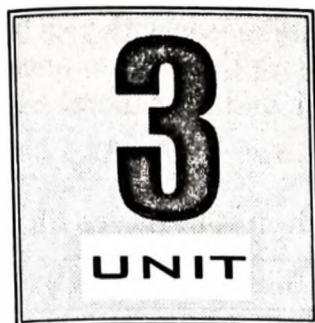
1. Plaster on wall, ceiling.
2. Moulded and casted articles of decoration.
3. For orthopedic cast to protect limbs with broken bones.
4. It is used for quick sealing.
5. At high temperatures, gypsum loses all the water of crystallization to give anhydrous calcium sulphate.
6. It is used in manufacture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

VERY IMPORTANT QUESTIONS

Following questions are very important. These questions may be asked in your SESSIONALS as well as UNIVERSITY EXAMINATION.

- Q. 1. What is lead storage battery ? Give its construction and working.**
Ans. Refer Q. 3.6, Unit-3.
- Q. 2. What is electrochemical corrosion ? Write down the mechanism involved in electrochemical corrosion.**
Ans. Refer Q. 3.9, Unit-3.
- Q. 3. Discuss the electrochemical theory of corrosion along with equations. Explain why sheets of Zinc metal are hung around the ship hull of ocean going ships.**
Ans. Refer Q. 3.12, Unit-3.
- Q. 4. What are corrosion inhibitors ? Explain the mechanism of their action.**
Ans. Refer Q. 3.13, Unit-3.
- Q. 5. What is Portland cement ? Give the chemical reactions involved during setting and hardening of cement.**
Ans. Refer Q. 3.19, Unit-3.
- Q. 6. Explain different cause of deterioration in the cement and how to prevent it.**
Ans. Refer Q. 3.21, Unit-3.





Electrochemistry (2 Marks Questions)

3.1. What is corrosion of metal ?

Ans. Corrosion is the process of destruction of metals by the chemical or electrochemical attack of environment, starting at surface.

3.2. What are the corrosion inhibitors ?

Ans. Corrosion inhibitor is a substance which when added in small quantity to the aqueous corrosive environment, effectively decreases the corrosion of metal.

The type of inhibitors are :

- i. Anodic inhibitors
- ii. Cathodic inhibitors

3.3. Why is a block of magnesium attached through an insulated metallic wire to the hull of the ship and underground iron pipeline ?

Ans. A block of magnesium is attached through an insulated metallic wire to the hull of the ship (or pipe) because magnesium shows sacrificial anode protection. Mg becomes anode, shows oxidation, gets corroded while ship (or pipe) made up of iron becomes cathode and is protected from corrosion.

3.4. Explain why a pure metal rod half immersed vertically in water starts corroding at the bottom ?

AKTU 2017-18 (Sem-2), Marks 02

Ans.

1. This is due to differential aeration. The rod above and closely adjacent to the waterline is more strongly-aerated and hence, becomes cathodic; while the lower part of rod immersed in water is less-oxygenated and hence become anodic.
2. So a difference of potential is created and electrochemical corrosion takes place. This causes corrosion of the anodic part. Hence, metal rod starts corroding at the bottom.

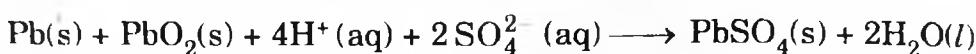
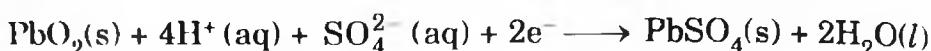
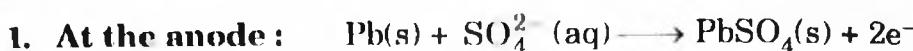
3.5. How does corrosion get effected with temperature ?

Ans. The rate of any chemical reaction (corrosion) 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.

- 3.6. Give reactions of lead-acid storage cell when it behaves like a galvanic cell.**

AKTU 2017-18 (Sem-2), Marks 02

Ans.



- 3.7. Define primary cell.**

Ans. A primary cell or battery is a type of non-rechargeable cell and cannot be reused once its electrolyte is all consumed.

- 3.8. Define secondary cell.**

Ans. A secondary cell or battery is the one that is rechargeable and serves multiple purposes for longer span.

- 3.9. Define cement.**

Ans. Cement is the binding material used for binding bricks, gravel, tile and plastering on walls.

- 3.10. List reasons for deterioration of the cement.**

Ans. Different reasons for cement deterioration

- i. Alkali-Silica reaction ii. Sulphate attack
- iii. Acid attack

- 3.11. Comment on the use of aluminum in place of zinc for cathodic protection of iron from rusting.**

AKTU 2018-19 (Sem-1), Marks 02

AKTU 2021-22 (Sem-1), Marks 02

Ans. The standard electrode potential of aluminium is more than that of zinc. So aluminium is more anodic than zinc. Thus we can better use aluminium in place of zinc for cathodic protection of from rusting iron.

- 3.12. Why does part of a nail inside the wood undergoes corrosion easily ?**

AKTU 2018-19 (Sem-2), Marks 02

Ans. Wood is a hygroscopic material so it can absorb large quantity of water. Iron nail in contact with the water will lead to faster corrosion.

3.13. How much rust ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) can be produced by 3 g of iron ?

AKTU 2020-21 (Sem-1), Marks 02

Ans. The number of moles of Fe

$$= 3 / 56 = 0.05 \text{ moles}$$

0.05 moles of Fe will give

$$0.05 \times 2 / 4 = 0.025 \text{ moles of } \text{Fe}_2\text{O}_3$$

The molar mass of $\text{Fe}_2\text{O}_3 = 2 \times 56 + 3 \times 16 = 160 \text{ g/mole}$

Mass of $\text{Fe}_2\text{O}_3 = 160 \times 0.025 = 4 \text{ g}$





Water Technology, Fuel and Combustion

CONTENTS

- Part-1 : Sources and Impurities of Water..... 4-2B to 4-3B**
- Part-2 : Hardness of Water..... 4-3B to 4-5B**
- Part-3 : Boiler Troubles 4-6B to 4-8B**
- Part-4 : Technique for Water Softening 4-8B to 4-24B
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and Reverse Osmosis Process)**
- Part-5 : Determination of Hardness 4-24B to 4-26B
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- Part-6 : Definition, Classification and 4-26B to 4-28B
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- Part-7 : Calorific Values-Gross and 4-28B to 4-28B
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- Part-8 : Determination of Calorific 4-29B to 4-33B
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- Part-9 : Theoretical Calculation of 4-33B to 4-35B
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- Part-10 : Ranking of Coal 4-36B to 4-37B**
- Part-11 : Analysis of Coal by Proximate 4-37B to 4-44B
and Ultimate Analysis of Coal.**
- Part-12 : Chemistry of Biogas Production 4-44B to 4-47B
from Organic Waste Material and
Their Environmental Impact on Society**

PART - 1*Sources and Impurities of Water.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 4.1. Explain different sources of water.

Answer**A. Surface water :**

1. Rivers, streams, lakes, and ponds are widely used as water sources in rural areas.
2. When rainfall is limited, the supply of surface water will vary considerably between wet and dry seasons.
3. One way to overcome this problem is to construct a dam across a river to create a reservoir that provides water storage.
4. Large surface water reservoirs may be used for hydroelectric power generation, regulating water releases to control river flows, for recreational purposes and to provide water for agricultural, municipal and industrial uses.

B. Groundwater :

1. An aquifer is an underground layer of water-bearing rock. Groundwater is the water contained in these aquifers.
2. This is replenished by water seeping from precipitation as well as other bodies of surface water, such as lakes and wetlands.
3. Its level fluctuates seasonally and from year to year as the inputs from precipitation and the outputs vary.
4. The depth of the water table also varies with location, from being near to the land surface in areas close to surface water bodies and in humid climates, to being hundreds of metres below the land surface in drier regions.
5. Groundwater reaches the surface naturally through springs or artificially through wells. Springs typically rise up where the water table meets the land surface.
6. Wells and boreholes are dug by hand or drilled by machine. These have to be deep enough to extend below the water table so that water can be drawn up by bucket or by pumping.

3. Rainwater :

1. Rainwater is also an important source of water, although on a relatively small scale. Collecting rain from roofs or other hard-surfaced areas and storing it until it is needed can provide a valuable source of water for many purposes.

Que 4.2. Discuss different types of impurities in water.

Answer

Impurities in water classified as :

A. Physical impurities :

1. The presence of physical impurities in water affects physical characteristics such as colour, odour, taste and turbidity.
2. Colour, odour and taste in water are due to the presence of organic matter, minerals, microorganisms etc.
3. Turbidity in water is chiefly due to suspended matters whereas colloidal also liable for turbidity.

B. Chemical impurities :

1. The presence of chemical impurities in water affects the chemical salts of minerals, characteristics of water such as PH, solids, hardness, alkalinity, chloride, nitrogen etc.
2. The presence of chemical impurities may cause various types of diseases.

C. Biological impurities :

1. Biological impurities in water are caused by the presence of living organisms.
2. These include algae, protozoa, pathogens, bacteria, viruses, microbes, and parasites along with their cysts (eggs) in contaminated water.
3. Microorganisms that can reproduce at alarming rates and contaminate water that causes diseases in human beings.

PART-2**Hardness of Water.****Questions-Answers****Long Answer Type and Medium Answer Type Questions**

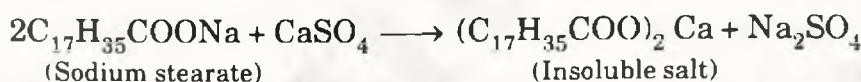
Que 4.3. What is hardness of water ? What are its types ?

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,



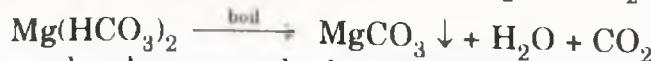
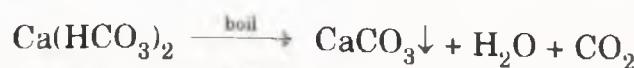
4. Thus, a white scum or precipitate of insoluble soap of calcium and magnesium is formed. Lather is not produced until the cations, Ca^{2+} and Mg^{2+} are completely precipitated out in the form of insoluble salts.
5. As a result, a large quantity of soap is required to produce lather with hard water.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

Types of hardness :

- a. Temporary hardness
- b. Permanent hardness

a. Temporary hardness :

1. 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 ($\text{Ca}(\text{OH})_2$).



- b. **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 4.4. | What are the disadvantages of hardwater ?

Answer

1. Domestic Problems :

- a. **Cooking :** Vegetables and other like pulses etc. do not cook well in hard water.
- b. **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.
- c. **Spoiling of 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.

2. Industrial Problems :

- a. **Textile industry :** The water used in textile and dyeing industries should be free from hardness (Ca^{2+} and Mg^{2+} ions), organic matter, suspended particles etc. Hard water precipitates basic dyes. Iron and manganese salt produce coloured spots on fabrics.
- b. **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.
- c. **Aluminium industry :** The water should be of high quality. Any type of impurity and hardness make it low grade.

Que 4.5. | Differentiate between temporary and permanent hardness.

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, etc.
2.	It can be removed by 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 , FeS_4 , MgSO_4 etc.

PART-3*Boiler Troubles.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 4.6. Write a short note on boiler troubles.

Answer

1. Water is mainly used in boilers for the generation of steam (for industries and power houses).
2. 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.
3. **A boiler feed water should correspond with the following composition :**
 - i. Its hardness should be below 0.2 ppm.
 - ii. Its caustic alkalinity (due to OH^-) should lie in between 0.15 and 0.45 ppm.
 - iii. 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.

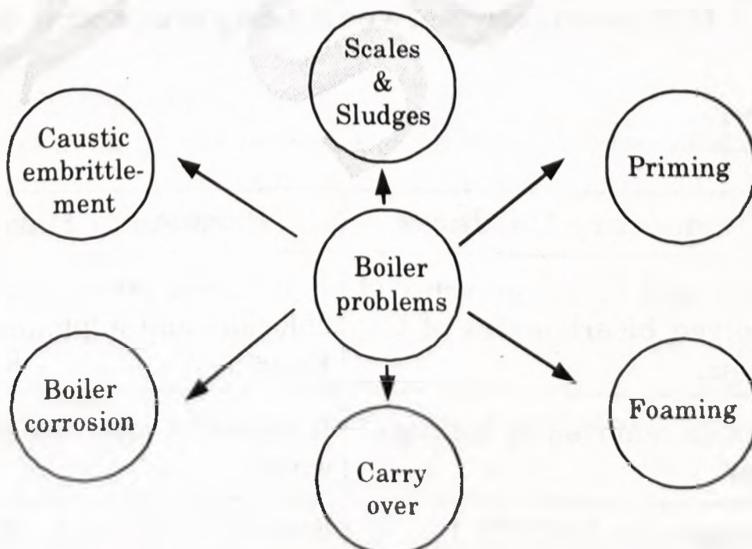
Boiler problems :

Fig. 4.6.1.

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.

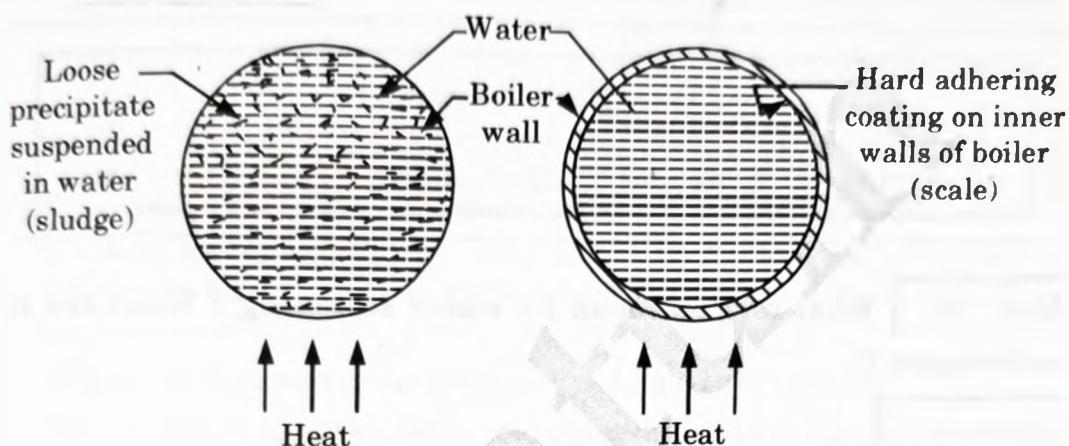


Fig. 4.6.2. Sludge and scale formation in boilers.

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.

PART-4

Technique for Water Softening (Lime-Soda, Zeolite, Ion-Exchange and Reverse Osmosis Process).

Questions-Answers

Long Answer Type and Medium Answer Type Questions

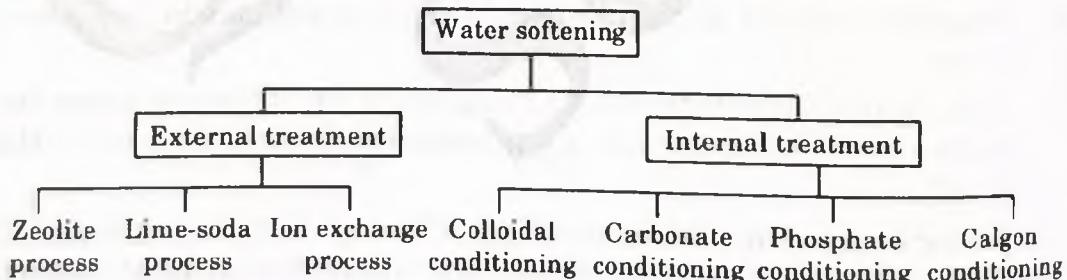
Que 4.7. What do you mean by water softening ? What are its techniques ?

Answer

A. 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. **Application :** Softening of water need to be done used in the steam production, for generation of electricity before feeding to the boiler.

B. Techniques :



The hardness causing salts can be removed from water by following two ways :

- a. **External Treatment :** The treatment of water is carried out before its entry into the boiler.
- b. **Internal Treatment :** Conditioning of water in the boiler itself by the addition of chemicals.

Que 4.8. Explain the Lime-Soda process for making soft water from hard water.

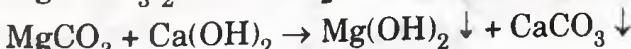
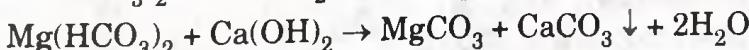
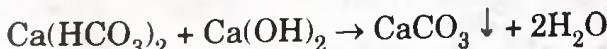
Answer

A. Principal of Lime-Soda Process :

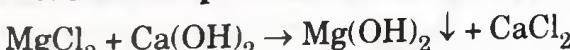
1. The basic principle of lime-soda process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration.
2. For this purpose, a suspension of milk of lime, $\text{Ca}(\text{OH})_2$, together with a calculated amount 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, $\text{Mg}(\text{OH})_2$; ferric hydroxide, $\text{Fe}(\text{OH})_3$ and aluminium hydroxide, $\text{Al}(\text{OH})_3$, so precipitated 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 [$\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$]; Aluminium sulphate [$\text{Al}_2(\text{SO}_4)_3$] or Sodium aluminate [NaAlO_2] are added, they hydrolyse to precipitate of aluminium hydroxide which entraps the fine precipitate of CaCO_3 , and $\text{Mg}(\text{OH})_2$.
8. Thus, coagulant helps in the formation of coarse precipitate.

B. Reactions with Lime :

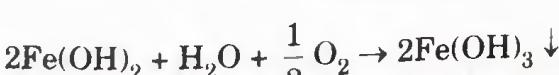
1. Removal of temporary hardness :



2. Removal of permanent Mg hardness :

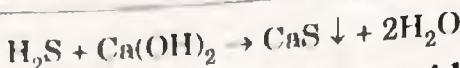
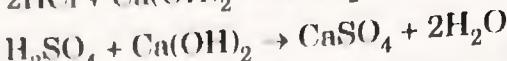
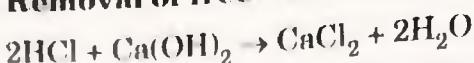
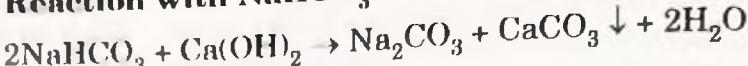


3. Removal of dissolved iron and aluminium salts :



4. Removal of dissolved CO_2 and H_2S :



**5. Removal of free mineral acids :****6. Reaction with NaHCO_3 :****C. Reactions of Soda :****D. Advantages of Lime-Soda Process :**

1. The process is highly economical.
2. The treatment leads to an increase in the pH value of water, thus reducing the corrosion of the distribution pipes.
3. This treatment also helps in reducing the total mineral content of water.

E. Disadvantages of Lime-Soda Process :

1. 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.
2. Careful operation and skilled supervision is required to get good results.
3. This process cannot produce water having zero hardness. This is because CaCO_3 , though very slightly, is soluble in water.

Que 4.9. Explain the basic principle of Lime-Soda process.

Calculate the amount of Lime and Soda required for softening 30000 liters of water, using 20 ppm of sodium aluminate as coagulant. Impurities in water are as follows :

$\text{Ca}^{2+} = 160 \text{ ppm}$, $\text{Mg}^{2+} = 96 \text{ ppm}$, dissolved $\text{CO}_2 = 34 \text{ ppm}$ and $\text{HCO}_3^- = 403 \text{ ppm}$.

AKTU 2017-18 (Sem-1), Marks 07

Answer

A. Principle of Lime-Soda Process : Refer Q. 4.8, Page 4-9B, Unit-4.

B. Numerical :

Given : Volume of water = 30000 L, $\text{NaAlO}_2 = 20 \text{ ppm}$, $\text{Ca}^{2+} = 160 \text{ ppm}$, $\text{Mg}^{2+} = 96 \text{ ppm}$, $\text{CO}_2 = 34 \text{ ppm}$, $\text{HCO}_3^- = 403 \text{ ppm}$

To Find : Amount of Lime and Soda.

1. Conversion to CaCO_3 Equivalent :

Constituent	Amount (ppm)	Multiplication Factor	CaCO_3 Equivalent (ppm)
Ca^{2+}	160	100/40	400
Mg^{2+}	96	100/24	400
CO_2	34	100/44	77.27
HCO_3^-	403	100/61 × 2	330.33
NaAlO_2	20	100/82 × 2	12.19

2 Lime Requirement :

$$= \frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{NaAlO}_2 \text{ all in terms of } \text{CaCO}_3 \text{ equivalent}]$$

$$= \frac{74}{100} [400 + 330.33 + 77.27 + 12.19] = 606.64 \text{ g/L}$$

Lime requirement for softening 30000 L

$$= \frac{606.64 \times 30000}{1000} \text{ g} = 18199.34 \text{ g}$$

3 Soda Requirement :

$$= \frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{NaAlO}_2 - \text{HCO}_3^- \text{ all in terms of } \text{CaCO}_3 \text{ equivalent}]$$

$$= \frac{106}{100} [400 + 400 + 12.19 - 330.33] = 510.782 \text{ g/L}$$

Soda requirement for softening 30000 L

$$= \frac{510.782 \times 30000}{1000} \text{ g} = 15323.46 \text{ g}$$

Que 4.10. A sample of water contains the following impurities :

$\text{Ca}^{2+} = 20 \text{ ppm}$, $\text{Mg}^{2+} = 18 \text{ ppm}$, $\text{HCO}_3^- = 183 \text{ ppm}$ and $\text{SO}_4^{2-} = 24 \text{ ppm}$. Calculate the Lime and Soda needed for softening.

AKTU 2017-18(Sem-2), Marks 3.5

Answer

Given : $\text{Ca}^{2+} = 20 \text{ ppm}$, $\text{Mg}^{2+} = 18 \text{ ppm}$, $\text{HCO}_3^- = 183 \text{ ppm}$, $\text{SO}_4^{2-} = 24 \text{ ppm}$

To Find : Amount of Lime and Soda.

1. Conversion to CaCO_3 Equivalent :

Constituent	Amount (ppm)	Multiplication Factor	CaCO_3 Equivalent (ppm)
Ca^{2+}	20	100/40	50
Mg^{2+}	18	100/24	75
HCO_3^-	183	100/61 × 2	150
SO_4^{2-}	24	100/96	25

2. Lime Requirement = $\frac{74}{100} [\text{Mg}^{2+} + \text{HCO}_3^- + \text{SO}_4^{2-}]$ all in terms of CaCO_3 equivalent]

$$= \frac{74}{100} [75 + 150 + 25] = \frac{74}{100} [250] = 185 \text{ ppm}$$

3. Soda Requirement = $\frac{106}{100} [\text{Ca}^{2+} + \text{Mg}^{2+} + \text{SO}_4^{2-} - \text{HCO}_3^-]$ all in terms of CaCO_3 equivalent]

$$= 106 / 100 [50 + 75 + 25 - 150] = 0 \text{ ppm}$$

Que 4.11. Calculate the quantities of lime (74 %) and soda (92 %) required for cold softening of 125,000 L of water with the following analysis, using 10 ppm of NaAlO_2 as coagulant. Analysis of raw water : $\text{Ca}^{2+} = 160 \text{ ppm}$, $\text{Mg}^{2+} = 48 \text{ ppm}$, $\text{CO}_2 = 66 \text{ ppm}$, $\text{HCO}_3^- = 264 \text{ ppm}$, $\text{H}^+ = 20 \text{ ppm}$, $\text{NaCl} = 4.7 \text{ ppm}$.

Analysis of treated water : $\text{CO}_3^{2-} = 45 \text{ ppm}$ and $\text{OH}^- = 68 \text{ ppm}$.

AKTU 2018-19 (Sem-2), Marks 10
Answer

Ion / Salt	Quantity	M.F.	Lime	Soda
Ca^{2+}	160	100/40	—	+ 400
Mg^{2+}	48	100/24	+ 200	+ 200
CO_2	66	100/44	+ 150	—
HCO_3^-	264	100/(61 × 2)	+ 216.39	- 216.39
H^+	20	100/2	+ 1000	+ 1000
NaCl	4.7	—	—	—
CO_3^{2-}	45	100/60	—	- 75
OH^-	68	100/(17 × 2)	+ 200	+ 200
			1766.39	1508.61

$$1. \text{ Lime requirement} = \frac{74}{100} \times 1766.39 \times \frac{125000}{10^6} = 163.39 \text{ kg}$$

$$\text{If 74 % pure} = \frac{163.39}{74/100} = 220.79 \text{ kg}$$

$$2. \text{ Soda requirement} = \frac{106}{100} \times 1508.61 \times \frac{125000}{10^6} = 199.89 \text{ kg}$$

$$\text{If 92 % pure} = \frac{199.89}{92/100} = 217.27 \text{ kg}$$

Que 4.12. Write the different chemical reactions taking place in soda-lime process. A sample of water on analysis gives following result :

Analysis of Raw water : $\text{Ca}^{2+} = 80 \text{ mg/l}$; $\text{Mg}^{2+} = 24 \text{ mg/l}$, $\text{CO}_2 = 33 \text{ mg/l}$, $\text{HCO}_3^- = 132 \text{ mg/l}$, $\text{H}^+ = 10 \text{ mg/l}$ & $\text{NaCl} = 4.3 \text{ ppm}$.

Analysis of treated water : $\text{CO}_3^{2-} = 12 \text{ mg/l}$ and $\text{OH}^- = 34 \text{ mg/l}$. Calculate the quantity of lime (74% pure) and soda (92 % pure) needed for softening 50000 L of water.

AKTU 2021-22 (Sem-1), Marks 10

Answer

Different chemical reactions taking place in soda-lime process : Refer Q. 4.8, Page 4-9B, Unit-4.

Constituent	Amount (mg/l) (w)	Equivalent weight $E = \times \left(\frac{\text{Molecular}}{\text{Valency}} \right)$	CaCO_3 Equivalent (mg/l) $\frac{w}{E} \times 50$
Ca^{2+}	80	$\frac{40}{2} = 20$	$\frac{80}{20} \times 50 = 200$
Mg^{2+}	24	$\frac{24}{2} = 12$	$\frac{24}{12} \times 50 = 100$
CO_2	33	$\frac{44}{2} = 22$	$\frac{33}{22} \times 50 = 75$
HCO_3^-	132	$\frac{61}{1} = 61$	$\frac{132}{61} \times 50 = 108.2$
H^+	10	$\frac{1}{1} = 1$	$\frac{10}{1} \times 50 = 500$
NaCl	4.3 ppm	$\frac{58.5}{1} = 58.5$	$\frac{4.3}{58.5} \times 50 = 3.7$

$$\text{Lime requirement} = \frac{74}{100} (\text{Mg}^{2+} + \text{HCO}_3^- + \text{CO}_2 + \text{H}^+) \\ = \frac{74}{100} (100 + 108.2 + 75 + 500) = 579.568 \text{ mg/l}$$

For 100 % pure and 1 litre lime required = 579.568 mg

$$\text{For 74 % pure and 50000 litre lime require} = \frac{579.568}{100} \times 74 \times 50000 \\ = 21444016 \text{ mg} = 21444 \text{ kg}$$

$$\text{Soda requirement} = \frac{106}{100} [\text{C}_n^{2+} + \text{M}_g^{2+}] = \frac{106}{100} [200 + 100] \\ = 318 \text{ mg/l}$$

For 100 % pure 1 litre soda require = 318 mg

$$\text{For 92 % pure 50,000 litre soda require} = 318/100 \times 92 \times 50,000 \\ = 1462800 \text{ mg} = 14628 \text{ kg}$$

Que 4.13. Write the process of lime soda softening. Calculate the amount of lime and soda required for the treatment of 20000 lts of water whose analysis is as follows : $\text{Ca}(\text{HCO}_3)_2 = 40.5$; $\text{Mg}(\text{HCO}_3)_2 = 36.5 \text{ ppm}$; $\text{MgSO}_4 = 30 \text{ ppm}$; $\text{CaCl}_2 = 27.75 \text{ ppm}$.

AKTU 2021-22(Sem-2), Marks 10

Answer

i. Lime-soda process : Refer Q. 4.8, Page 4-9B, Unit-4.

ii.

Impurities (ppm)	Multiplication factor	CaCO_3 equivalent mg/l	Requirement
$\text{Ca}(\text{HCO}_3)_2$ (40.5 ppm)	$\frac{100}{162}$	$40.5 \times \frac{100}{162} = 25$	Lime
$\text{Mg}(\text{HCO}_3)_2$ (36.5 ppm)	$\frac{100}{146}$	$36.5 \times \frac{100}{146} = 25$	2 × Lime
MgSO_4 (30 ppm)	$\frac{100}{120}$	$30 \times \frac{100}{120} = 25$	Lime + soda
CaCl_2 (27.75 ppm)	$\frac{100}{111}$	$27.75 \times \frac{100}{111} = 25$	Soda

Line requirement = $\frac{74}{100}$ [CaCO₃ equivalent of Cr (HCO₃)₂ +

$$2 \times \text{Mg} (\text{HCO}_3) \times \frac{\text{Volume of water}}{1000}$$

$$= \frac{74}{100} [25 + 2 \times 25 + 25] * \frac{20000}{1000} = 1480 \text{ gm}$$

Soda requirement = $\frac{106}{100}$ [CaCO₃ equivalent of Mg SO₄ + CaCl₂] ×

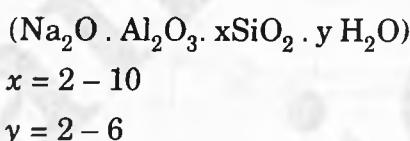
$$\frac{\text{Volume of water}}{1000} = \frac{106}{100} [25 + 25] \times \frac{2000}{1000}$$

$$= 1060 \text{ gm}$$

Que 4.14. | What do you understand by the term Zeolite ? Explain the types of Zeolite.

Answer

A. **Zelolite :** Zeolites are naturally occurring hydrated, sodium alumino-silicate minerals and also known as boiling stone. It is denoted as :



B. **Types of Zeolites :**

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

For example : Natrolite : Na₂O · Al₂O₃ · 4SiO₂ · 2H₂O

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.

OR

What is hardness of water ? What do you mean by term Permutit (Zeolite) ? Describe Zeolite or Permutit process for softening of hard water.

AKTU 2018-19 (Sem-1), Marks 10

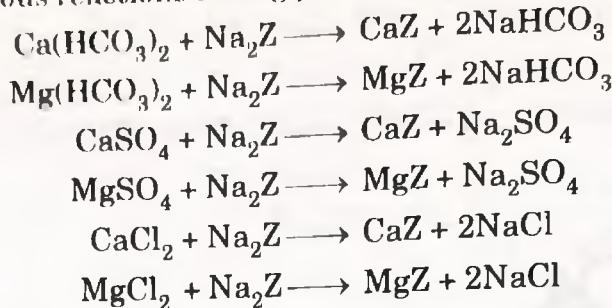
Answer

A. **Hardness of Water :** Refer Q. 4.3, Page 4-3B, Unit-4.

B. **Zeolite :** Zeolites can be represented as Na₂Z, where Z is the insoluble radical framework.

C. Principle :

- 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.
- The various reactions taking place may be indicated as follows :



- It is clear from these reactions that sodium zeolite is converted to calcium and magnesium zeolites.

D. Working :

- A zeolite softener consists of a steel tank packed with a thick layer of permuitit or zeolite.

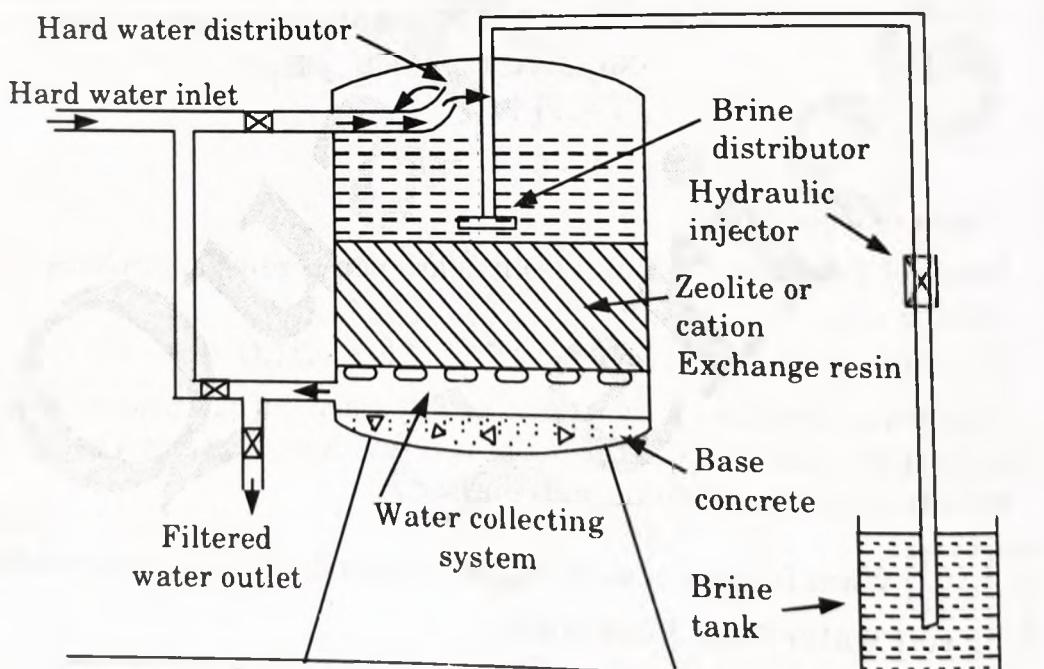


Fig. 4.15.1. Sectional view of Zeolite process for water softening.

- The hard water is percolated at a specified rate through the bed of zeolite.
- Calcium and magnesium ions present in it are retained by the zeolite in the form of CaZ and MgZ respectively.
- The outgoing water becomes rich in sodium salts. The softened water is collected from the bottom.

5. 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.
6. The soluble CaCl_2 and MgCl_2 so formed in regeneration process are washed with soft water and washings are led to sink.
7. The zeolite bed is ready for use again for softening purpose.
8. Theoretically each mg/L of CaCO_3 hardness requires 1.17 mg/L of NaCl solution.
9. But thrice the amount of theoretically required amount of NaCl is used to make regeneration reaction more efficient.

E. Advantages of Zeolite process :

1. Water having very low hardness of about 10 ppm hardness is produced. Even water having zero hardness can be produced.
2. The plant is compact and occupies less space.
3. No sludge is formed and hence there is no problem of sludge disposal.

F. Disadvantages of Zeolite process :

1. 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.
2. 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.
3. The process leaves sodium bicarbonate in water, which causes priming and foaming in industrial or boiler feed waters.

Que 4.16. | Describe Zeolite process of water softening. A zeolite softener was 90 % exhausted by removing the hardness completely when 10,000 litres of hard water was passed through it. The exhausted zeolite bed required 200 litres of 3 % sodium chloride solution for its complete regeneration. Calculate the hardness of water sample.

AKTU 2017-18 (Sem-1), Marks 07

Answer

Zeolite Process of Water Softening : Refer Q. 4.15, Page 4-15B, Unit-4.

Given : Exhaust % = 90 %, Volume of water = 10,000 L, Volume of NaCl = 200 L, NaCl % = 3 %

To Find : Hardness of water

$$3 \% \text{ NaCl} = \frac{3 \text{ g NaCl}}{100 \text{ ml}} = 30 \text{ g/L}$$

1. 200 L of 3 % NaCl required

$$= 200 \times 30 = 6000 \text{ g NaCl}$$

2. Amount of substance

$$(w) = 6000 \text{ g}$$

3. Equivalent mass of

$$\text{NaCl} (E) = 58.5$$

$$4. \text{ Equivalent of } \text{CaCO}_3 = \frac{w \times 50}{E} = \frac{6000 \times 50}{58.5}$$

$$= 5128 \text{ g CaCO}_3$$

$$5. 90 \% \text{ Hardness of } 10000 \text{ L of water} = 5128 \text{ g equivalent of CaCO}_3$$

$$6. 1 \text{ of L water} = \frac{5128 \times 1000}{10000 \times \frac{90}{100}} = \frac{5128}{9}$$

$$= 569.8 \text{ ppm}$$

Que 4.17. Explain the Zeolite process of water softening ? The hardness of 10,000L of a sample of water was removed by passing it through a zeolite softener. The zeolite softener then required 200 L of NaCl solution containing 150 gm/L of NaCl for regeneration. Find the hardness of water sample.

AKTU 2017-18(Sem-2), Marks 07

Answer

A. Zeolite Process : Refer Q. 4.15, Page 4-15B, Unit-4.

B. Numerical :

Given : Volume of NaCl = 200 L, Density of NaCl = 150 g/L,
Volume of water = 10,000 L

To Find : Hardness of water.

$$1. 1 \text{ L of NaCl} = 150 \text{ g}$$

$$200 \text{ L of NaCl} = 150 \times 200 = 30000 \text{ g}$$

$$2. \text{ Amount of substance } (w) = 30000 \text{ g}$$

$$3. \text{ Equivalent mass of NaCl} (E) = 58.5$$

$$4. \text{ Equivalent of } \text{CaCO}_3 = \frac{w \times 50}{E} = \frac{30,000 \times 50}{58.5} = 25641.02 \text{ g CaCO}_3$$

$$5. 10000 \text{ L water} = 25641.02 \times 1000 \text{ mg CaCO}_3$$

$$6. 1 \text{ L water} = \frac{25641.02 \times 1000}{10000} = 2564.102 \text{ ppm}$$

Que 4.18. Write the chemical name and molecular formula of zeolite. Give different chemical reactions taking place in zeolite process. A zeolite softener was regenerated by passing 50 ltrs of NaCl solution having strength of 14.625 g/l of NaCl. Calculate the hardness of water if 10000 ltrs of hard water was softened by using this zeolite.

AKTU 2021-22 (Sem-1), Marks 10

Answer

Chemical Name and Molecular Formula of Zeolite :
Refer Q. 4.14, Page 4-15B, Unit-4.

Given : Volume of NaCl = 50 ltr, Strength of NaCl = 14.625 gm/l

Volume of water = 10,000 ltr

To Find : Hardness of water.

$$1 \text{ litre of NaCl} = 14.625 \text{ gm}$$

$$50 \text{ ltr of NaCl} = 50 \times 14.625 = 731.25 \text{ gm}$$

$$\text{Amount of substance (w)} = 731.25 \text{ gm}$$

$$\text{Equivalent mass of NaCl (E)} = 58.5$$

$$\text{Equivalent of CaCO}_3 = \frac{w \times 50}{E} = \frac{731.25 \times 50}{58.5} = 625 \text{ g CaCO}_3$$

$$10,000 \text{ ltr water} = 625 \times 1000 \text{ mg CaCO}_3$$

$$\begin{aligned} 1 \text{ ltr water} &= \frac{625 \times 1000}{10,000} \text{ mg/l} \\ &= 62.5 \text{ ppm} \end{aligned}$$

Que 4.19. What are Ion exchange resins ? How will you purify water by using the resins ?

OR

What are Ion exchange resins ? Discuss their role in Ion exchange process of water softening.

Answer**A. Ion Exchange Resins :**

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 :**

- Resins containing acidic groups like – COOH or – SO₃H group are termed as cation exchange resins and are represented as RH⁺.
- 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.

b. **Anion Exchange Resins :**

- Resin containing basic functional groups like amine, substituted amine or quaternary ammonium groups as their hydroxide salts is termed as anion exchange resins and is represented as ROH⁻.
- 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.

B. Working :

- The ion exchange unit consists of two tanks. Cation exchange resins and anion exchange resins are placed in first and second tank respectively.
- First, hard water is made to pass through cation exchange resin which exchanges its H⁺ ions for Ca²⁺ and Mg²⁺ ions in water.



- The anions originally associated with Ca²⁺ or Mg²⁺ will be associated with H⁺ ions.
- Thus water after passing through cation exchanger is free of Ca²⁺ and Mg²⁺ ions.
- This water is then passed through another column having anion exchange resin.
- Here the anions like SO₄²⁻, Cl⁻ etc., present in water are exchanged for OH⁻ ions of the resin.



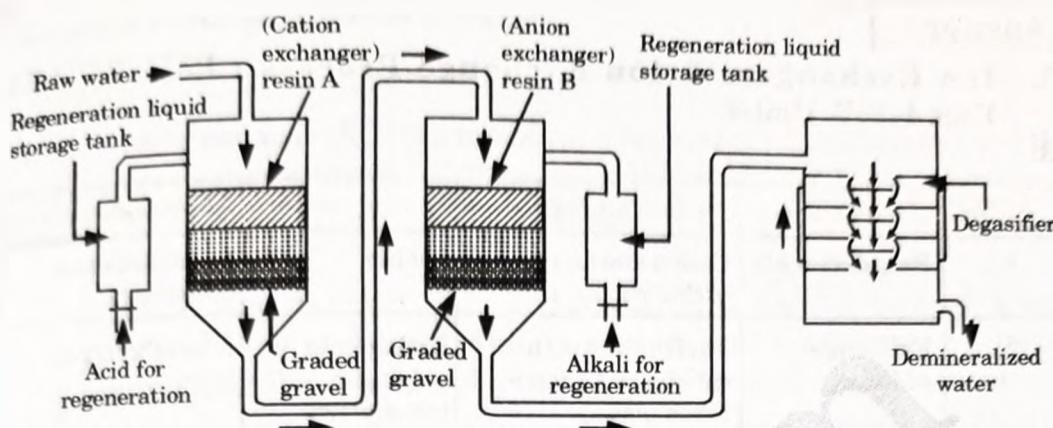
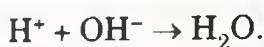


Fig. 4.19.1. Softener for demineralization.

7. The water coming out of the anion exchanger is completely free from cations and anions responsible for hardness.
8. It is known as deionized water or demineralized water. It is as pure as distilled water.
9. H^+ released from cation exchanger and OH^- released from anion exchanger combine to form unionized water.



C. Advantages :

1. Highly acidic or alkaline water can be softened.
2. Water of very low hardness is produced (about 2 ppm).

D. Disadvantages :

1. The equipments are costly. Moreover costly chemicals are required for regeneration.
2. Turbid water decreases the efficiency of the process.

Que 4.20. Give comparison between Ion Exchange, Zeolite and Lime-Soda process.

OR

What are ion exchangers ? With the help of neat sketch, discuss ion-exchange process for water softening. Compare its merit over zeolite process.

AKTU 2018-19 (Sem-2), Marks 10

Answer

A. Ion Exchangers & Ion Exchange Process : Refer Q. 4.19, Page 4-19B, Unit-4.

B.

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.	Automation	Possible	Possible	Not possible
6.	Residual hardness	Least (0-2 ppm)	Low (0-15 ppm)	High (15-50 ppm)

Que 4.21. Explain ion exchange process of water softening. Zeolite softener was 90 % exhausted when 10,000 L hard water was passed through it. The softener required 200 L of NaCl solution of strength 50 g/L. Calculate the hardness of water.

AKTU 2020-21 (Sem-1), Marks 10

Answer

A. Ion Exchange Process : Refer Q.4.19, Page 4-19B, Unit-4.

B. Numerical :

Given : Exhaust % = 90 %, volume of water = 10,000 L, Volume of NaCl = 200 L, NaCl strength = 50 g/L

To Find : Hardness of water.

- Equivalent mass of NaCl (E) = 58.5
- Amount of substance (w) = $200 \times 50 = 10000$ g
- Equivalent of $\text{CaCO}_3 = \frac{w \times 50}{E} = \frac{10000 \times 50}{58.5} = 8547$ g of CaCO_3
- 90 % of hardness of 10000 L of water = 8457 g equivalent of CaCO_3
- Hardness = $\frac{8457 \times 1000}{10,000 \times 90/100} = \frac{8457}{9} = 939.66$ ppm

Que 4.22. Discuss the process of reverse osmosis.

OR

Explain reverse osmosis process.**Answer**

- 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.
- Reverse osmosis pressurizes and passes impure water through a semi-permeable membrane and removes many of the impurities (approximately 90 % 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.
- 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.
- Reverse osmosis (RO) units removes 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.

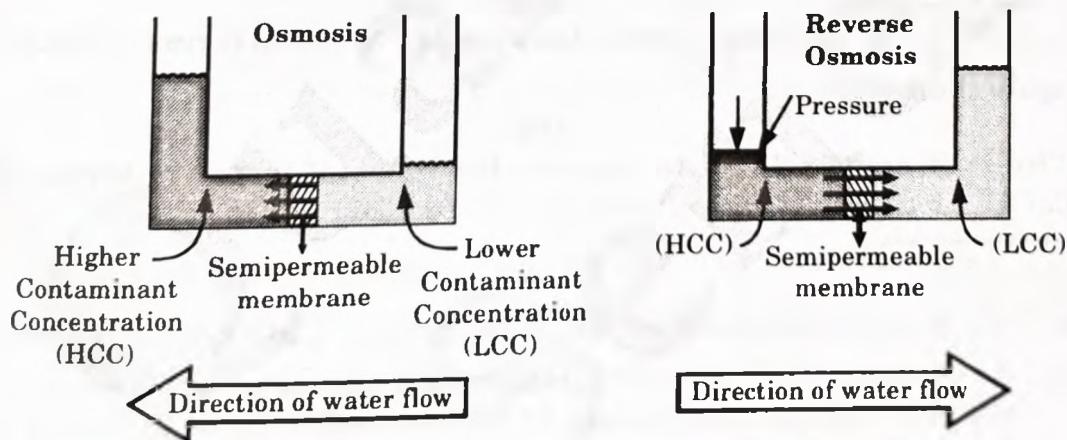


Fig. 4.22.1. Diagrammatic representation of osmosis and reverse osmosis processes.

Que 4.23. Explain reverse osmosis with its advantages.

A water sample on analysis gives the following data : $\text{Ca}^{2+} = 20 \text{ ppm}$, $\text{Mg}^{2+} = 25 \text{ ppm}$, $\text{CO}_2 = 30 \text{ ppm}$, $\text{HCO}_3^- = 150 \text{ ppm}$, $\text{K}^+ = 10 \text{ ppm}$. Calculate the lime (87 % pure) and soda (91 % pure) required to soften 106 liter of sample water.

AKTU 2018-19 (Sem-1), Marks 10

Answer

Reverse osmosis : Refer Q. 4.22, Page 4-22B, Unit-4.

Advantages of reverse osmosis (RO) :

1. Energy requirement is low.
2. Very high salt rejection rate.
3. Excellent rejection of microorganisms and organic compounds.

Numerical : The procedure is same as Q. 4.11, Page 4-12B, Unit-4.

(Ans. Lime = 0.019 kg, Soda = 0.027 kg)

PART-5

Determination of Hardness and Alkalinity.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.24. Why do we express hardness of water in terms of CaCO_3 equivalent ?

OR

Why is it conventional to express hardness of water in terms of CaCO_3 at the international level ? Write other units also.

Answer

- A. We express Hardness of Water 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. 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 to convert various hardness salts CaCO_3 equivalents we may use,
Equivalents of CaCO_3

$$= \frac{\text{Mass of the substance} \times \text{Equivalent weight of } \text{CaCO}_3}{\text{Equivalent weight of the substance}} \quad \dots(4.23.1)$$

5. As equivalent weight of most of the hardness causing substances and that of CaCO_3 = Molecular weight/2, hence to make mathematical calculations more easier, the eq.(4.4.1) can be written in terms of molecular weights i.e.,

Equivalents of CaCO_3

$$= \left[\frac{\text{Mass of the substance}}{\text{Molecular mass of the substance} / 2} \times 100 \right] / 2$$

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

B. Units :

- Parts Per Million (ppm) :** ppm is the parts of calcium carbonate equivalent hardness per 10^6 parts of water.
- Milligrams Per Litre (mg/L) :** It is the number of milligrams of CaCO_3 equivalent hardness present per liter of water.

$$1 \text{ mg/L} = 1 \text{ mg of } \text{CaCO}_3 \text{ equivalent hardness per L of water.}$$

But 1 L of water weighs = 1000 gm = 1000×1000 mg

$$1 \text{ mg/L} = 1 \text{ mg}/10^6 \text{ mg} = 1 \text{ ppm.}$$

- Clarke's Degree (${}^{\circ}\text{Cl}$) :** It is the number of grains (1 grains = 1/7000 lb) of CaCO_3 equivalent hardness per gallon (10 lb) of water. Or simply, it is the parts of CaCO_3 equivalent hardness per 70,000 parts of water.
 $1 {}^{\circ}\text{ Clarke} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent hardness per 70,000 parts of water.}$
- Degree French (${}^{\circ}\text{Fr}$) :** It is the part of CaCO_3 equivalent hardness per 10^5 parts of water.

C. Relationship between various Units of Hardness :

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1 {}^{\circ}\text{Fr} = 0.07 {}^{\circ}\text{Cl}$$

$$1 {}^{\circ}\text{Fr} = 10 \text{ ppm} = 10 \text{ mg/L} = 0.7 {}^{\circ}\text{Cl}$$

$$1 {}^{\circ}\text{Cl} = 14.3 \text{ ppm} = 14.3 \text{ mg/L} = 1.43 {}^{\circ}\text{Fr}$$

Que 4.25. 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 $\text{CaSO}_4 = 12.6 \text{ mg/L}$.

Answer

Given : $Mg(HCO_3)_2 = 9.3 \text{ mg/L}$, $Ca(HCO_3)_2 = 17.4 \text{ mg/l}$, $MgCl_2 = 8.7 \text{ mg/L}$ and $CaSO_4 = 12.6 \text{ mg/L}$.

To Find : Temporary and total hardness of water.

1. Calculation of $CaCO_3$ equivalent :

Constituent	Amount (ppm)	Multiplication Factor	$CaCO_3$ Equivalent (ppm)
$Mg(HCO_3)_2$	9.3	100/146	6.36 mg/L
$Ca(HCO_3)_2$	17.4	100/162	10.74 mg/L
$MgCl_2$	8.7	100/95	9.15 mg/L
$CaSO_4$	12.6	100/136	9.264 mg/L

2. Temporary Hardness :

Temporary hardness of water is due to $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$.
 $\text{Temporary hardness} = 6.36 + 10.74 = 17.10 \text{ mg/L}$

3. Permanent Hardness :

Permanent hardness of water is due to $MgCl_2$ and $CaSO_4$.
 $\text{Permanent hardness} = 9.15 + 9.26 = 18.41 \text{ mg/L}$

4. Total Hardness = 35.51 mg/L

PART-6

Definition Classification and Characteristic of a Good Fuel.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.26. Define fuel. Give its classification and also list the characteristics of a good fuel.

Answer

A. Fuel :

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.

B. Classification :**1. On the basis of their Occurrence :**

- a. **Natural or Primary Fuels** : Fuels which are found in nature are called natural fuels.

Examples : Wood, coal, peat, petroleum and natural gas.

- b. **Artificial or Secondary Fuels** : Fuels which are prepared artificially generally from primary fuels are called artificial fuels.

Examples : Coke, kerosene oil, petrol, coal gas etc.

2. On the basis of Physical State of Aggregation :

Table 4.26.1. Classifications of chemical fuels.

Types of fuel	Natural or Primary	Artificial or Secondary
Solid	Wood, peat, lignite, 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.

C. Characteristics of a Good fuel :

- High calorific value** : 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** : Fuel with low ignition temperature is safe for storage, handling and transport but there might be some difficulty during ignition of fuel.

i. 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.

- 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 :** Too high combustion rates are 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, SO₂, H₂S and other poisonous gases.
7. Low cost
8. Easy to transport
9. Low storage cost.

PART-7

Calorific Values Gross and Net Calorific Values.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.27. Define calorific value. What are gross and net calorific values ?

Answer

- A. **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.
- B. **Higher or Gross Calorific Value (HCV or GCV) :**
 1. 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.
 2. Example : 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.
- C. **Lower or Net Calorific Value (LCV or NCV) :**
 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 vapour escapes as such along with hot combustion gases.
 3. 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.
 Hence, $\text{LCV} = \text{HCV} - \text{Mass of hydrogen} \times 9 \times \text{Latent heat of steam.}$

PART-B*Determination of Calorific Value By Bomb Calorimeter.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 4.28. With the help of neat sketch, explain construction, principle and working of a Bomb Calorimeter.

OR

What do you understand by the term GCV and NCV ? Explain the construction and working of Bomb Calorimeter.

AKTU 2017-18 (Sem-2), Marks 07

OR

Explain the process of determination of calorific value using Bomb calorimeter method.

AKTU 2021-22 (Sem-2), Marks 10

Answer

A. GCV and NCV : Refer Q. 4.27, Page 4-28B, Unit-4.

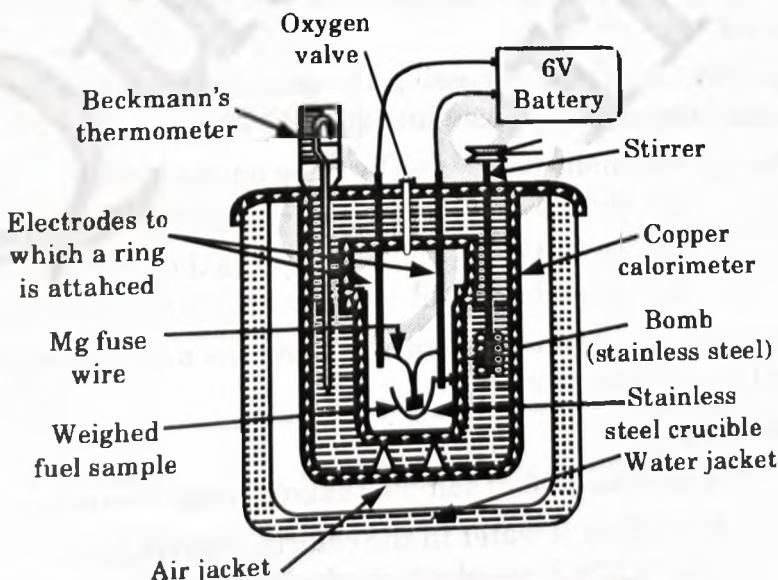


Fig. 4.28.1. Bomb calorimeter.

B. 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.

ii. Construction :

1. It consists of a strong cylindrical stainless steel bomb capable of withstanding 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.

iii. 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 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.

iv. Calculations :

1. 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
 $(= \text{Wt. of apparatus} \times \text{Specific heat} = W' \times S)$
 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.)

2. Heat liberated by burning of fuel = $x L$ cal.
3. Heat absorbed by water = $\{W \times S \times (T_2 - T_1)\}$
4. Heat absorbed by apparatus = $\{W' \times S \times (T_2 - T_1)\} = w (T_2 - T_1)$
5. 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
6. Hence, total heat absorbed by water, apparatus etc.
 $= [W \times 1 \times (T_2 - T_1) + w \times 1 \times (T_2 - T_1)]$
 $= [(W + w) \times 1 (T_2 - T_1)] \text{ cal}$
7. But, heat liberated by the fuel = Heat absorbed by water, apparatus etc.
 $x L = (W + w) (T_2 - T_1)$
8. HCV of fuel (L) = $\frac{(W + w) (T_2 - T_1)}{x} \text{ cal/gm}$ or $\frac{\text{kcal}}{\text{kg}}$

Que 4.29. What is the basic principle of Bomb Calorimeter ? A 0.80 g sample of solid fuel was completely combusted in the excess of oxygen using Bomb Calorimeter. The rise in temperature of water in calorimeter was 2.5°C . Calculate the high calorific value of the fuel. If water taken in calorimeter is 2000 g and water equivalent of calorimeter is 2200 (Given % H in fuel = 2.2).

AKTU 2017-18 (Sem-1), Marks 07

Answer

- A. Principle of Bomb Calorimeter : Refer Q. 4.28, Page 4-29B, Unit-4.
 B. Numerical :

Given : $x = 0.8 \text{ g}$, $w = 2200 \text{ g}$, $W = 2000 \text{ g}$, $H = 2.2 \%$, $t_2 - t_1 = 2.5^\circ\text{C}$,

Latent heat of water = 587 cal/g

To Find : HCV and LCV.

1. $\text{HCV} = \frac{(W + w) (t_2 - t_1)}{x} = \frac{(2000 + 2200)(2.5)}{0.8} = 13125 \text{ cal/g}$
2. $\text{LCV} = \text{HCV} - 0.09 \times H \times 587 = 13125 - 0.09 \times 2.2 \times 587$
 $= 13008 \text{ cal/g}$
3. In mega joules per kilogram :
 $\text{HCV} = 13008 \times 4.18 \text{ J/g}$
 $= \frac{54373.44 \times 10^3}{10^6} \text{ MJ/kg}$
 $= 54.37 \text{ MJ/kg}$

Que 4.30. With the help of a neat diagram, explain the working of bomb calorimeter. A sample of coal contain C = 91 %, H = 5.5 %, N = 2.5 % and ash = 2 %. The following data were obtained when the above coal was tested in bomb calorimeter :

Weight of coal burnt = 1.029 g

Weight of water taken = 570 g

Water equivalent of bomb and calorimeter = 2200 g

Rise in temperature = 3.3 °C

Fuse wire correction = 3.8 cal

Acid correction = 62.6 cal

Cotton thread correction = 1.6 cal

Cooling correction = 0.047 °C

Assuming that the latent heat of condensation of steam is 587 cal / gm, calculate gross and net calorific values of the coal.

AKTU 2018-19 (Sem-2), Marks 10

Answer

A. Bomb Calorimeter : Refer Q. 4.28, Page 4-29B, Unit-4.

$$\begin{aligned} 1. \quad GCV &= \frac{(2200 + 570)(3.3 - 0.047) - [3.8 + 62.6 + 1.6]}{1.029} \\ &= 8690.78 \text{ cal/gm} \\ 2. \quad NCV &= GCV - 0.09 \times H \times \text{Latent heat} \\ &= 8690.78 - 0.09 \times 5.5 \times 587 = 8400.21 \text{ cal/gm} \end{aligned}$$

Que 4.31. Explain the construction and working principle of Bomb calorimeter. A sample of coal contains 80 % C, 15 % H, and 5 % Ash. The following data were obtained when the above coal sample was tested in bomb calorimeter : Weight of coal burnt = 0.98 g Weight of water taken = 1000 g Water equivalent of bomb calorimeter = 2500 g Observed rise in temperature = 2.5 °C Fuse wire correction = 8 cal Acid correction = 50 cal Cooling correction = 0.02 °C Calculate gross and net calorific value of coal if the latent heat of condensation of water is 580 cal/g.

AKTU 2021-22 (Sem-1), Marks 10

Answer

A. Bomb Calorimeter : Refer Q. 4.28, Page 4-29B, Unit-4.

Given : Wt. of coal burnt (x) = 0.98 g

Wt. of water taken (w) = 1000 g

Water equivalent of bomb calorimeter (W) = 2500 g

Rise in temp ($t_2 - t_1$) = 2.5 °C

Fuse wire correction = 8 cal

Acid correction = 50 cal

Cooling correction $\Delta t = 0.02^\circ\text{C}$

$$\begin{aligned} \text{GCV} &= \frac{(W + w)(t_2 - t_1 - \Delta t) - [\text{Acid correction} \\ &\quad + \text{Fuse wire Correction}]}{x} \\ &= \frac{(1000 + 2500)(2.5 - 0.02) - (50 + 8)}{0.98} \\ &= 8797.95 \approx 8798 \text{ cal/gm} \\ \text{NCV} &= \text{GCV} - 0.09 \times H \times \text{latent heat} \\ &= 8798 - 0.09 \times 15 \times 580 \\ &= 8015 \text{ cal/gm} \end{aligned}$$

PART-9

Theoretical Calculation of Calorific Value by Dulong Method.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.32. | What is Dulong Formula for calculation of theoretical calorific value of fuel ?

Answer

1. The theoretical gross or higher calorific value of a coal sample from ultimate analysis data can be calculated by Dulong formula.
2. On the basis of calorific values of elements :

Carbon = 8080 cal/g,

Hydrogen = 34500 cal/g

Sulphur = 2240 cal/g,

$$3. \text{ GCV in cal/gm} = \frac{1}{100} \left[8080 \text{ C} + 34500 \left(\text{H} - \frac{\text{O}}{8} \right) + 2240 \text{ S} \right] \text{ cal / gm}$$

where C, H, O, S represent the percentages of carbon, hydrogen, oxygen and sulphur respectively in the coal.

Que 4.33. | Describe proximate analysis of fuels.

A coal sample has the following composition by weight : C = 90 %, O = 3 %, S = 0.5 %, N = 0.5 % and Ash = 2.5 %. Net calorific value of the coal was found to be 8,490.5 kcal/kg. Calculate the percentage of hydrogen and Gross calorific value.

AKTU 2018-19 (Sem-1), Marks 10

Answer

Proximate analysis : Refer Q. 4.37, Page 4-37B, Unit-4.

Numerical :

$$\begin{aligned} 1. \quad H \% &= 100 \% (C + O + S + N + \text{Ash}) \\ &= 100 \% - (90 + 3 + 0.5 + 0.5 + 2.5) \\ &= 3.5 \% \end{aligned}$$

$$\begin{aligned} 2. \quad GCV &= \frac{1}{100} \left[8080(C) + 3400\left(H - \frac{O}{8}\right) + 2240(S) \right] \\ &= 7389.45 \text{ kcal / kg} \end{aligned}$$

Que 4.34. | The percentage composition of coal sample is C = 70 %,

H₂ = 10 %, O₂ = 1 %, S = 5 %, ash = 0.5 % and N = 0.3 %.

- Calculate the quantity of air needed for complete combustion of 1 kg of coal. If 60 % excess of air is supplied.
- Calculate the gross and net calorific value of the coal using Dulong's formula.

AKTU 2020-21 (Sem-1), Marks 10

Answer

- 1kg of coal contains :

$$C = 700 \text{ g}, H_2 = 100 \text{ g}, O_2 = 10 \text{ g}, S = 50 \text{ g}$$

$$\begin{aligned} \text{Net } O_2 &= \left[\frac{32}{12} \times C + \frac{16}{2} \times H + \frac{32}{32} \times S \right] - O_2 \text{ in fuel} \\ &= \left[\frac{32}{12} \times 700 + \frac{16}{2} \times 100 + \frac{32}{32} \times 50 \right] - 10 = 2706.67 \text{ g} \end{aligned}$$

Quantity of air needed

$$= \text{Net } O_2 \times \frac{100}{23} \times \frac{160}{100} = 18829.01 \text{ g} = 18.83 \text{ kg}$$

$$\begin{aligned} \text{ii. GCV or HCV} &= \frac{1}{100} \left[8080 C + 34500 \left(H - \frac{O}{8} \right) + 2240 S \right] \\ &= \frac{1}{100} \left[8080 \times 700 + 34500 \left(100 - \frac{10}{8} \right) + 2240 \times 50 \right] \end{aligned}$$

$$= 9174.87 \text{ kcal/kg}$$

$$\text{NCV or LCV} = \text{GCV} - 0.09 H \times 587$$

$$= 9174.87 - 0.09 \times 10 \times 587 = 8646.57 \text{ kcal/kg}$$

Que 4.35. What is calorific value ? Explain the construction and working of bomb calorimeter ? A coal has the following composition by weight C = 92 %, O = 2.0 %, S = 0.5 %, N = 0.5 % and ash = 2.5 % Net calorific value of the coal was found to be 9,430 kcal/Kg ,Calculate the percentage of hydrogen and gross calorific value of coal ?

AKTU 2021-22 (Sem-2), Marks 10
Answer

Calorific Value : Refer Q. 4.27, Page 4-28B, Unit-4.

Bomb Calorimeter : Refer Q. 4.28, Page 4-29B, Unit-4.

Given : C = 92 %, O = 2 %, S = 0.5 %, N = 0.5 % and ash = 2.5 %

Net calorific value (NCV) = 9430 kcal/kg

To Find : i. Percentage of Hydrogen
ii. Gross calorific value of coal

Gross calorific value (GCV)

$$= \frac{1}{100} \left[8080 C + 34500 \left(H - \frac{0}{8} \right) + 22405 \right] \text{ k cal/kg}$$

Net calorific value (NCV)

$$= \left[\text{GCV} - \frac{9H}{100} \times 587 \right] \text{ k cal/kg}$$

$$\text{GCV} = \frac{1}{100} \left[8080 \times 92 + 34500 \left(H - \frac{2}{8} \right) + 2240 \times 0.5 \right]$$

$$= 7433.6 + 345 (H - 0.25) + 11.2$$

$$= 7444.8 + 345 H - 86.28$$

$$\text{GCV} = 7358.55 + 345 H$$

Net calorific value

$$= 7358.55 + 345 H - \frac{9H}{100} \times 587$$

$$9430 = 7358.55 + 345 H - 52.83 H$$

$$9430 - 7358.55 = 292.17 H$$

$$H = \frac{2071.45}{292.17} = 7.089 \%$$

$$H = 7.1 \%$$

Gross calorific value GCV

$$= 7358.55 + 345 \times 7.1$$

$$= 9808.05 \text{ k cal/kg}$$

PART-10*Ranking of Coal.***Questions-Answers****Long Answer Type and Medium Answer Type Questions**

Que 4.36. | What is coal ? What is rank or types of coal ?

Answer

- A. **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.
- B. **Types or Rank of Coal :**
 - 1. **Peat :**
 - i. Peat is brown and fibrous in texture.
 - ii. Air dried peat contains 15-25 % moisture and it crumbles into powder during air drying. Calorific value of peat is about 5400 cal/gm.
 - iii. It has low density.
 - iv. It contains 57 % C, 6 % H, 35 % O, 3-6 % Ash.
 - 2. **Lignite :**
 - i. It is the intermediate stage between peat and black coal.
 - ii. It is brownish black and more compact than peat
 - iii. It contains 45-50 % volatile matter and burns with long flame.
 - iv. Its calorific value is 6000 – 6700 cal/gm and C % = 65-70 %.
 - v. It contains 5 % H, 20 % O, 10-15 % Ash.
 - 3. **Bituminous Coals :**
 - a. **Sub-bituminous Coal :**
 - i. This coal has characters between lignite and bituminous coal.
 - ii. It is harder and denser than lignite. It is grey black and has dull waxy lustier.
 - iii. Its calorific value is about 7000 cal/gm and 70-75 % C. It contains large volatile matter 35-40 %. It crumbles into pieces on air drying and during transportation.
 - iv. It is non-caking coal.
 - v. This coal is used for domestic and industrial purposes.

b. Bituminous Coal :

- i. This coal has banded or laminated structure with alternate bright and dull layers.
- ii. It has cubical fracture.
- iii. It is black, dense and hard.
- iv. It contains 75-85 % C and has calorific value 8000 – 8500 cal/gm.
- v. It is a caking coal, and forms coke and coal gas on carbonizations, as it contains 20-30 % of volatile matter.

c. Semi bituminous Coal :

- i. It has characters between bituminous and anthracite coals.
- i. It has low volatile matter and has coking property.
- iii. Its calorific value is about 840 cal/gm, C % = 85-90 %.

4. Anthracite Coal :

- i. It has calorific value about 8700 cal/gm and 92-98 % C.
- ii. It contains very low volatile matter, ash, moisture.
- iii. It is highly lustrous black and hard coal.
- iv. It burns with non-smoky short blue flame of high temperature.

PART - 11*Analysis of Coal by Proximate and Ultimate Analysis of Coal.***Questions-Answers****Long Answer Type and Medium Answer Type Questions****Que 4.37. | Explain Proximate Analysis.****OR**

Draw diagram of bomb calorimeter. Explain proximate analysis of coal.

AKTU 2020-21 (Sem-1), Marks 10**Answer**

Bomb Calorimeter : Refer Q. 4.28, Page 4-29B, Unit-4.

Proximate analysis is the study of coal sample in which following parameters are found out :

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.

Method : 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 $105 - 110^{\circ}\text{C}$. Then the crucible is taken out, cooled in a desiccator and weighed. The amount of weight loss is reported as moisture.

$$\text{Formula :} \quad \text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

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.

Method : The moisture free coal is taken in silica crucible covered with lid and kept in a multiple furnace at $925 \pm 25^{\circ}\text{C}$ for 7 minute. 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.

Formula : 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.

Method : 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 $700 - 750^{\circ}\text{C}$ for half an hour in a muffle furnace. Heating, cooling and weighing is repeated till a constant weight is obtained.

$$\text{Formula :} \quad \text{Ash \%} = \frac{\text{Weight of Ash}}{\text{Weight of coal sample taken}} \times 100$$

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.

Formula :

$$\text{Fixed carbon \%} = 100 \% - \% \text{ of (Moisture + Volatile + Ash matter)}$$

Que 4.38. What is rank of coal ? Describe Proximate and Ultimate

Analysis of coal.

AKTU 2017-18 (Sem-1), Marks 07

Answer

A. **Rank of Coal :** Refer Q. 4.36, Page 4-36B, Unit-4.

B. **Proximate Analysis :** Refer Q. 4.37, Page 4-37B, Unit-4.

C. Ultimate Analysis : It includes the exact estimation of carbon, hydrogen, nitrogen, sulphur and oxygen present in fuel.

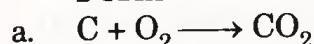
i. **Determination of C and H :**

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.

Method :

- a. 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 CO_2 and H_2O respectively.
- b. The gaseous products of combustion are passed through two bulbs.
- c. One containing weighed amount of anhydrous CaCl_2 which absorbs water, $\text{CaCl}_2 + 7 \text{H}_2\text{O} \rightarrow \text{CaCl}_2 \cdot 7 \text{H}_2\text{O}$ and the other containing weighed amount of KOH which absorbs carbon dioxide $2 \text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$.
- d. The weights of CaCl_2 and KOH in the bulbs are then determined.
- e. The increase in the weight of CaCl_2 bulb represents the weight of water formed, while the increase in the weight of KOH bulb represents the weight of CO_2 formed.

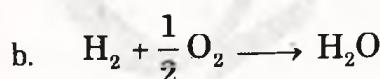
Formula :



$$\frac{\text{Wt. of Carbon (C)}}{\text{Wt. of } \text{CO}_2 [\text{= Increase in wt. of KOH tube}]} = \frac{\text{Wt. of C (= 12)}}{\text{Mol. wt. of } \text{CO}_2 (= 44)}$$

$$\% \text{ C} = \frac{\text{Wt. of C}}{\text{Wt. of coal}} \times 100$$

$$\% \text{ C} = \frac{\text{Increase in wt. of KOH tube} \times 12}{\text{wt. of coal sample taken} \times 44} \times 100$$



$$\frac{\text{Wt. of Hydrogen (H}_2\text{)}}{\text{Wt. of H}_2\text{O} [\text{= Increase in wt. of CaCl}_2 \text{ tube}]} = \frac{\text{Mol. Wt. of Hydrogen (H}_2 = 2\text{)}}{\text{Mol. Wt. of H}_2\text{O} (= 18)}$$

$$\% \text{ H} = \frac{\text{Wt. of Hydrogen}}{\text{Wt. of coal}} \times 100$$

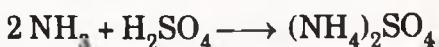
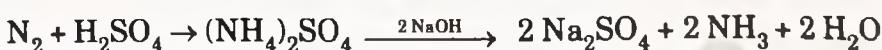
$$\therefore \% \text{ of H} = \frac{\text{Increase in Wt. of CaCl}_2 \text{ tube} \times 2}{\text{Wt. of coal sample taken} \times 18} \times 100$$

2. **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.

Method : 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.
- 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.
- The ammonia thus produced is distilled over and absorbed in a known volume (V_1) of standard H_2SO_4 solution ($N/10$)



- 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,

$$= N/10 \times V_1 - N/10 \times V_2$$

$$= 0.1(V_1 - V_2) \text{ milli equivalents}$$

$$= \frac{0.1(V_1 - V_2)}{1000} \text{ equivalents}$$

$$\text{Wt. of N} = \frac{0.1(V_1 - V_2)}{1000} \times 14$$

$$\begin{aligned} \text{iii. Formula : } \% \text{ of N} &= \frac{\text{Wt. of N}}{\text{Wt. of coal sample taken (1 gm)}} \times 100 \\ &= \frac{0.1(V_1 - V_2)/1000}{1} \times 14 \times 100 \\ &= 0.1(V_1 - V_2) \times 1.4 \\ \Rightarrow \% \text{ of N} &= 0.1(V_1 - V_2) \times 1.4 \end{aligned}$$

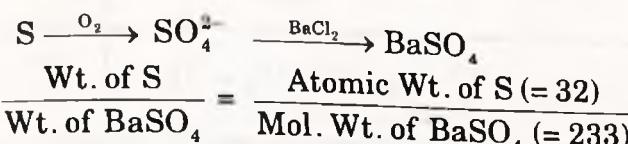
3. Determination of Sulphur :

- 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.
- Sulphur 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.

Method :

- 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.

- b. The ash from the bomb calorimeter is extracted with dil. hydrochloric acid.
- c. The acid extract is then treated with barium chloride solution to precipitate sulphate as BaSO_4 .
- d. The ppt. of BaSO_4 is filtered, washed, dried and heated to constant weight.



- e. Let weight of BaSO_4 precipitate is W_2 gm and of coal is W_1 g

$$\text{Hence, wt. of S} = \frac{32}{233} \times W_2 \text{ gm.}$$

Formula :

$$\therefore \% \text{ of S in coal} = \frac{\text{Wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Wt. of coal sample taken in bomb} \times 233}$$

$$\Rightarrow \% \text{ of S in coal} = \frac{W_2}{W_1} \times \frac{32}{233} \times 100$$

- 4. **Determination of Ash :** Determination is carried out as in proximate analysis.

5. **Determination of Oxygen :**

- a. Oxygen is present in combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than the actual one.
- b. High oxygen content coals have high inherent moisture and low calorific value.
- c. An increase in 1% oxygen content decreases the calorific value by about 1.7 %.
- d. Thus, a good quality coal should have low % of oxygen.

Method : It is determined indirectly by deducting the combined

Formula : % of (C, H, N, S and ash) from 100.

$$\% \text{ of Oxygen} = 100 - \% \text{ of (C + H + N + S + Ash).}$$

Que 4.39. Calculate the minimum weight of air required for complete combustion of 1kg of fuel containing C = 90 %, H = 3.5 %, O = 3.0 %, S = 0.5 %, H_2O = 1 %, N = 0.5 % and ash = rest.

AKTU 2017-18 (Sem-2), Marks 3.5

Answer

Given : C = 90 %, H = 3.5 %, O = 3 %, S = 0.5 %, H_2O = 1 %,

N = 0.5 %, Ash = 1.5 %

To Find : Weight of air.

1. Calculation of weight of O₂:

Constituent	Amount (%)	Combustion Reaction	Weight of O ₂ Required
Carbon (C)	90	C (12 g) + O ₂ (32 g) → CO ₂	$\frac{32 \times 90}{12} = 240$
Hydrogen (H)	3.5	H ₂ (2 g) + 1/2 O ₂ (16 g) → H ₂ O	$\frac{16 \times 3.5}{2} = 28$
Sulphur (S)	0.5	S (32 g) + O ₂ (32 g) → SO ₂	$\frac{32 \times 0.5}{32} = 0.5$
Oxygen (O ₂)	3	—	—
Water (H ₂ O)	1	—	—
Nitrogen (N ₂)	0.5	—	—

2. Nitrogen, Water, Oxygen, does not burn hence does not consume oxygen.

3. Theoretical oxygen required for 100 kg of fuel

$$= 240 + 28 + 0.5 = 268.5 \text{ kg}$$

4. Net amount required = O₂ required - O₂ present in fuel

$$= 268.5 - 1 = 267.5 \text{ kg of O}_2$$

5. Air required

$$= 267.5 \times 100/23$$

$$= 1163.043 \text{ kg}$$

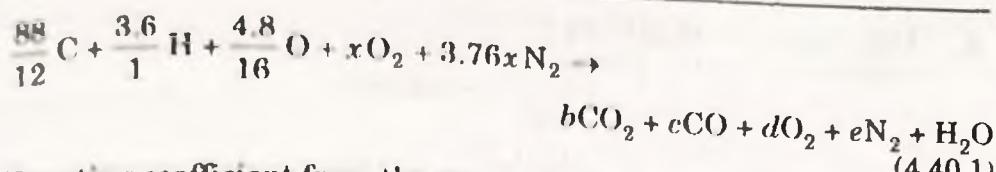
Que 4.40. The analysis of the coal in a boiler trial was C = 88 %, H = 3.6 %, O = 4.8 %, other matters 3.6 % and the fuel gas analysis by volume was CO₂ = 10.9 %, CO = 1 %, O₂ = 7.1 %, N₂ = 81 %. Find the proportion of carbon burned to CO and the air required for kg of fuel for the combustion as it actually occurred and also the weight of fuel gas per kg of fuel burned.

Answer

Given : CO₂ = 10.9 %, CO = 1 %, O₂ = 7.1 %, N₂ = 81 %, C = 88 %, H = 3.6 %, O = 4.8 %, other matters = 3.6 %

To Find : Proportion of carbon burned to CO.

1. Since, the fuel analysis is given on mass basis, so let us consider 100 kg of fuel.
2. Let x mole of oxygen are supplied for combustion.
3. The combustion equation on mole basis is given as,



4. Equating coefficient from the eq. (4.40.1)

Carbon : $\frac{88}{12} = b + c$

Hydrogen : $\frac{3.6}{1} = 2f$
 $f = 1.8$

Oxygen : $\frac{4.8}{32} + x = b + \frac{c}{2} + d + \frac{f}{2}$

Nitrogen : $3.76x = e$

5. Based on volumetric analysis of dry fuel gases

$$\frac{b}{b+c+d+e} = 0.109 \quad \dots(4.40.2)$$

$$\frac{c}{b+c+d+e} = 0.01 \quad \dots(4.40.3)$$

$$\frac{d}{b+c+d+e} = 0.071 \quad \dots(4.40.4)$$

$$\frac{e}{b+c+d+e} = 0.81 \quad \dots(4.40.5)$$

6. Dividing eq. (4.40.2) by eq. (4.40.3), we have

$$\frac{b}{c} = \frac{0.109}{0.01} = 10.9$$

$$b = 10.9c$$

$$b + c = \frac{88}{12}$$

$$10.9c + c = \frac{88}{12}$$

$$c = \frac{\frac{88}{12}}{12 \times 11.9} = 0.61625$$

$$b = 6.7170$$

7. By eq. (4.40.2) and eq. (4.40.4),

$$\frac{b}{d} = \frac{0.109}{0.071} = 1.53521$$

$$d = \frac{6.7170}{1.53521} = 4.375$$

8. Dividing eq. (4.40.2) by eq. (4.40.5),

$$\frac{b}{e} = \frac{0.109}{0.81} = 0.13456$$

$$e = \frac{6.7170}{0.13456} = 49.9153$$

9. From oxygen balance, we have

$$\frac{4.8}{32} + x = b + \frac{c}{2} + d + \frac{f}{2}$$

$$x = 6.7170 + \frac{0.61625}{2} + 4.375 + \frac{1.8}{2} - \frac{4.8}{32}$$

$$x = 12.150 \text{ moles}$$

10. Thus, the mass of oxygen supplied = $12.150 \times 32 = 388.804 \text{ kg}$

11. The mass of actual air supplied for 100 kg fuel,

$$= \frac{388.804}{232} \times 10^3 = 1675.87 \text{ kg}$$

12. Therefore, the mass of actual air supplied per kg of fuel,

$$= \frac{1675.873}{100} = 16.75 \text{ kg}$$

13. Proportion of carbon burned to CO,

$$= \frac{c}{b+c} = \frac{0.61625}{6.717 + 0.61625} = 0.084035 = 8.4035 \%$$

14. Weight of fuel gas 100 kg of fuel burned,

$$= b\text{CO}_2 + c\text{CO} + d\text{O}_2 + e\text{N}_2$$

$$= 6.7170 \times 44 + 0.61625 \times 28 + 4.375 \times 32 + 28 \times 49.9153$$

$$= 1850.4314$$

15. Weight of the gas per kg of fuel burned,

$$= \frac{1850.4314}{100} = 18.50 \text{ kg}$$

PART - 1 2

Chemistry of Biogas Production from Organic Waste Material and Their Environmental Impact on Society.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 4.41. | What is biogas ? Discuss the mechanism of biogasification.

OR

Give the composition of biogas. With the help of diagram explain a biogas plant.

AKTU 2017-18 (Sem-2), Marks 3.5

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.
 - b. A 'gas holder' which covers digester and made up of weld steel sheets.
 - c. A 'pipeline', 10 cm in diameter.

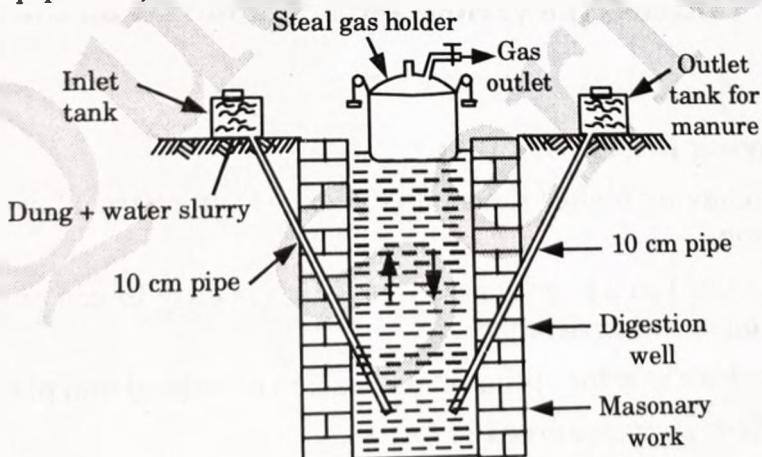


Fig. 4.41.1. Gobar gas plant.

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°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 4.42. | Discuss the various impact of biogas on the society.

Answer

1. Resolving Energy Issues :

1. Bio gas having higher thermal efficiency than charcoal, cow dung and kerosene.
2. So, it is used as a energy resource which is easy to use and cause less pollution in the environment.
3. It provides a way for optimum utilization of animal and plant waste.

2. Fertilizer Requirement :

1. Waste of anaerobic fermentation by bio gas plant is called organic fertilizer.
2. Nitrogen which is found in the fermented manure is mainly ammonium form, which is more suitable for the development of plants
3. Thus, using of commercial fertilizer is reduced. Especially, weed seeds found in the animal wastes lost germinating property during the anaerobic fermentation.

3. Health-Related Effects :

1. People who live in rural areas dispose wood and plant wastes by direct combustion without chimney cause variety of respiratory diseases. Using of biogas eliminates these problems.
2. In addition, flies which live on waste and diseases threaten the health of people living in the area. During anaerobic fermentation most of the pathogens and parasites are disposed. Thus, reduction occurs in health care expenses caused by bacteria and other pathogens.

4. Development :

1. Biogas systems provide the development of rural living standards.
2. The employment of local installation and construction workers increases.
3. Social pressure, caused by waste and environmental problems, is decreased on farmers.
4. It prevents deforestation with replacing the non-commercial fuels and there are also some non-financial benefits such as reduced time for collecting firewood and plant waste.

5. Economic Effects :

1. Biogas systems, established in regions causes an increase of savings and income.
2. It decreases economic fluctuations by means of the local energy and fertilizer production.
3. It reduces dependence for energy and foreign fertilizer on macro-level.

6. Emission :

1. Emission of green house gases like methane and ammonia is reduced, which occurs mainly during storage of animal waste.
2. In addition, use of synthetic nitrogen fertilization which creates N_2O decreased with the use of organic fertilizers.
3. Ammonia emissions which create health, environmental, and odor problem, are decreased by the anaerobic processes of biogas plant.

VERY IMPORTANT QUESTIONS

Following questions are very important. These questions may be asked in your SESSIONALS as well as UNIVERSITY EXAMINATION.

Q. 1. Write a short note on boiler troubles.

Ans. Refer Q. 4.6, Unit-4.

Q. 2. What is hardness of water ? Describe Zeolite process for making soft water from hard water.

Ans. Refer Q. 4.15, Unit-4.

Q. 3. What are Ion exchange resins ? How will you purify water by using the resins ?

Ans. Refer Q. 4.19, Unit-4.

Q. 4. With the help of neat sketch, explain construction, principle and working of a Bomb Calorimeter.

Ans. Refer Q. 4.28, Unit-4.

Q. 5. Explain Proximate Analysis.

Ans. Refer Q. 4.37, Unit-4.

Q. 6. What is biogas ? Discuss the mechanism of biogasification.

Ans. Refer Q. 4.41, Unit-4.





Water Technology, Fuel and Combustion (2 Marks Questions)

4.1. What is soft water and hard water ?

- Ans.** **Soft water :** Water which form lather with a soap easily on shaking, and persist for at last two minutes, is soft water.
Hard water : Water which does not form lather with a soap easily but first form a sticky, curve like precipitate, is hard water.

4.2. Explain temporary hardness.

- Ans.** Hardness due to dissolved bicarbonates of calcium and magnesium, iron, etc, is known as temporary hardness.

4.3. 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.

4.4. Give the example of salts offering temporary or carbonates hardness ?

- Ans.** Temporary hardness in water is due to dissolved bicarbonates of heavy metals, i.e., $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, FeCO_3 and MgCO_3

4.5. 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^{2-} if water is used in high pressure boilers for steam generation. NaHCO_3 if present in water sample liberates CO_2 and causes corrosion.

4.6. What is permanent hardness ? Write the constituent responsible for permanent hardness.

- Ans.** Permanent or noncarbonate hardness is the hardness in water due to dissolved salts of heavy metals other than bicarbonates. Examples : CaSO_4 , CaCl_2 , MgSO_4 , MgCl_2 , FeSO_4 , MnCl_2 etc.

4.7. Explain why value of GCV is greater than NCV.

Ans. GCV (gross calorific value) is the quantity of heat produced by combustion when the water produced by combustion is allowed to return to the liquid state. NCV (net calorific value) is the quantity of heat produced by combustion when the water produced by combustion remains gaseous. Since water releases heat when it condenses, hence GCV is greater than NCV.

4.8. What is principle of bomb calorimeter ?

Ans. A known weight of solid / liquid fuel is burnt in the presence of excess oxygen in the closed pot, and the products of combustion are cooled, to get GCV of the fuel.

4.9. Explain when will the value of GCV = NCV ?

AKTU 2017-18 (Sem-1), Marks 02

Ans. As, NCV = GCV - Latent Heat. So, when latent heat = 0. NCV becomes equal to GCV.

4.10. A sample of coal contains 60 % Carbon, 33 % oxygen, 6.0 % Hydrogen, 0.5 % Sulphur, 0.2 % Nitrogen and 0.3 % Ash. Calculate GCV and NCV of coal.

AKTU 2017-18 (Sem-2), Marks 02

Ans.

Given : C = 60 %, O = 33 %, H = 6 %, S = 0.5 %

N = 0.2 %, Ash = 0.3 %.

To Find : GCV and NCV.

$$\begin{aligned}
 1. \quad GCV &= \frac{1}{180} \left[8080C + 34400 \left(H - \frac{O}{8} \right) + 2240S \right] \\
 &= \frac{1}{180} \left[8080 \times 60 + 34400 \left(6 - \frac{33}{8} \right) + 2240 \times 0.5 \right] \\
 &= 5504.2 \text{ cal/gm}
 \end{aligned}$$

$$\begin{aligned}
 2. \quad NCV &= GCV - \left(\frac{9}{100} \times H \times \text{Latent heat of water} \right) \\
 &= 5504.2 - \left(\frac{9}{100} \times 6 \times 587 \right) \\
 &= 5187.22 \text{ cal/gm}
 \end{aligned}$$

4.11. 100 mL of water sample has hardness equivalent to 12.5 ml of 0.08 N MgSO_4 solution. Calculate the hardness of this water sample.

AKTU 2017-18 (Sem-1), Marks 02

Ans.

Given : Water sample = 100 mL, $MgSO_4$ = 12.5 mL of 0.08 N
To Find : Hardness

1. 100 mL of water sample

$$\begin{aligned} &= 12.5 \text{ mL of } 0.08 \text{ N } MgSO_4 \\ &= 12.5 \times 0.08 \text{ mL } 1\text{N } MgSO_4 \\ &= 1 \text{ mL of } 1\text{N } MgSO_4 \\ &= 1 \text{ mL of } 1\text{N } CaCO_3 \text{ equivalent} \\ &= 0.001 \text{ of } 1\text{N } CaCO_3 \text{ equivalent} \\ &= 0.05 \text{ g } CaCO_3 \text{ equivalent} \\ &= 50 \text{ mg } CaCO_3 \text{ equivalent} \end{aligned}$$

2. 1000 mL (or / L) of water sample

$$\begin{aligned} &= \frac{50 \text{ mg } CaCO_3 \times 1000 \text{ mL}}{100 \text{ mL}} \\ &= 500 \text{ mg } CaCO_3 \text{ eq.} \end{aligned}$$

Hence, hardness of water is 500 mg $CaCO_3$ equivalent per litre or 500 ppm.

- 4.12. 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.

- 4.13. 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

- 4.14. Why does magnesium bicarbonate require double amount of lime for softening ? AKTU 2018-19 (Sem-1), Marks 02

Ans. $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow + Mg(OH)_2 + 2H_2O$

From the above chemical reaction,

1 mol of $Mg(HCO_3)_2$ = 2 mol of $Ca(OH)_2$ (lime)

Thus, for water softening, magnesium bicarbonate require double amount of lime.

- 4.15. Calculate GCV of the coal sample having C = 0 %, H = 9 % O = 4 %, N = 1.5 %, and ash = 3 %

AKTU 2018-19 (Sem-2), Marks 02

Ans. Given : C = 80 %, S = 2.5 %, H = 9 %, O = 4 %, N = 1.5 %
Using Dulong's formula

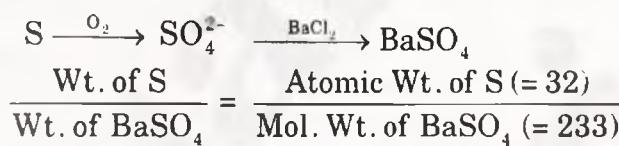
$$\begin{aligned} \text{GCV} &= \frac{1}{100} \left[8080(\text{C}) + 34500 \left[\text{H} - \frac{O}{8} \right] + 2240(\text{S}) \right] \\ &= \frac{1}{100} \left[8080 \times 80 + 34500 \left[9 - \frac{4}{8} \right] + 2240(2.5) \right] \\ &= 9452.5 \text{ Kcal/kg} \end{aligned}$$

4.16. How can sulfur be estimated by ultimate method ?

AKTU 2020-21 (Sem-1), Marks 02

Ans.

1. 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.
2. Then ash from the bomb calorimeter is extracted with dil. hydrochloric acid.
3. The acid extract is then treated with barium chloride solution to precipitate sulphate as BaSO_4 .
4. The ppt. of BaSO_4 is filtered, washed, dried and heated to constant weight.



5. Take weight of BaSO_4 precipitate is W_2 gm and of coal is W_1 g

$$\text{Hence, wt. of S} = \frac{32}{233} \times W_2 \text{ gm.}$$

4.17. What is calgon conditioning ? Explain.

AKTU 2017-18 (Sem-2), Marks 02

Ans. Calgon conditioning involves adding calgon [sodium hexa phosphate ($\text{NaPO}_3)_6$] to boiler water. It prevents scale and sludge formation by forming soluble complex compound with CaSO_4 .

4.18. Why calgon is better than other internal process for water treatment ?

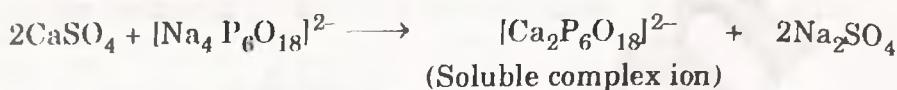
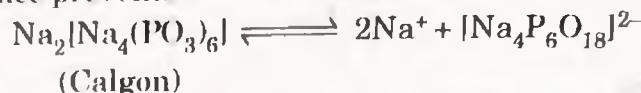
AKTU 2020-21 (Sem-1), Marks 02

Ans. In calgon conditioning, the added calgon forms soluble complex compound with CaSO_4 , thereby it prevents the scale and sludge formation in boiler. Since the complex formed is soluble, so it does not cause any problem to the boiler.

- 4.19. Show with the help of reactions, how scale formation can be prevented by Calgon conditioning ?**

AKTU 2018-19 (Sem-2), Marks 02

Ans. Calgon is added to the boiler water. It forms soluble complex compound with calcium salt like CaSO_4 , CaCl_2 etc., present in water and hence prevents from the formation of scale and sludge.



- 4.20. Calculate the hardness of water sample containing impurity of $\text{Ca}(\text{HCO}_3)_2 = 81 \text{ mg/l}$. Give your answer in ${}^\circ\text{F}$ also.**

AKTU 2021-22 (Sem-1), Marks 02

Ans. Hardness of given water sample as

$$\begin{aligned} \text{Ca}(\text{HCO}_3)_2 &\equiv \text{CaCO}_3 \\ 40 + (1 + 12 + 48) \times 2 &\equiv 40 + 12 + 16 \times 3 \\ \Rightarrow 162 \text{ ppm} &\equiv 100 \text{ ppm} \\ 81 \text{ ppm} &\equiv \frac{100}{162} \times 81 = 50 \text{ ppm} \\ 1 \text{ ppm} &= 0.1 {}^\circ\text{Fr} \\ 50 \text{ ppm} &= 50 \times 0.1 {}^\circ\text{Fr} \\ &= 5 {}^\circ\text{Fr} \end{aligned}$$

- 4.21. 4.2 g of a sample of coal was Kjeldahlized and evolved ammonia gas was absorbed in 30 ml of 0.1 N H_2SO_4 . After absorption excess acid required 5 ml of 0.1N NaOH for neutralization. Calculate the % of nitrogen in coal sample.**

AKTU 2021-22 (Sem-1), Marks 02

Ans. Calculation of Nitrogen Percentage :

Given : Weight of coal = 4.2 g

Volume of H_2SO_4 = 30 ml

Volume of NaOH = 5 ml

Normality of H_2SO_4 = 0.1 N

Normality of NaOH = 0.1 N

Solution : + H_2SO_4 consumed = 30 - 5
= 25 ml

Equivalent of consumed H_2SO_4

$$= 25 \times 0.1$$

$$= 2.5 \times 10^{-3} \text{ milli equivalent}$$

$$\begin{aligned} \text{Weight of N}_2 &= 14 \times \text{Equivalent of consumed H}_2\text{SO}_4 \\ &= 14 \times 2.5 \times 10^{-3} \end{aligned}$$

$$\begin{aligned}\text{Percentage nitrogen} &= \frac{\text{Wt. of N}_2}{\text{Wt of Coal sample}} \times 100 \\ &= \frac{14 \times 2.5 \times 10^{-3} \times 100}{4.2} \\ &= 0.83 \%\end{aligned}$$

- 4.22. 0.4 gm of a coal sample was used in bomb calorimeter for the determination of calorific value .The ash formed in the bomb calorimeter was extracted with acid and the acid extracted was heated with BaCl_2 solution and a precipitate of BaSO_4 was formed .The precipitate was filtered dried and weighted. The weighted of precipitate was to 0.04 gm Calculate the percentage of sulphur in the sample ?

AKTU 2021-22 (Sem-2), Marks 02

$$\begin{aligned}\text{Ans. } \% \text{ of S coal} &= \frac{\text{wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{wt. of coal simple} \times 233} \\ &= \frac{0.04 \times 32 \times 100}{0.4 \times 233} \% = 1.37 \%\end{aligned}$$

- 4.23. A sample of hard water has hardness 500 ppm. Express the hardness in °fr and °Cl. AKTU 2021-22 (Sem-2), Marks 02

$$\begin{aligned}1 \text{ ppm} &= 0.07^\circ \text{ Cl} \\ 1 \text{ ppm} &= 0.1^\circ \text{ Fr} \\ 500 \text{ ppm} &= 500 \times 0.07^\circ \text{ Cl} \\ &= 35^\circ \text{ Cl} \\ 500 \text{ ppm} &= 500 \times 0.1^\circ \text{ Fr} \\ &= 50^\circ \text{ Fr}\end{aligned}$$



5

UNIT

Materials Chemistry

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- Part-1 : Polymers 5-2B to 5-2B**
- Part-2 : Classification of Polymers 5-2B to 5-6B**
- Part-3 : Polymerization Process 5-6B to 5-8B**
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- Part-5 : Polymer Blends and Composites 5-9B to 5-12B**
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Lucite, Bakelite, Kevlar, Dacron,
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- Part-8 : Environmental Impact of 5-27B to 5-28B
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- Part-9 : Speciality Polymers 5-28B to 5-30B**
- Part-10 : General Methods of Preparation 5-30B to 5-38B
and Applications of Organometallic
Compounds (R-Mg-X and LiAlH₄)**

Que 5.2. | How are polymers classified? Explain.

OR

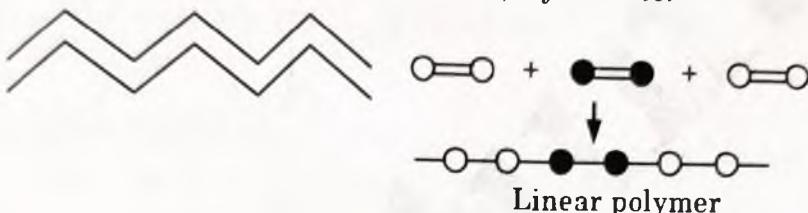
What is meant by tacticity? With suitable examples, explain Isotactic, Syndiotactic and Atactic polymers.

Answer

1. Based on Polymeric Structure :

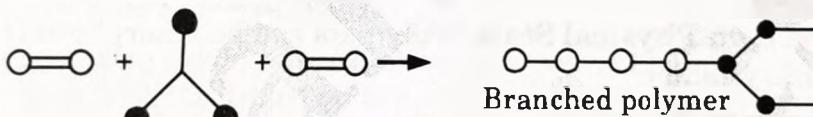
- a. **Linear Polymer** : In linear polymers, the monomer units are joined together end to end in a single chain.

Example : High density polyethylene, Nylons etc.



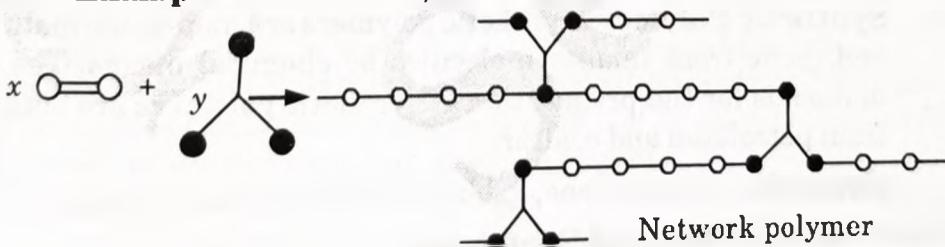
- b. **Branched Polymer** : Branched polymers are the polymers in which the same side chains or branches are connected to the main chain.

Example : low density polyethylene, starch etc.



- c. **Cross linked or Network Polymer** : Polymers in which monomers are cross linked together in all three dimensions to form three dimensional network structure are termed as network polymers.

Example : Thermosets, Rubbers etc.



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

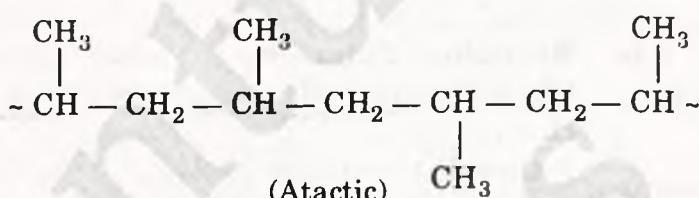
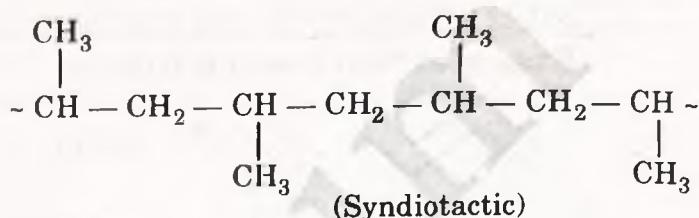
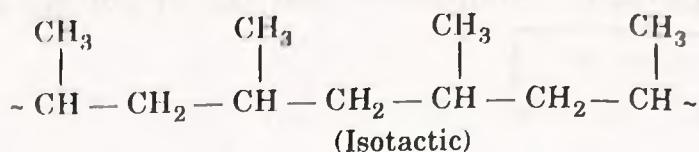
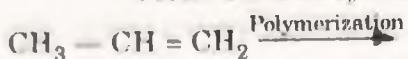
- a. **Isotactic Polymer** : In isotactic polymers all the functional groups or alkyl groups lie on one side of the chain and the hydrogen atoms on the other side.

Example : Natural rubber.

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

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 etc.

4. Based on its Origin:

- a. **Natural Polymers** : The polymers obtained from natural sources (such as plants & animals) are natural polymers.

Example : starch etc

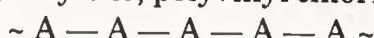
- b. **Synthetic Polymer**: Synthetic polymers are man-made materials and made from smaller molecules by chemical means. The raw materials for the preparation of synthetic polymers are obtained from petroleum and coal tar.

Example : polyethylene, rubber (synthetic), terylene etc.

5. Based on the Chemical Structure :

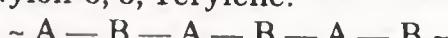
- a. **Homopolymer**: The polymers in which the entire polymer chain is made up of one single repeating unit.

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. This process is known as co-polymerization.

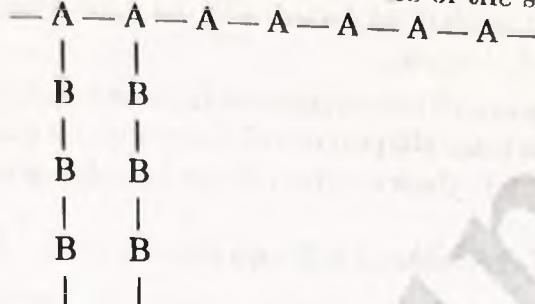
Example : Nylon-6, 6 Terylene



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.
 $\text{---A---A---A---B---B---B---A---A---A---}$
(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 co-polymer. Thus,



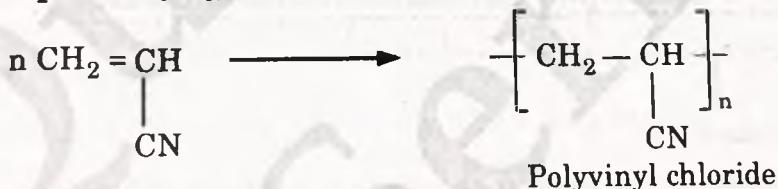
- d. **Alternating Copolymers** : The two monomers are incorporated alternatively along the chain of the copolymer. Thus,



7. Based on the Mode of Synthesis :

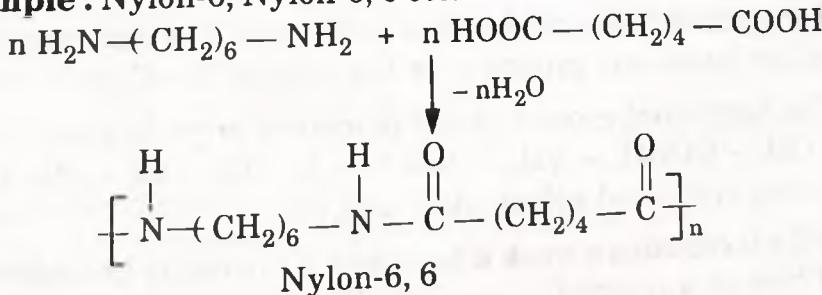
- a. **Addition Polymers** : The addition polymer is one in which the monomers with multiple bonds undergo true addition, to form the polymers.

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.

Example : Nylon-6, Nylon-6, 6 etc.



8. Based on the Behaviour when Heated :

- a. **Thermoplastics** : The polymers which gets soften on heating and hardened on cooling without or with little change in their properties.

Example : LDPE, HDPE, Nylon-6, 6, etc.

- b. **Thermosetting** : The polymers which once hardened cannot be softened again.

Example : Bakelite.

9. On the Basis of Ultimate Form :

- 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.

- 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.

Example : Synthetic rubbers etc.

PART-3

Polymerization Process.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.3. Define polymerization and monomer.

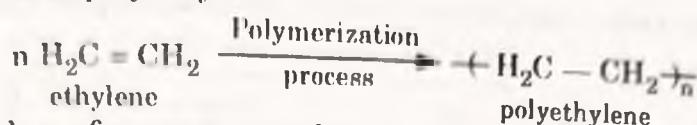
Answer

A 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 $C = C$.
- 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 $C = C$ 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.

Polymerization:

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



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

Que 5.4. What do you mean by degree of polymerization and functionality of polymers ?

Answer

A Degree of Polymerization:

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

B. 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. Example : $\text{CH}_2 = \text{CHX} \longrightarrow -\text{CH}_2-\text{CHX}-$
Thus, vinyl monomers can be considered as bifunctional because they have two reactive (or bonding) sites.
 4. For a substance to act as a monomer, it must have at least two reactive (or bonding) sites.

Que 5.5. What are the necessary conditions for a monomer to undergo condensation polymerization ?

Answer

- Instead of double bonds, monomer should have functional groups like alcohol, amine, or carboxylic acid groups.
 - Each monomer should have at least two reactive sites, which usually means two functional groups.
 - Purity of monomers should be high.

Que 5.6. Giving suitable example distinguish between chain growth and step growth polymerization process.

Answer

Difference between Chain or Addition and Step or Condensation Polymers :

S. No.	Chain or Addition Growth Polymerization	Step or Condensation Growth Polymerization
1.	Monomer molecule has C = C π -bond.	Monomer molecule has functional group.
2.	Catalyst is essential.	Catalyst may or may not be required.
3.	It is exothermic reaction.	It is 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 is not formed.	Generally by-product is obtained along with polymer.
6.	Polymer chain ends are dead.	Polymer chain ends are live.
7.	Molecular weight relatively lower.	Molecular weight 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.

PART-4

Thermosetting and Thermoplastic Polymers.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.7. Giving suitable examples, distinguish between thermoplastic and thermosetting polymers.

OR

**Differentiate between (i) Thermoplastic and Thermosetting
(ii) Addition and Condensation polymerization.**

AKTU 2017-18 (Sem-1), Marks 07

Answer

A. Differentiate between addition and Condensation polymerization : Refer Q. 5.6, Page 5-8B, Unit-5.

B.

S. No.	Thermoplastic Polymers	Thermosetting Polymers
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.
8.	Examples : Polythene, polypropylene, polyvinylchloride etc.	Examples : Bakelite, epoxy resin, melamine etc.

PART-5

Polymer Blends and Composites.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.8. What are the polymer blends ? State their characteristics.

Answer**A. Polymer Blends :**

1. Blended polymer is the mixture of two or more polymers, having better properties than the components polymers.
2. For making a blend of polymers it is essential that they are compatible with each other i.e., both the polymers should be friendly in structure.

3. Example :

- i. Two hydrocarbon polymers can be blended (polyethylene and polypropylene).
- ii. Cellulose nitrate and polyglycols are possible to blend.
- iii. Polyester and cotton (cellulose fibres) can be blended.

B. Characteristics :

1. The blend possesses better strength, more toughness, higher T_g , glass transition temperature and better moulding property.
2. The purpose of blending sometimes is specific e.g. polyester is having high tensile strength, crease resistant, durable but does not absorb sweat easily and gets heated by sunlight.
3. By making blend with cotton, good properties of both polymers are present in the blended product.

Que 5.9. What are composites materials ? Give classification of composite materials.

AKTU 2020-21 (Sem-1), Marks 10

OR

What are composite materials ? Give the classification of composite materials.

AKTU 2017-18 (Sem-2), Marks 07

AKTU 2018-19 (Sem-2), Marks 10

OR

Write a note on polymer blends and polymer composites.

AKTU 2018-19 (Sem-1), Marks 10

OR

What are polymer composites ? Discuss the classification and applications of polymer composites.

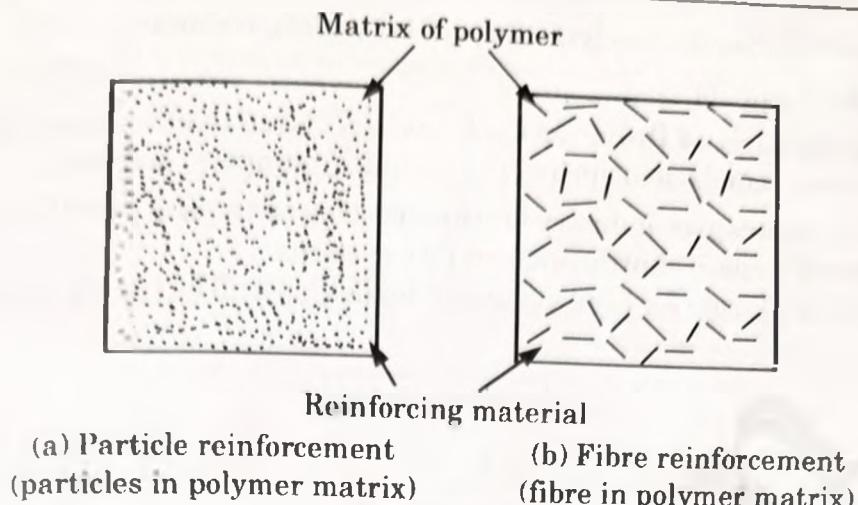
AKTU 2021-22 (Sem-1), Marks 10

Answer

A. Polymer blends : Refer Q. 5.8., Page 5-9B, Unit-5.

B. Polymer Composites :

1. A polymer and a reinforcing material as a two phase mixture, with interfaces between them, is known as polymer composite.

**Fig. 5.9.1.**

2. The polymer composite has properties of both the materials in combination.
3. The polymer phase is called as matrix phase and the composite used for mixing is known as dispersed phase.
4. The boundaries between the matrix and dispersed phase are known as interface.

C. Classification of Composites :

1. Particle Reinforced Composites :

- i. The particles are evenly dispersed in all directions.
- ii. The strength of the bonding at matrix-particle interface dictates the mechanical properties of the composite.

2. Fibre reinforced composites (Fibre plastics) :

- i. The dispersed phase in the composite is in the form of fibres.
- ii. The fibres provide very high strength.
- iii. The fibres are either continuous, aligned or discontinuous.
- iv. The mechanical properties of composite depend upon the magnitude of interfacial bond between fibre and the matrix, fibre orientation and concentration, fibre length and fibre properties.

D. Properties of Polymer Composites :

1. Low coefficients of expansion.
2. High dimensional stability.
3. High tensile strength.
4. High heat stability and therefore usable at higher working temperature.

E. Advantages of Composite Polymers :

1. High performance.
2. Laminate patterns and ply build up in a part can be tailored to give the required mechanical properties in various dissections.

3. Achieve smooth aerodynamic profiles to drag reduction.
 4. Low production cost.
- E. Application of Polymer Composites :** Used in automotive industry for body panels, leaf spring, drive shafts, bumpers, doors etc.
- Use in Aerospace industry for constructing structural parts for military aircrafts, space shuttle and satellite systems.
- Used in Marine for fibre glass boat bodies, as well as canoes and kayaks.

PART-6

Conducting and Biodegradable Polymers.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.10. Explain the conductivity of polymers with conjugated π -electron system. How is this conductivity enhanced by doping ?

OR

Explain intrinsically conducting polymers.

AKTU 2017-18 (Sem-2), Marks 3.5

OR

What are conducting polymers ? How can we improve the conducting property of a polymer ?

OR

What are conducting polymers ? Classify conducting polymers and mention their important applications.

AKTU 2018-19 (Sem-2), Marks 10

AKTU 2021-22 (Sem-2), Marks 10

Answer

- A. Difference between Thermoplastic and Thermosetting Polymers :** Refer Q. 5.7, Page 5-8B, Unit-5.
- B. Conducting Polymers :** A polymer which can conduct electricity is termed as conducting polymer.

Examples :

- i. Polyaniline is used to make rechargeable batteries in the shape as flat buttons or as laminated rolled films.

- ii. Polypyrrole is used in 'smart' windows. These smart windows can change their colour in response to changes in temperature.

C. Classification of Conducting Polymers :

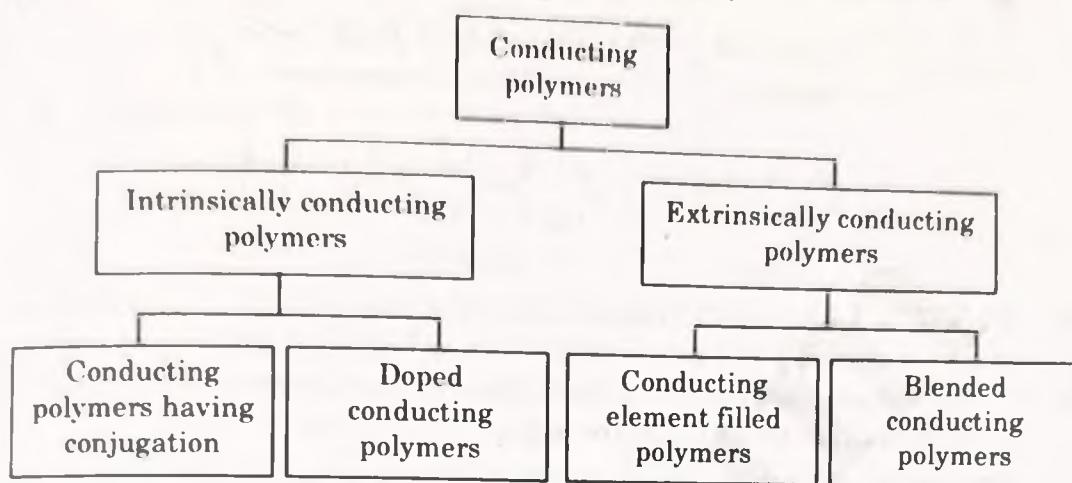
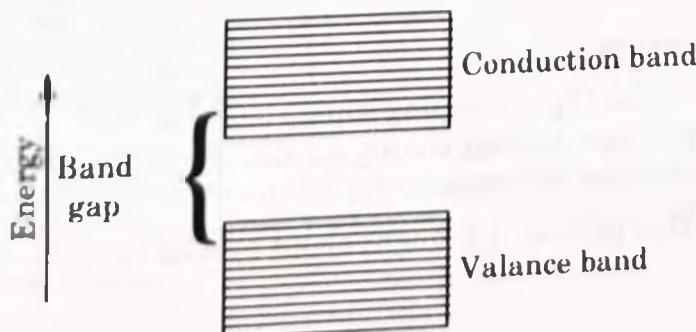


Fig. 5.10.1.

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

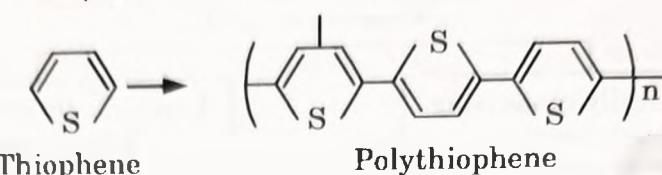
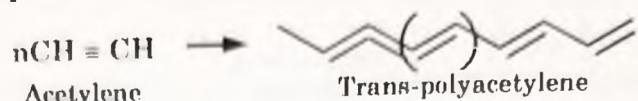
i. Conjugated π -electrons Conducting Polymers :

- A key property of a conductive polymer is the presence of conjugated doublets along the backbone of the polymer.
- The orbital's 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.



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

g. Examples:

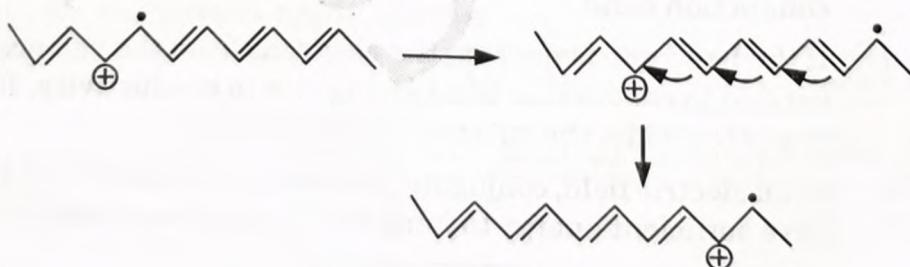


- ii. **Doped Conducting Polymers :** Electrical conductivity of polyacetylene can be increased by a factor of $10^{12} \text{ S cm}^{-1}$ when it was doped with an electron donor, such as alkali metal ion or an electron acceptor, such as arsenic pentaflouride (AsF_5) or iodine.

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

A. Oxidation:

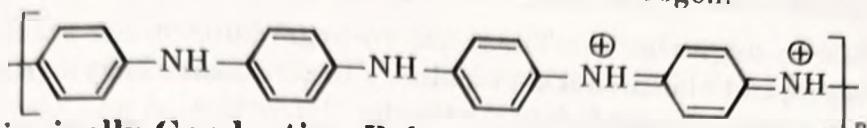
- a. In this process, doping typically removes some electrons from π -bond of the conjugated double bonds as they have low ionization potentials.
 - b. The holes so created can move along the molecule i.e., the polymer becomes electrically conductive.
 - c. Thus, when an electron is removed from the top of the valence bond of a conjugated polymer, a hole is created, causing partial delocalization, extending over several monomeric units.
 - d. The radical cation is called ' polaron'. It stabilizes itself by polarizing the medium around it.
 - e. The polarons are mobile and can move along the polymer chain by rearrangement of double and single bonds and hence the polymer become conducting.



B. Reduction:

- a. In this type of doping some electrons are introduced into the polymer having conjugate double bonds as they have high electron affinities.
 - b. This process is brought about by adding Lewis bases.

- c. 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. Extrinsic Conducting Polymers :

- i. **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.
- d. 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.
- ii. **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.

D. Applications :

1. They are used in manufacturing of polymeric batteries.
2. These are also used in electroluminance displays like in mobile phones etc.
3. Conductive polymers used in analytical sensors.
4. It can also be used in photovoltaic devices.

Que 5.11. Define biodegradable polymers with its requirements and limitation. Write down the types and applications of biodegradable polymers.

OR

What are biodegradable polymers ? Discuss their application.

Answer

A. Biodegradable Polymers :

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

B. Requirements of Biodegradation : There are essentially following three elements for the biodegradation process which needs to be simultaneously present :

1. **Micro-organisms :** These micro-organisms must exist with the appropriate biochemical machinery to synthesize enzymes specific for the target polymer to initiate the depolymerization process.

2. **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

3. **Substrate :** 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.

C. Types of Biodegradable Polymers :

1. **Natural Biodegradable Polymers :** Natural rubber, collagen, lignin, poly-(gamma-glutamic acid) are some of the examples of natural biodegradable polymers.

2. **Synthetic Biodegradable Polymers :** Polyvinyl alcohol, polyanhydrides, poly-(3 Hydroxybutyrate-CO-3-Hydroxyvalerate) or PHBV are some of the examples of synthetic biodegradable polymers.

D. Need for Biodegradable Polymers : To solve problems with traditional, non-biodegradable polymers :

1. Solid waste problems, particularly with regard to decreasing availability of landfills.

2. Litter problems.

3. Entrapment or ingenious hazards to marine life.

E. Applications of Biodegradable Polymers :

1. Poly (β -hydroxy butyrate) or PHB is used in the manufacture of shampoo bottles.

2. β -hydroxy butyrate- β -hydroxy valerate or HB-HV copolymers are suitable as matrices for controlled release of drugs due to their favorable biocompatibility and biodegradation properties.
3. Poly (lactic acid) or PLA breaks down in the environment back to lactic acid, which can be metabolized; it has found commercial use in medical applications such as drug-delivery systems and wound clips.
4. It is also used in some agricultural applications, such as timed-release coatings for fertilizers and pesticides.

F. Limitations of Biodegradable Polymers :

1. Biodegradable polymers are not suitable in the recycling of commingled plastics.
2. Biodegradable polymers are very expensive.
3. Biodegradable polymers are not easily available.
4. In order to store potentially hazardous materials, landfills are built to be free of moisture and airtight.

Que 5.12. | How do natural biodegradable polymers undergo biodegradation ?

Answer

1. Biodegradation is the breakdown of polymer by microbial organisms (such as bacteria etc.,) into smaller compounds.
2. The microbial organisms degrade the polymer through metabolic or enzymatic processes.
3. The biodegradability of a given polymeric material is defined by the chemical structure of the polymer.
4. Photodegradation is often subsequently followed by microbial or biodegradation.
5. Natural products which are susceptible to biological attack are starch, cellulose etc.
6. Biodegradation of any organic material under controlled aerobic and anaerobic conditions produces compost. The process is termed as composting.
7. Hence, a plastic that undergoes degradation by microbial action during composting to yield CO_2 , H_2O and inorganic compounds, leaves no toxic residue.

PART-7

*Preparation, Properties and Industrial Applications of
Teflon, Lucite, Bakelite, Kevlar, Dacron, Thiokol, Nylon,
Buna-N and Buna-S.*

Questions-Answers

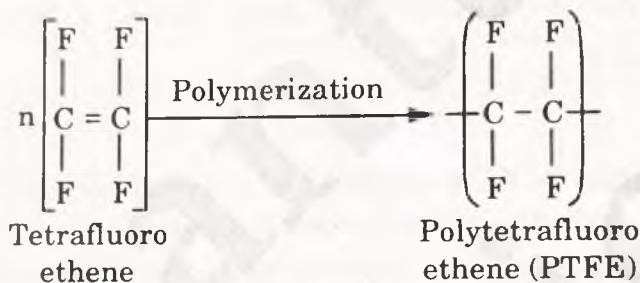
Long Answer Type and Medium Answer Type Questions

Que 5.13. Give the preparation, properties and applications of the following polymers.

- A. Teflon
B. Lucite
C. Kevlar

Answer

A Teflon : Teflon is obtained by polymerization of water-emulsion of tetrafluoro ethylene, under pressure in presence of benzoyl peroxide as catalyst.



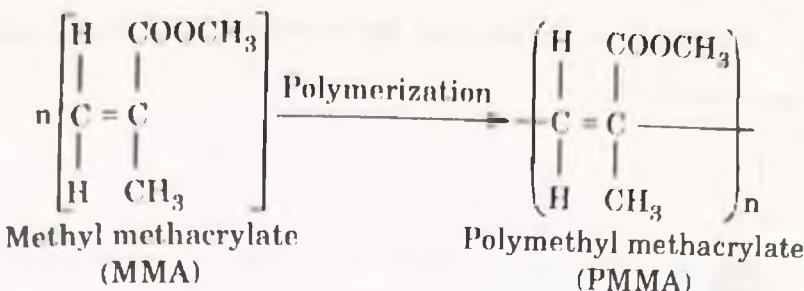
Properties :

1. Due to the presence of highly electronegative fluorine atoms and the regular configuration of the polytetrafluoro ethylene molecule results in very strong attractive forces between the different chains.
 2. These strong attractive forces give the material extreme toughness, high softening point (about 350°C), exceptionally high chemical-resistance towards all chemicals (except hot alkali metal and hot fluorine), high density (2.1 to 2.3 gcm^{-3}), waxy touch, very low coefficient of friction, extremely good electrical and mechanical properties.
 3. The material however, has the disadvantage that it cannot be dissolved and cannot exist in a true molten state.

Uses :

1. It is used as insulating material (for motors, transformers, cables, wires, fittings, etc.)
 2. It is also used for making gaskets, packings, chemical-carrying pipes, and tanks.
 3. It is used for coating and impregnating glass fibres, asbestos fibres and clothes.

- B. Lucite :** Lucite is obtained by polymerization of methyl methacrylate (ester of methyl acrylic acid, $\text{CH}_2 = \text{C}(\text{CH}_3)\text{COOH}$) in presence of acetyl peroxide of hydrogen peroxide. It is an acrylic polymer.

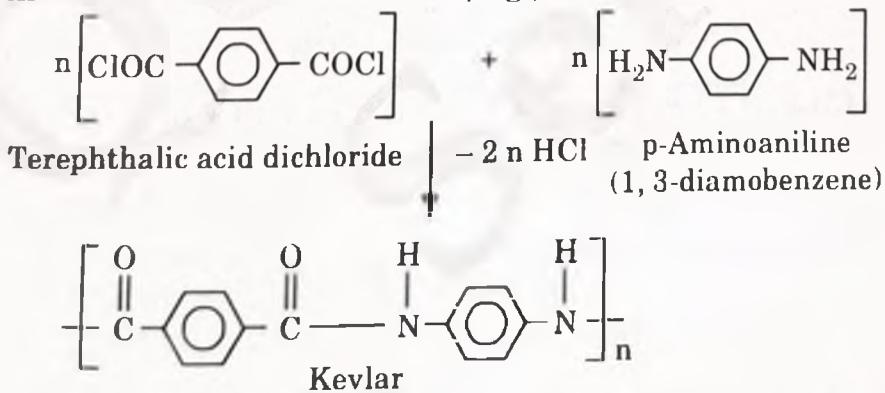


Properties :

1. Polymethyl methacrylate (PMMA) is hard, fairly rigid material with a high softening point of about 130–140 °C, but it becomes rubber-like at a temperature above 65 °C.
2. This relatively wide span of temperature accounts for the outstanding shape-forming properties of polymethyl methacrylate.
3. It has high optical transparency, high resistance to sunlight and ability of transmitting light accurately, even in curved section.
4. However, it has low chemical-resistance to hot acids and alkalis and low scratch-resistance.

Uses : For making lenses, aircraft light fixtures, gun turrets, cockpit canopies, dentures, paints, adhesives, jewellery, wind T.V. screens etc.

- C. Kevlar :** Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide groups – CONH –. It is prepared by polycondensation between aromatic dichloride and aromatic diamines, e.g.,



Properties :

1. Kevlar is exceptionally strong (5 times stronger than steel and 10 times stronger than Al on a weight-for-weight basis).
2. It has high heat stability and flexibility. The unique properties of Kevlar are due to the delocalized bonding which causes the benzene rings to be inflexible.
3. The high electron-density in the chains of Kevlar also results in relatively stronger Van der Waals intermolecular forces between neighbouring polymer molecules.

Uses : Kevlar is used extensively in the aerospace and aircraft industries, car parts (such as tyres, brakes, clutch linings, etc.), ropes, cables, bullet-proof vests, motorcycle helmets and other high performance materials.

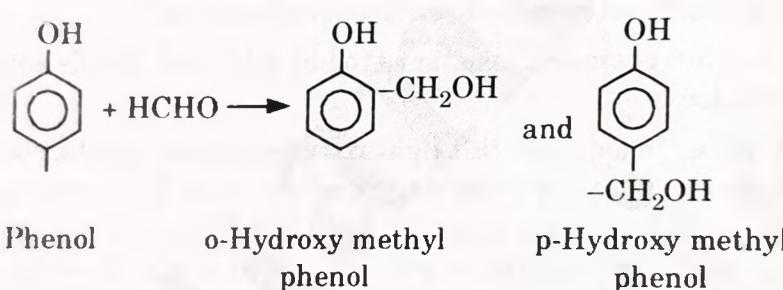
Que 5.14. Explain preparation, properties and applications of Bakelite and Thiokol.

Answer

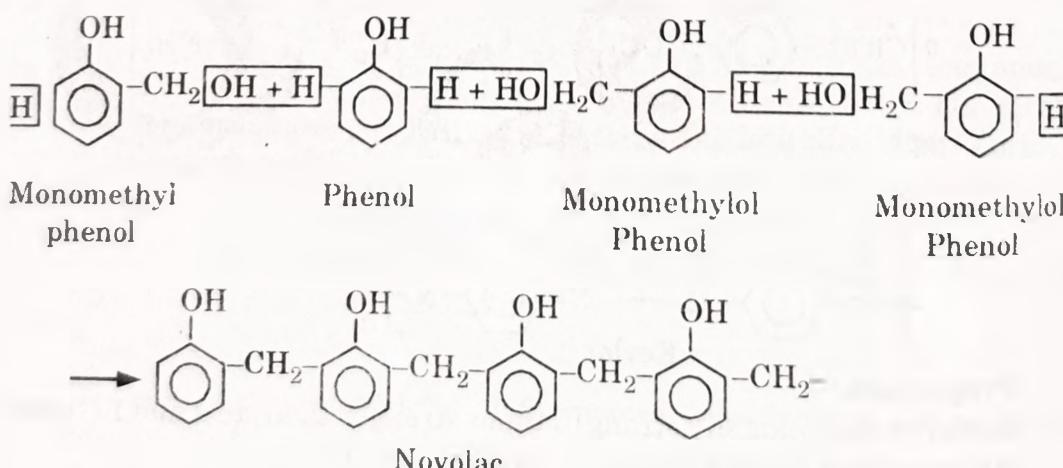
A. Bakelite :

1. Phenolic resins or phenoplasts are condensation polymerization products of phenolic derivatives with aldehydes.
2. Most important member of this class is bakelite or phenol formaldehyde resin. It is prepared by condensing phenol with formaldehyde in presence of acidic/alkaline catalyst.
3. The initial reaction results in the formation of *o* - and *p* - hydroxy methyl phenol, which reacts to form linear polymer, novolac. Thus :

a.

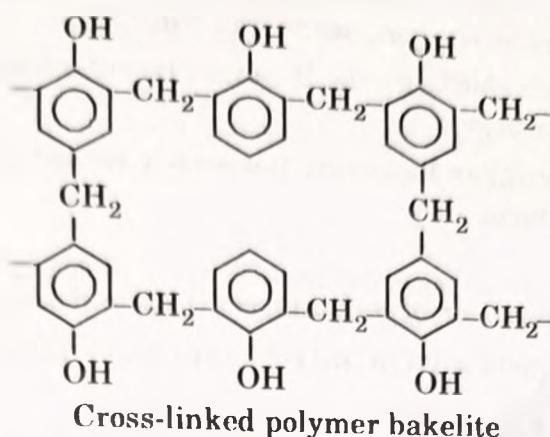


b.



During moulding, hexamethylene telamine $[(\text{CH}_2)_6\text{N}_4]$ are added, which converts the soluble and fusible novolac into a hard, infusible and insoluble solid of cross-linked structure.

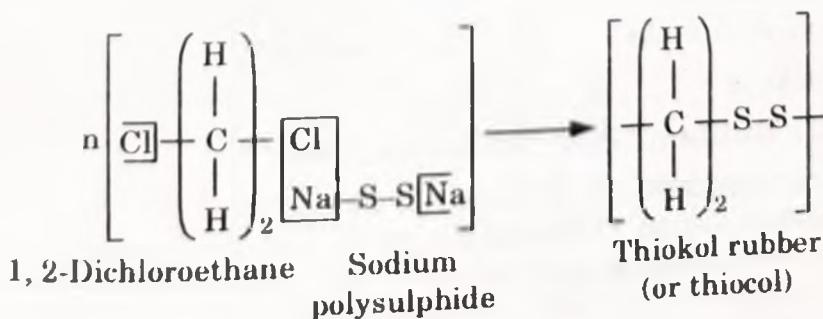
c.

**Properties :**

1. Phenolic resins (Bakelite) set to rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids, which are resistant to non-oxidizing acids, salts and many organic solvents.
2. They can be attacked by alkalis, because of the presence of free hydroxyl group in their structures.
3. They possess excellent electrical insulating character.

Uses :

1. It is used for making electric insulator parts like switches, plugs, switchboards, heater-handles, etc.
 2. It is used for making moulded articles like telephone parts, cabinets for radio and television.
 3. It is used for impregnating fabrics, wood and paper.
 4. It is used as adhesives (e.g., binder) for grinding wheels.
 5. It is used in paints and varnishes.
 6. It is used as hydrogen-exchanger resins in water softening.
 7. It is used for making bearings, used in propeller shafts for paper industry and rolling mills.
- B.** **Thiokol :** Thiokol is made by the reaction between sodium poly-sulphide (Na_2S_2) and ethylene dichloride.



Properties :

1. Polysulphide rubber possesses extremely good resistance to mineral oils, fuels, solvents, oxygen, ozone and sunlight.
2. It is also impermeable to gases. It cannot be vulcanized and hence, does not form hard rubber.
3. Polysulphide rubber however, possesses rather poor strength and abrasion-resistance.

Uses :

1. It is used in preparation of sealants, coatings and other rubber products.
2. They also show good solvent, oil resistant and adhesive properties.

Que 5.15. | Give the preparation, structure, properties and applications of following polymers :

1. Buna-N
2. Buna-S

OR

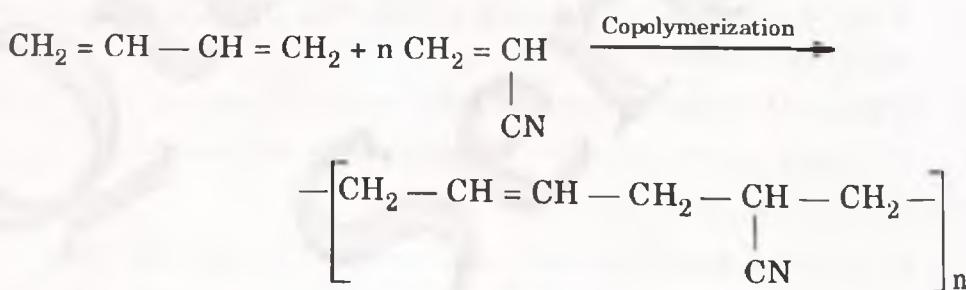
What are Copolymers ? How does Buna-S differs from Buna-N ?

Answer

A. Copolymers : Refer Q. 5.2, Page 5-3B, Unit-5.

B. Nitrile Rubber, GR-A, Buna-N or NBR :

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



2. Properties :

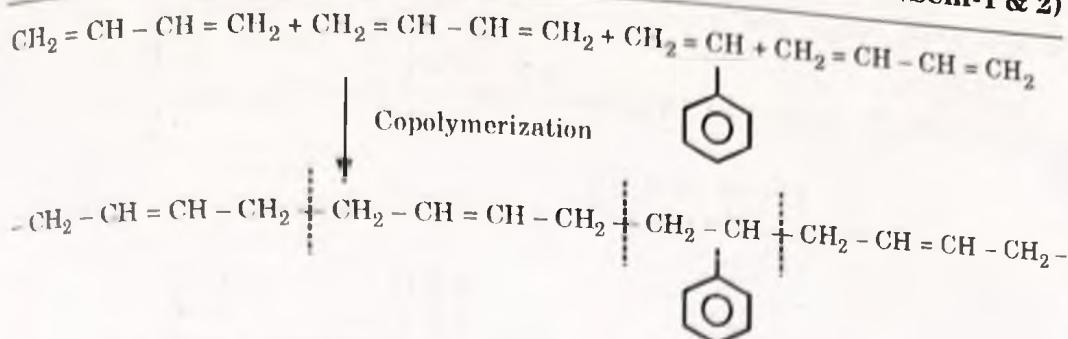
- i. Resistant to acids, heat and oils.
- ii. It has high temperature and wear resistance.

3. Applications :

- | | |
|-------------------|----------------------|
| i. Conveyer belts | ii. Adhesives |
| iii. Gaskets | iv. Printing rollers |

C. Styrene Rubber, GR-S, Buna-S or SBR :

1. **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.)

2. Properties :

- i. High wear resistance
- ii. High load bearing capacity
- iii. Low oxidation resistance.

3. Applications :

- i. Shoe soles ii. Motor tyres
- iii. Gaskets iv. Adhesives

D. Difference between Buna-N and Buna-S :

S.No.	Basis	Buna-N	Buna-S
1.	Monomers	Butadiene and acrylonitrile	75 % Butadiene and 25 % styrene
2.	Application	Conveyer belts, Printing rollers	Shoe soles, Motor tyres

Que 5.16. Give preparation, properties and application of buna-N and Terylene.

AKTU 2017-18 (Sem-2), Marks 3.5

OR

Give preparation, properties and applications of following polymers :

Buna-N, Nylon-6, 6, Terylene.

AKTU 2018-19 (Sem-2), Marks 10

OR

Write the preparation properties and application of Nylon-6 and Bakelite.

AKTU 2017-18 (Sem-1), Marks 07

AKTU 2021-22 (Sem-2), Marks 10

Answer

- A. **Buna-N :** Refer Q. 5.15, Page 5-22B, Unit-5.
- B. **Buna-S :** Refer Q. 5.15, Page 5-22B, Unit-5.
- C. **Bakelite :** Refer Q. 5.14, Page 5-20B, Unit-5.
- D. **Nylon-6 :**
1. **Preparation :** Nylon-6 can be made either by self-condensation of ε-amino caproic acid



or by ring opening polymerization of caprolactum

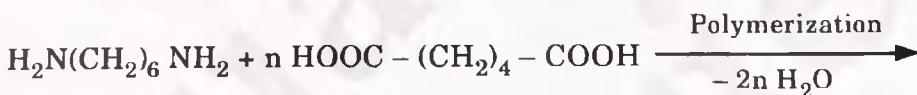


2. Properties :

- i. It has high tensile strength, high impact strength, melting point 160-200 °C.
- ii. It can be easily moulded into fibers, components of machines. It is milky white but can be given attractive colors.
- 3. Application : Bristles, textiles, light machine gears, bearings, moulded articles, ropes, types cords, fabrics.

E. Nylon-6, 6 :

- 1. Preparation : It is made by the condensation polymerization of hexamethylene diamine and Adipic acid in 1 : 1 molar ratio.



Nylon-6 6 (or Polyhexamethylene adipamide)

2. Properties :

- i. Nylons have high crystallinity which imparts high strength, high melting point, elasticity, toughness, wear resistance and retention of good mechanical properties upto 125 °C.
- ii. They are also sterilisable.
- iii. 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.

3. Applications :

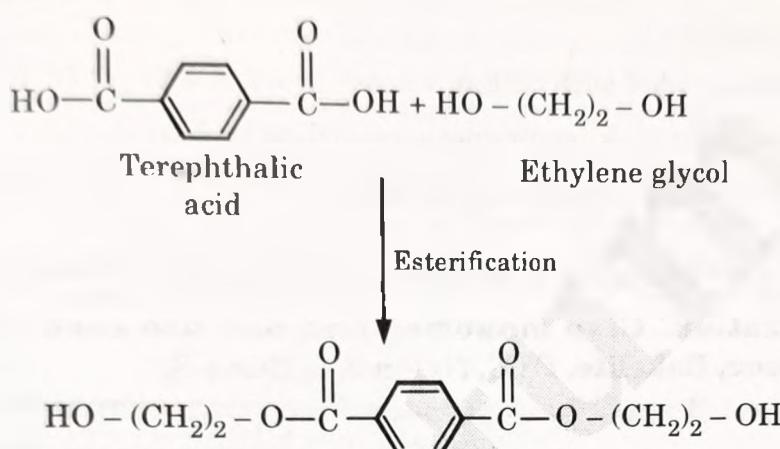
- i. Nylon-6, 6 is primarily used for fibers, which find use in making socks, tinder-garments, carpets etc.
- ii. Nylon-6, 6 is also used in mechanical engineering for well known applications like gears, bearings, bushes, cams etc.

- iii. Mouldings having application in medicine and pharmacy because of sterilisability.

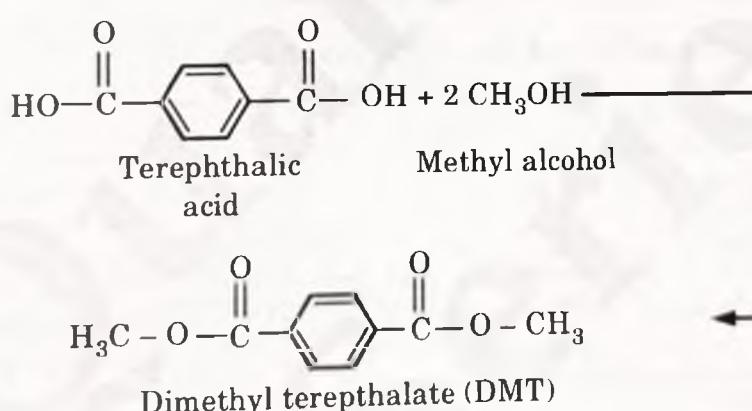
F. PET (Polyethylene Terephthalate), Dacron or Terylene :

1. Preparation :

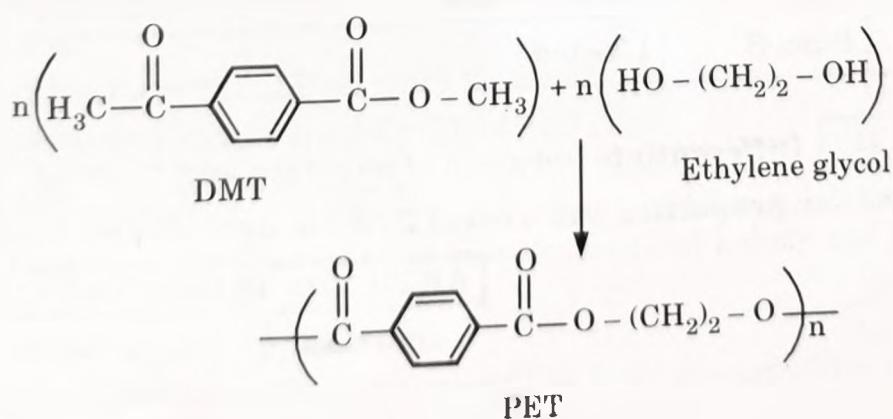
- i. It is prepared by dimethyl terephthalic acid and ethylene glycol with esterification.



- ii. Now terephthalic acid is converted into dimethyl ester by reacting with methyl alcohol.



- iii. By esterification dimethyl terephthalate reacts with ethylene glycol to form PET as a byproduct.



2. Properties :

- It forms crystalline polymer.
- It can be easily converted to fine fibers to very good tensile strength.
- It has good impact strength and better thermal stability.
- Fibres of PET are crease resistant, low moisture absorbing.

3. Applications :

- It can be blended with cotton, viscose, wool, silk to get better fabrics.
- It is useful for making magnetic recording tapes.
- It can be converted to films and bottles.

Que 5.17. | Distinguish between addition and condensation polymerization. Give monomer and one use each of PMMA, Polyethylene, Bakelite, PVC, Nylon 6, 6, Buna-S.

AKTU 2020-21, Marks 10**Answer**

A. Difference: Refer Q. 5.6, Page 5-8B, Unit-5.

B. Monomer and Use of given Polymer :

S. No.	Polymer	Monomer	Use
1.	PMMA	Methyl methacrylate	Shatterproof windows
2.	Polyethylene	Ethylene	Fruit juice containers
3.	Bakelite	Phenol and formaldehyde	Switches and other electrical appliances
4.	PVC	Vinyl chloride	Drainage pipe
5.	Nylon 6, 6	Hexamethylenediamine and adipic acid	Fibers for textiles and carpets
6.	Buna-S	1,3 – but	

Que 5.18. | Differentiate between elastomers and fibers. Give the preparation, properties and uses of Buna-S, Buna-N and Neoprene.

AKTU 2018-19 (Sem-1), Marks 10

Answer**A. Difference :**

S. No.	Elastomers	Fibres
1.	In these polymers, the polymer chain are held together by the weakest intermolecular forces.	In these polymers, the chains are held together by the strong intermolecular forces like hydrogen bonding.
2.	Elastomers are characterized by the absence of stiffening groups, the presence of molecular symmetry, low amount of crystallinity.	Fibres are characterized by presence of stiffening groups, molecular symmetry, high amount of crystallinity.

B. Preparation, properties and uses of Buna-S and Buna-N :
Refer Q. 5.15, Page 5-22B, Unit-5.**PART-8***Environmental Impact of Polymers in Society.***Questions-Answers****Long Answer Type and Medium Answer Type Questions****Que 5.19. What are the role of polymers in the society ?****Answer**

Role of polymers in the society includes several positive and negative impacts :

A. Positive Impacts of Polymers :**1. Medical and Biomedical Applications :**

Both natural and synthetic polymers are used in medical prosthetic applications like heart valves, dental problems, cartilage scaffolds, joints, making of artificial skin, blood vessels, artificial kidney and also in systems for drug delivery.

2. Transportation Applications :

Fuel cell mainly made of polymers has been developed for energy efficiency and to prevent burning of fossils fuel.

Natural and synthetic rubbers in equal proportion are used in production of tyres.

3. Packaging :

LDPE (low density polyethylene) blends were made into the reusable bags used for carrying rubbish or groceries. Bio polymer called polysaccharide have been used for food packaging application while poly-L-lactic acid (PLLA) has been used as fast food containers.

Polymer packaging makes storage of food and goods more efficient because polymer packaging replace the metal packaging which can be corroded with time which may spoil food.

4. Agriculture :

Polymers of different grades are used in restrained release of nutrient and pesticides, seed coating, soil conditioning, and plants protection. Starch, Cellulose, chitin and alginic acid are among of the natural polymer used as control release.

5. Communication :

Polymers are used to provide insulation to underground and aerial cables that are used in telecommunication, broadband and radio equipments.

B. Negative Impacts :

Pollution :

1. Pollution in oceans and water from the production of the synthetic polymers lead to the disturbance in the marine life.
2. They also prove as a significant challenge on land because they are often disposed in landfills where they will remain for centuries into the future slowly leaking toxins into soil as time passes.
3. Burning of plastics lead to production of harmful gases like, carbon dioxide and carbon monoxide.

PART-9

Speciality Polymers.

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.20. | What are speciality polymers ? Explain their types and applications.

Answer**A. Speciality Polymers :**

Speciality Polymers are the class of some High Performance Polymers (HPP), including plastics, polymers, fluids, membranes, smart hydrogels and elastomers that are designed to meet the critical requirements that engineers face every day in key industries including, Automobiles, Aeronautics, Smart Devices, Pharmacy, Energy Production and Storage.

B. Different Types of Speciality Polymers are :**1. Ionic Polymer-metal Composites (IPMCs) :**

- i. They are synthetic composite nanomaterials that display artificial muscle behavior under an applied voltage or electric field.
- ii. IPMCs are composed of an ionic polymer like Nafion or Flemion whose surfaces are chemically plated with conductors such as platinum or gold.

2. Liquid Crystal Polymers (LCPs) :

- i. They are polymers with the property of liquid crystal, usually containing aromatic rings as mesogens.
- ii. LCPs have unique properties like thermal actuation, anisotropic swelling, and soft elasticity. Therefore, they used as sensors.
- iii. One of the most famous and classical applications for LCPs is Kevlar, a strong but light fiber with wide applications including bulletproof vests. They are also widely used in the digital display market.

3. Synthetic Polymer Membranes :

- i. It is a synthetically created membrane which is usually intended for separation purposes in laboratory or in industry.
- ii. The best known synthetic membrane separation processes are water purification reverse osmosis, dehydrogenation of natural gas, removal of microorganisms from dairy products, and Dialysis.

4. Smart Hydrogels :

- i. Smart hydrogels, or stimuli-responsive hydrogels, are three-dimensional networks composed of cross-linked hydrophilic polymer chains that are able to dramatically change their volume and other properties in response to environmental stimuli such as light, temperature, pH and certain chemicals.
- ii. Hydrogels are used for producing contact lenses, hygiene products and wound dressings. Other commercial uses of hydrogels are in drug delivery and tissue engineering.

5. Dendritic Polymers :

- i. Dendritic polymers are highly branched polymers with controllable structures, which possess a large population of terminal functional groups, low solution or melt viscosity, and good solubility.

- ii. Their size, degree of branching and functionality can be adjusted and controlled through the synthetic procedures.
- iii. They are found to be useful in delivery systems for drugs and genes, some dendrimers have medicinal uses of their own, mostly due to their antifungal, antibacterial and cytotoxic properties.

Que 5.21. Discuss biomedical polymers with their medical applications. Also give its properties.

Answer

- A. **Biomedical polymers :** Biomedical polymers are essentially a biomaterial that is used and adapted for a medical application.
- B. **Properties :**
 1. Biomedical polymers are thermoplastic, low-melting polymeric implant materials based on lactide / caprolactone-monomers.
 2. This polymer has low melting point.
 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. The degradation times of these polymers are typically in the range of 3 – 12 months.
- C. **Medical Applications of Biodegradable Polymers :** Wound management, dental applications, orthopedic devices, cardiovascular applications, intestinal applications.
- D. **Biodegradable Polymers used in Medical Applications :**
 - 1. **Natural Polymers :**

a. Fibrin	b. Collagen
c. Chitosan	d. Gelatin
 - 2. **Synthetic Polymers :**

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

PART- 1 □

General Methods of Preparation and Applications of Organometallic Compounds (R-Mg-X and LiAlH₄).

Questions-Answers

Long Answer Type and Medium Answer Type Questions

Que 5.22. What is organometallic compound? Give classification of organometallic compounds.

Answer

A. Organometallic Compounds :

1. The compounds in which the carbon atoms of organic group are bound to metal atoms are known as organometallic compounds.
2. 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).

B. Classification of Organometallics :

1. **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 $R^x - M^{x+}$.
2. **Sigma-Bonded Organometallic Compounds :** In these compounds the organic group (R) is bound to a metal atom (of lower electropositivity) or non-metallic elements by a normal two-electron covalent bond.
3. **Non-Classically Bonded Organometallic Compounds :**
 - i. Here the bonding is not explained in terms of ionic or electron-pair sigma bonds.
 - ii. 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 $C_5H_5^-$.

Que 5.23. Define the term organometallic compounds. Explain general methods of synthesis of organometallic compound preparation and applications with suitable examples.

OR

What are organometallic compounds? Write their classification, preparation and applications. AKTU 2017-18 (Sem-1), Marks 07

Answer

- A. **Organometallic Compounds and its Classification :** Refer Q. 5.22, Page 5-31B, Unit-5.

B. Methods of Synthesis of Organometallic Compounds :

1. Direct reactions of metals :

- i. 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.

- ii. Grignard reagents ($RMgX$) are synthesized by this method.



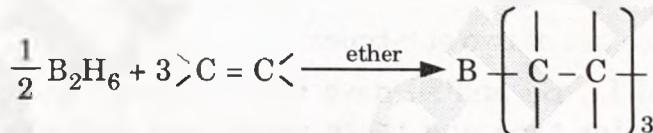
2. Use of alkylating agents :

- i. Here alkylating agents are used to make organometallic compounds. Alkylating agents can be Grignard and lithium reagents, aluminium and mercury alkyls etc.
- ii. The alkylation is generally done either in ether or hydrocarbon solvents.



3. Interaction of metal or non-metal hydrides with alkenes or alkynes :

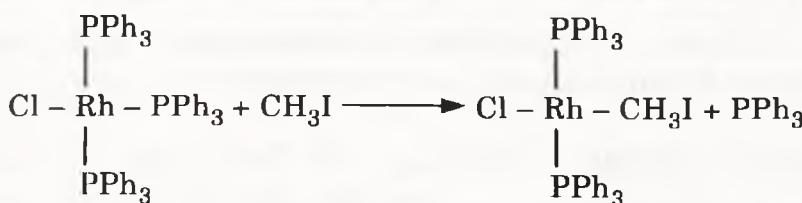
- i. Hydroboration reaction is one of the best examples for such synthesis. It can also be regarded as insertion of alkene in M-H bond.
- ii. Example :



4. Oxidative addition reactions or Oxad reactions :

- i. Here metal-carbon bonds are made by the addition of alkyl or aryl halides to coordinatively unsaturated transition metal compounds.

ii. Example :



C. Applications of Organometallic Compounds :

- Lithium alkyls are widely used as stereospecific catalysts for the polymerization of alkenes.
- The alkyls of aluminium are important because of their industrial use as catalysts for the polymerization of ethylene and propylene.

3. Organo-titanium compounds got importance mainly because of the discovery by ziegler and natta that ethylene can be polymerized in presence of a mixture of $TiCl_4$ and $AlEt_3$ in a hydrocarbon solvent at room temperature and atmospheric pressure.

For example,

Que 5.24. | What are Organometallic compounds ? How Grignard reagents are prepared ? Write any five synthetic applications of Grignard reagents.

AKTU 2021-22 (Sem-1), Marks 10

OR

What are Grignard reagents ? How are they prepared ? Give its applications.

AKTU 2017-18 (Sem-2), Marks 07

AKTU 2018-19 (Sem-2), Marks 10

OR

What are organometallic compounds ? How Grignard reagents are prepared ?

Write any five applications of Grignard reagents.

AKTU 2021-22 (Sem-2), Marks 10

Answer

A. Organometallic Compound : Refer Q. 5.22, Page 5-31B, Unit-5.

B. Grignard Reagent :

1. The organomagnesium halides are known as Grignard reagents.

2. The Grignard reagent is represented as $R-Mg-X$, where

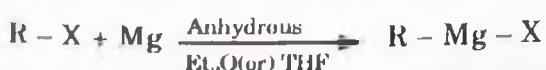
R = alkyl / aryl / alkenyl / allyl group

X = Cl / Br / I.

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

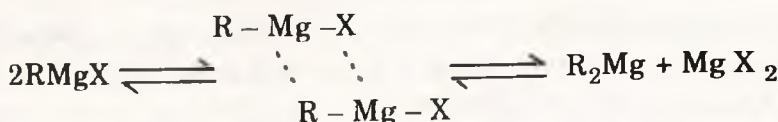
C. Preparations of Grignard Reagent :

1. The Grignard reagents are prepared by the action of activated magnesium (Rieke magnesium) on organic halides in suitable solvents like Diethyl ether, Et_2O or Tetrahydrofuran, THF in anhydrous conditions.



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

3. The Grignard reagents are in equilibrium with the dialkylmagnesium species R_2Mg and MgX_2 .

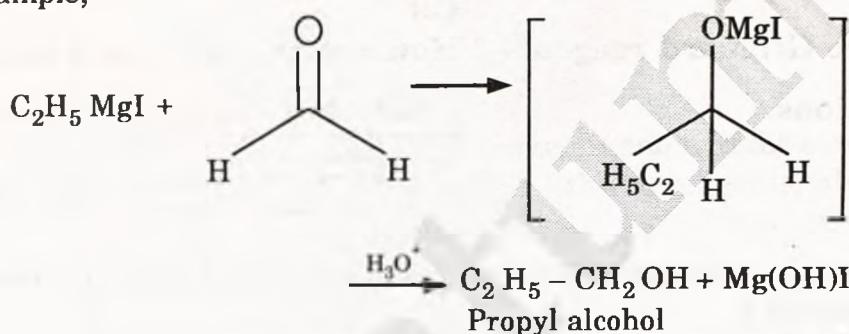


4. In the formation of Grignard reagent, the polarity of carbon attached to the halide group is reversed. This reversal in polarity is called as **umpolung**.

D. Applications of Grignard Reagent :

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

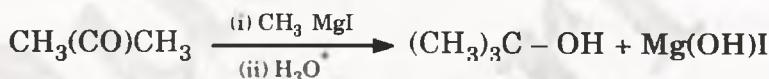
Example,



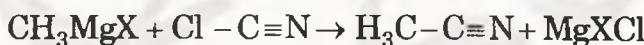
2. The Grignard reaction with aldehydes other than formaldehyde gives secondary alcohols.



3. The addition of Grignard reagent to ketones furnishes tertiary alcohols.



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



5. Amines can be prepared by reacting these reagents with Chloramine, NH_2Cl .



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



Que 5.25. | Describe $LiAlH_4$ alongwith its preparation and applications.

Answer**A. LiAlH₄:**

- Lithium aluminium hydride, also known as LiAlH₄, is a reducing agent that is commonly used in modern organic synthesis.
- It is a nucleophilic reducing agent that is best suited for reducing multiple polar bonds.
- The LiAlH₄ reagent is capable of converting aldehydes to primary alcohols, ketones to secondary alcohols, carboxylic acids and esters to primary alcohols, amides and nitriles to amines, epoxides to alcohols, and lactones to diols.

B. Preparation of LiAlH₄:

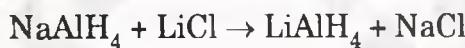
- The reaction of lithium hydride and aluminium chloride produces lithium aluminium hydride.



- In addition to this method, the industrial synthesis requires the initial preparation of sodium aluminium hydride under high pressure and temperature:



Following that, LiAlH₄ is synthesized via a salt metathesis reaction as follows :

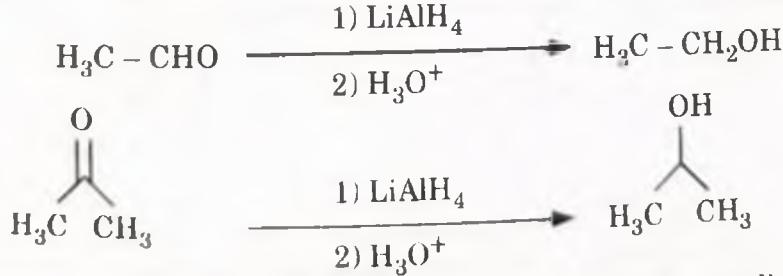


It proceeds in a high yield. Filtration is used to remove LiCl from an ethereal solution of LAH.

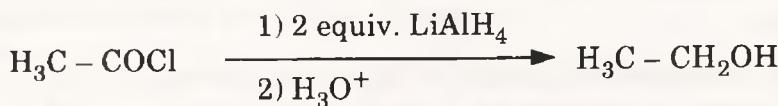
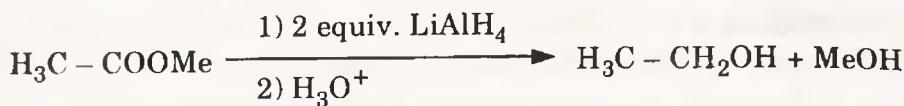
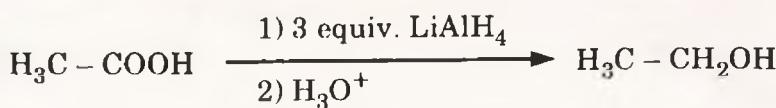
C. Applications of LiAlH₄:

- LiAlH₄ reduces aldehydes or ketones to the corresponding primary or secondary alcohols.
Acetaldehyde, for example, is reduced to ethyl alcohol, while acetone is reduced to isopropyl alcohol.

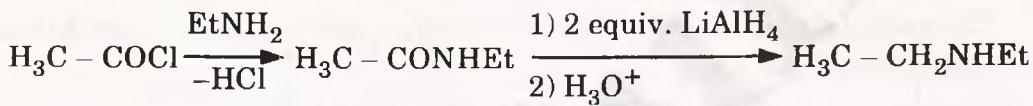
LiAlH₄ reduction of carbonyl compounds



- LiAlH₄ is used to reduce carboxylic acids, esters, and acid halides to their corresponding primary alcohols.
For example, LiAlH₄ reduction of acetic acid, methyl acetate, and acetyl chloride yield the same ethyl alcohol.

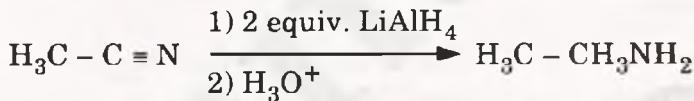


3. Lithium aluminium hydride, LiAlH_4 , reduces the amides to amines. This method is particularly useful for obtaining secondary amines.
Diethylamine, for example, can be synthesized from acetyl chloride.



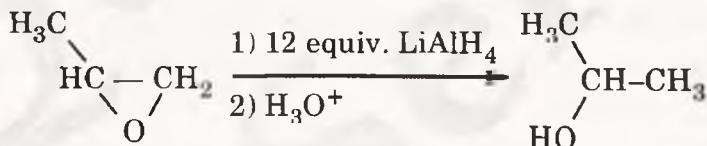
4. LiAlH_4 reduces the nitriles to primary amines.

For example, LiAlH_4 reduces acetonitrile to ethyl amine.



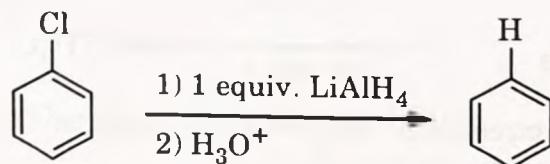
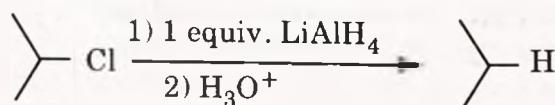
5. The oxiranes (epoxides) are converted to alcohol by lithium aluminium hydride. The mechanism involves a hydride attack on the epoxide's less hindered side.

For example, 2-methyloxirane primarily yields 2-propanol.



Reduction of epoxides by LiAlH_4

6. Lithium aluminium hydride is used to convert haloalkanes and haloarenes to their corresponding hydrocarbons.



Que 5.26. What are organometallic compounds? Explain various methods of preparation of Grignard reagent and also write reactions of Grignard reagent with HCHO , R_2NH , CO_2 , $\text{CH}_3\text{CH}_2\text{OH}$ and ester.

AKTU 2018-19 (Sem-1), Marks 10

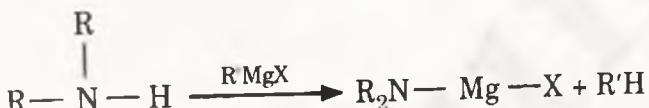
Answer

Organometallic compound and preparation : Refer Q. 5.23,
Page 5-31B, Unit-5.

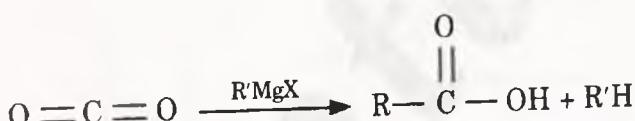
Reactions:

HCHO : Refer Q. 5.19, Page 5-27B, Unit-5.

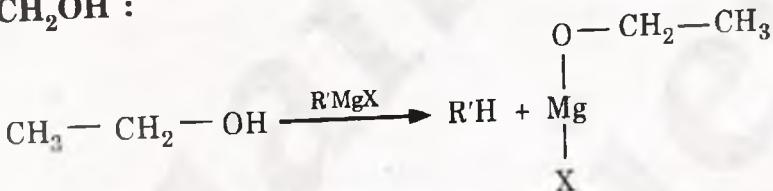
ii. R_2NH :



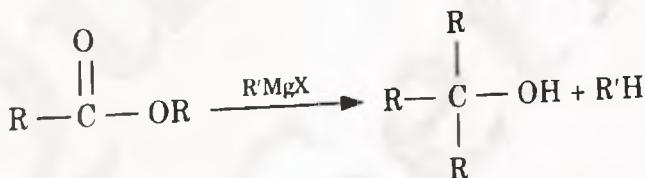
iii. CO₂:



iv. $\text{CH}_3\text{CH}_2\text{OH}$:



v. Ester:

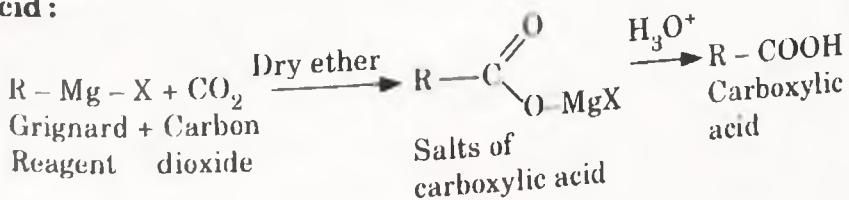


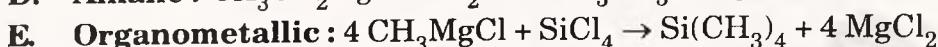
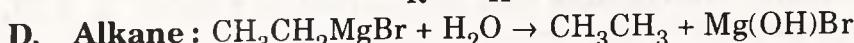
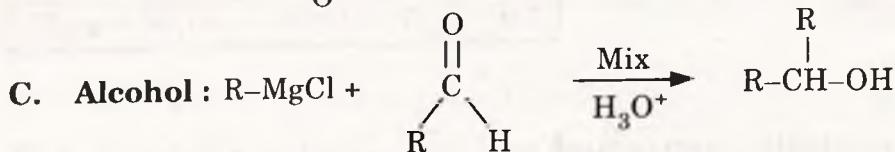
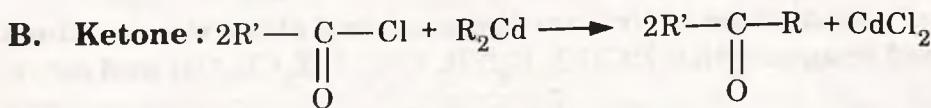
Que 5.27. Explain with equations preparation of acid, ketone, alcohol, alkane and organometallic compound from Grignard reagent.

AKTU 2020-21, Marks 10

Answer

A Acid:





VERY IMPORTANT QUESTIONS

Following questions are very important. These questions may be asked in your SESSIONALS as well as UNIVERSITY EXAMINATION.

Q. 1. Giving suitable examples, distinguish between thermoplastic and thermosetting polymers.

Ans. Refer Q. 5.7, Unit-5.

Q. 2. What are composites materials ? Give classification of composite materials.

Ans. Refer Q. 5.9, Unit-5.

Q. 3. Explain the conductivity of polymers with conjugated π -electron system. How is this conductivity enhanced by doping ?

Ans. Refer Q. 5.10, Unit-5.

Q. 4. Give preparation, properties and application of buna-N and Terylene.

Ans. Refer Q. 5.16, Unit-5.

Q. 5. Define the term organometallic compounds. Explain general methods of synthesis of organometallic compound preparation and applications with suitable examples.

Ans. Refer Q. 5.23, Unit-5.

Q. 6. What are organometallic compounds ? How Grignard reagents are prepared ? Write any five synthetic applications of Grignard reagents.

Ans. Refer Q. 5.24, Unit-5.





Materials Chemistry (2 Marks Questions)

5.1. Define and explain polymer.

Ans. A polymer is defined as the substance having very high molecular weight and is made by joining of large number of simple molecules. Therefore, the polymers molecules have certain structural unit repeating large number of times.

5.2. Why Teflon is highly chemical resistant ?

AKTU 2020-21 (Sem-1), Marks 02

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.

5.3. Why can human beings digest starch but cannot digest cellulose although both are made up of D-(+)-Glucose ?

Ans. Starch ($C_6H_{10}O_5$) is a biodegradable polymer and can degrade in the presence of micro-organisms so can be digestible while cellulose is not a biodegradable polymer.

5.4. Explain why ethylene polymerises but ethane does not ?

Ans. Ethane cannot polymerize because it does not have a property to show functionality. Double bonds are not available for combination in ethane while they are available in ethylene.



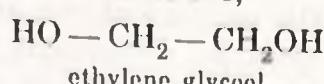
5.5. What do you understand by the term functionality of a polymer ? Explain by taking an example.

AKTU 2017-18 (Sem-2), Marks 02

Ans.

1. Functionality of monomers is defined as the number of reactive position or groups in the molecule of monomer.
2. The monomer having two reactive positions known as bifunctional monomer and similarly trifunctional, tetra functional, etc, monomers.

Examples of such monomers are,



- 5.6. Will you prefer to polymerize acrylonitrile under anionic or cationic conditions ? Explain.**

AKTU 2017-18 (Sem-1), Marks 02

Ans. We will prefer anionic polymerization to polymerize acrylonitrile because under anionic polymerization the active center of propagating species is negatively charged and the monomer containing electron withdrawing group such as acrylonitrile will thus favor the polymerization.

- 5.7. Differentiate between addition polymerization and condensation polymerization with suitable example.**

Ans.

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.

- 5.8. Give two examples of initiators used for free radical polymerization.**

Ans. Benzoyl peroxide and AIBN (Azobis Iso Butyo Nitrile).

- 5.9. 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.

- 5.10. What do you understand by polymer blends ?**

AKTU 2018-19 (Sem-2), Marks 02

Ans. Polymer blend is the mixture of two or more polymers, having better properties than the component polymers. For making a polymer blend it is essential that they are compatible with each other.

5.11. Classify the polymers on the basis of tacticity.

Ans.

- a. Isotactic polymer
- b. Atactic polymer
- c. Syndiotactic polymer

5.12. What is the main purpose of vulcanization ?

Ans. In vulcanization added sulphur combines chemically at the double bonds of different rubber chains, thereby making the product stiff.

5.13. Why is PVC used in chemical industries ?

Ans.

- i. Maintenance cost of PVC is low.
- ii. High resistance towards chemicals.
- iii. PVC can be processed in any form, even by hot welding.

5.14. Write the monomer of

- a. Neoprene
- b. Terylene.

AKTU 2018-19 (Sem-1), Marks 02

Ans.



5.15. Why a dry ether solvent important for the preparation of Grignard reagent ? **AKTU 2018-19 (Sem-1), Marks 02**

Ans. Dry ether is an especially good solvent for the formation of Grignard reagents because ethers are non-acidic.

5.16. What are Bio-degradable polymers ? Discuss their application. **AKTU 2018-19 (Sem-2), Marks 02**

Ans.

- A. **Bio-degradable Polymers** : The polymers which are degraded by micro-organisms within a suitable period so that the polymers and

their degraded products do not cause any serious effects on the environment are called biodegradable polymers.

B. Applications :

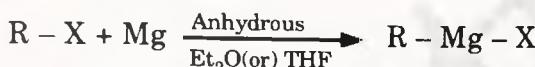
1. Poly (β -hydroxy butyrate) or PHB is used in the manufacture of shampoo bottles.
2. It is also used in some agricultural applications, such as timed-release coatings for fertilizers and pesticides.

5.17. Give the preparations of Grignard reagent.

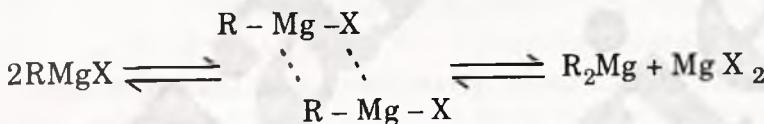
AKTU 2020-21 (Sem-1), Marks 02

Ans.

1. The Grignard reagents are prepared by the action of activated magnesium (Rieke magnesium) on organic halides in suitable solvents like Diethyl ether, Et_2O or Tetrahydrofuran, THF in anhydrous conditions.



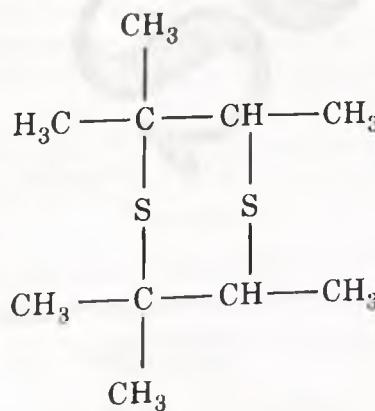
2. This is an oxidation insertion of magnesium between carbon and halogen bond, which involves oxidation of Mg(0) to Mg (II).
3. The Grignard reagents are in equilibrium with the dialkylmagnesium species R_2Mg and MgX_2 .



5.18. Give the structure of vulcanized rubber.

AKTU 2021-22 (Sem-1), Marks 02

Ans.



Sulphur cross-links vulcanized rubber.

5.19. Give two differences between addition and condensation polymers.

AKTU 2021-22 (Sem-1), Marks 02

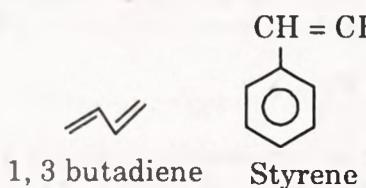
Ans. Differences between addition and condensation polymers :

S. No.	Addition Polymers	Condensation Polymers
1.	Monomers must have either a double or triple bond.	Monomers must have two similar or different functional groups.
2.	Addition of monomers results in polymers.	Condensation of monomers results in polymers.

5.20. Write monomers of Buna-S and Nylon 66 ?

AKTU 2021-22 (Sem-2), Marks 02

Ans. Monomers of Buna-S : – 1, 3 butadiene and styrene



Monomer of Nylon 66 : Hexamethylene diamine adipic acid
 $\text{NH}_2 - (\text{CH}_2)_6 - \text{NH}_2$ Hexamethylene diamine
 $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ Adipic acid

5.21. Write structure of Ferrocene and Dibenzene chromium.

AKTU 2021-22 (Sem-2), Marks 02

Ans. In ferrocene structure iron atom sandwiched between two cyclopentadienyl rings



In dibenzene chromium structure chromium atom sandwiched between two benzene rings.

