



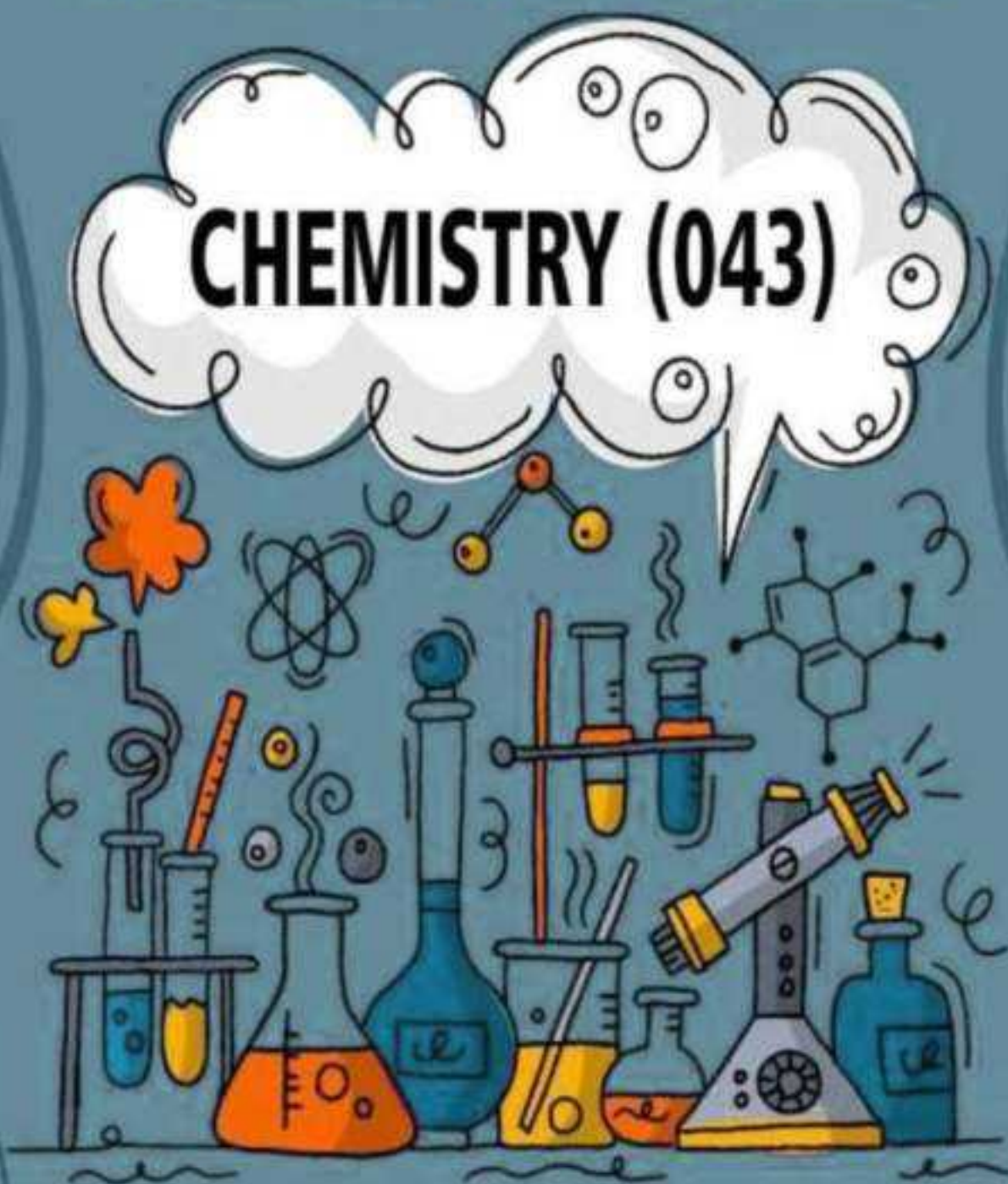
केन्द्रीय विद्यालय संगठन मुंबई संभाग

KENDRIYA VIDYALAYA SANGATHAN
MUMBAI REGION



STUDENT SUPPORT MATERIAL

CHEMISTRY (043)



CLASS XII
SESSION 2023-24

OUR INSPIRATION:

CHIEF PATRON	MRS. SONA SETH DEPUTY COMMISSIONER	
PATRON	MR. S.V. JOGLEKAR ASSISTANT COMMISSIONER	
COURSE DIRECTOR	MRS. SAVITA YADAV PRINCIPAL KV -2 COLABA	
RESOURCE PERSON	MRS. KIRAN DWIVEDI PGT CHEMISTRY KV ARMY AREA	
RESOURCE PERSON	MRS. SUBHASHINI SINGH PGT CHEMISTRY KV NO.3 9BRD, PUNE	

3D's of CHEMISTRY

DETERMINATION

DESTINATION

DEVOTION

KENDRIYA VIDYALAYA SANGATHAN, MUMBAI REGION

<u>S.No</u>	Name of KV	PGT CHEMISTRY	
		Name of the Contributor	Topics Alloted For Demo Lesson
2	INS Hamia	Mr. Ramswarup Buntolia	d and f Block- Reasoning Question-Answers
3	Koliwada	Vijay Kumar	Any Topic from Electrochemistry
5	BEG Pune	AVANTI NEGI	Any Topic from Structure of Atom
6	No. 1 AFS Pune	BINI MENON	Numericals from Solution -Based on Vant-Hoff Factor
7	Ganeshkhind	Mr Asif Equebal Mrs Indu Chib	Coordination Chemistry
8	NDA Khadakwasala Pune	MRS. VARSHA INDURKAR	Organic Mechanisms
10	OF Varangeon	SMT RAGINI GAJBHIYE	Organic - Reasoning Questions
11	Kamptee	1. KUNDAN KHAKSE 2. P.K.MESHRAM	Nernst Equation and Bonding in Coordination Compounds
12	Nagpur CRPF	PARVATHY KAMBLE	Any Topic from Thermodynamics
13	Nagpur VSN	1.MANISHA SANE 2. DIVYAJYOTI NAGOTRA	Distinguishing Tests
14	Nagpur Ambajhari	1)ASHWAJEET DIVE 2)VINEETA VIDYARTHI	Any Topic from Chemical Equilibrium
15	No. 1 AFS Pune	Archana Kumari Singh	Demonstration and Editing and Compiling of Study Material of Class 12th
16	No. 2 AFS Pune	Pragya Dwivedi	Demonstration and Editing and Compiling of Study Material of Class 11th

INDEX

S. No.	Title	Page No.
1	Weightage of marks	10
2	Syllabus	11-12
3	Solutions	13-31
4	Electrochemistry	32-51
5	Chemical Kinetics	52-64
6	d -and f -Block Elements	65-85
7	Coordination Compounds	86-105
8	Haloalkanes and Haloarenes	106-129
9	Alcohols, Phenols and Ethers	130-147
10	Aldehydes, Ketones and Carboxylic Acids	148-167
11	Amines	168-184
12	Biomolecules	185-208
13	MINIMUM LEARNING MATERIAL	209-255
14	ANNEXURE-1 SAMPLE PAPER 1 TO 5	256-322
15	ANNEXURE -2 NAME REACTION	323-332
16	ANNEXURE-3 REASON BASED QUESTION	333-337
17	ANNEXURE -4 WORD PROBLEMS	338-341
18	ANNEXURE-5 CONVERSIONS	342-349
19	CHAPTER WISE FORMULAE AND WORKSHEETS	
20	CHAPTER WISE MCQ	

MARKS DISTRIBUTION AS PER GIVEN CBSE
CLASS XII

SESSION 2022-23

MARKS 70

S.No.	Title	Marks
1	Solutions	7
2	Electrochemistry	9
3	Chemical Kinetics	7
4	d -and f -Block Elements	7
5	Coordination Compounds	7
6	Haloalkanes and Haloarenes	6
7	Alcohols, Phenols and Ethers	6
8	Aldehydes, Ketones and Carboxylic Acids	8
9	Amines	6
10	Biomolecules	7
	TOTAL	70

SYLLABUS CHEMISTRY (THEORY) CLASS XII (2023-24)

Unit I: Solutions (15 Periods)

Types of solutions, expression of concentration of solutions of solids in liquids, solubility of gases in liquids, solid solutions, Raoult's law, colligative properties - relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure, determination of molecular masses using colligative properties, abnormal molecular mass, Van't Hoff factor.

Unit II: Electrochemistry (18 Periods)

Redox reactions, EMF of a cell, standard electrode potential, Nernst equation and its application to chemical cells, Relation between Gibbs energy change and EMF of a cell, conductance in electrolytic solutions, specific and molar conductivity, variations of conductivity with concentration, Kohlrausch's Law, electrolysis and law of electrolysis (elementary idea), dry cell-electrolytic cells and Galvanic cells, lead accumulator, fuel cells, corrosion.

Unit III: Chemical Kinetics (15 Periods)

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Unit IV: d and f Block Elements (18 Periods)

General introduction, electronic configuration, occurrence and characteristics of transition metals, general trends in properties of the first-row transition metals – metallic character, ionization enthalpy, oxidation states, ionic radii, colour, catalytic property, magnetic properties, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$.

Lanthanoids – Electronic configuration, oxidation states, chemical reactivity and lanthanoids contraction and its consequences.

Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit V: Coordination Compounds (18 Periods)

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds, Bonding, Werner's theory, VBT, and CFT; structure and stereoisomerism, the importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Unit VI: Haloalkanes and Haloarenes (15 Periods)

Haloalkanes: Nomenclature, nature of C-X bond, physical and chemical properties, optical rotation mechanism of substitution reactions.

Haloarenes: Nature of C-X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, Iodoform, freons, DDT.

Unit VII: Alcohols, Phenols and Ethers (14 Periods)

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol.

Phenols: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses.

Unit VIII: Aldehydes, Ketones and Carboxylic Acids (15 Periods)

Aldehydes and Ketones: Nomenclature, nature of carbonyl group, methods of preparation, physical and chemical properties, mechanism of Nucleophilic addition, reactivity of alpha hydrogen in aldehydes, uses.

Carboxylic Acids: Nomenclature, acidic nature, methods of preparation, physical and chemical properties; uses.

Unit IX: Amines (14 Periods)

Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Unit X: Biomolecules (18 Periods)

Carbohydrates - Classification (aldoses and ketoses), monosaccharides (glucose and fructose), D-L configuration oligosaccharides (sucrose, lactose, maltose), polysaccharides (starch, cellulose, glycogen); Importance of carbohydrates.

Proteins - Elementary idea of - amino acids, peptide bond, polypeptides, proteins, structure of proteins - primary, secondary, tertiary structure and quaternary structures (qualitative idea only), denaturation of proteins; enzymes, Hormones - Elementary idea excluding structure.

Vitamins - Classification and functions.

Nucleic Acids: DNA and RNA

CHAPTER-1 – SOLUTIONS

Solutions are homogeneous mixtures of two or more than two substances. Binary solution is a solution which consists of two components.

A solution may be classified as solid, liquid or gaseous solution.

Terms to express the concentration of a solution

1	Mass percentage	Mass of solute per 100 g of solution.
2	Molarity	No of moles of solute in one litre of solution. $M = \frac{W_B \times 1000}{M_B \times V}$ W_B - Mass of solute (g) V - Volume of solution (mL) M_B - Molar mass of solute(gmol^{-1})
3	Molality	No of moles of solute in one kg of solvent. $m = \frac{W_B \times 1000}{M_B \times W_A}$ W_B - Mass of solute (g) W_A - Mass of solvent (g) M_B - Molar mass of solute (gmol^{-1})
4	Mole fraction	Ratio of no of moles of a component to the total no of moles of Solution
5	Parts per million	Number of parts of the component in 10^6 parts of solution

Solubility

Solubility is the maximum amount of solute that can be dissolved in a specified amount of solvent at a specified temperature or pressure (in the case of gaseous solutes)

Solubility of a solid in a liquid

A saturated solution contains the maximum amount of solute dissolved in a given amount of solvent at a particular temperature. The concentration of solute in such a solution is its solubility. Effect of temperature

- If the dissolution process is exothermic, the solubility decreases with increase in temperature
 - If the dissolution process is endothermic, the solubility increases with increase in temperature
- Effect of pressure
- No significant effect as solids are highly incompressible

Solubility of gases in liquids

Henry's law

Statement	Partial pressure of a gas in vapour phase is directly proportional to the mole fraction of the gas in the solution.
Mathematical expression	$p = K_H x$, p = pressure of the gas x = mole fraction of gas in solution K_H = Henry's law constant
Relation between K_H & x	K_H is inversely proportional to solubility of the gas
Applications	i) To increase the solubility of CO_2 in soft drinks, the bottles are sealed under high pressure ii) Scuba divers carry cylinders filled with air diluted with helium. Otherwise high concentration of N_2 in blood can cause 'bends'. ii) At high altitudes due to low pressure, there is less oxygen in the blood and people suffer from anoxia.

Solubility of gases in liquids decreases with rise in temperature, because dissolution of gas in a liquid is an exothermic process.

Raoult's Law: For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

$$p_A = p_A^0 x_A + p_B = p_B^0 x_B$$

where p_A^0 - Vapour pressure of pure A,

p_B^0 - Vapour pressure of pure B

$$p_{\text{total}} = p_A + p_B$$

Mole fraction of the components in vapour phase is

given by $y_A = p_A / p_{\text{total}}$, $y_B = p_B / p_{\text{total}}$

Raoult's law as a special case of Henry's law

Henry's law, $p = K_H x$ Raoult's Law - $p_A = p_A^0 x_A$

Raoult's law becomes a special case of Henry's law in which K_H becomes equal to p_A^0

Ideal solutions are the solutions which obey Raoult's law over entire range of concentration, A - B interactions are similar to that of A - A or B - B interactions,

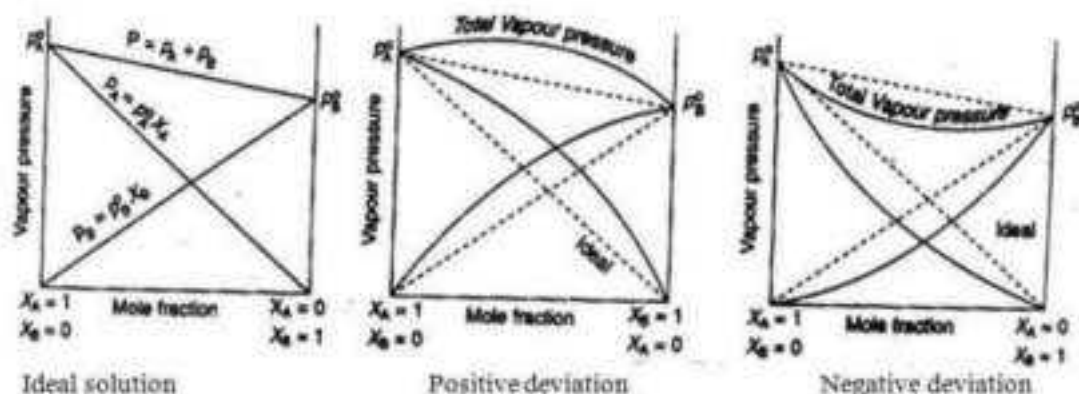
$$\Delta_{\text{mix}} H \text{ \& } \Delta_{\text{mix}} V = 0$$

Eg :- benzene & toluene, n-hexane & n-heptane

Non ideal solutions with components A & B

Showing positive deviation	Showing negative deviation
A - B interactions are weaker than A - A or B - B interactions	A - B interactions are stronger than A - A & B - B interactions
$\Delta_{\text{mix}} H > 0$, $\Delta_{\text{mix}} V > 0$	$\Delta_{\text{mix}} H < 0$, $\Delta_{\text{mix}} V < 0$
Examples : CS_2 & Acetone, Ethanol & water	Chloroform & acetone, Nitric acid & water

Graphical Representation of ideal and non-ideal solutions



Azeotropes

Azeotropes are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Minimum boiling azeotropes– These are solutions that show a large positive deviation from Raoult's law. Eg – Ethanol and water mixture (95% by volume).

Maximum boiling azeotropes – These are solutions that show large negative deviation from Raoult's law. Eg- Nitric acid and water mixture (68 % by mass).

Colligative properties are the properties that depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution.

There are four colligative properties as follows:

1. Relative lowering of vapour pressure

In a solution with non-volatile solute, the surface has both solute and solvent molecules; thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced. The decrease in the vapour pressure of solvent depends on the quantity of non-volatile solute present in the solution, irrespective of its nature.

For a solution of volatile liquids Raoult's law, is given as

$$P = P_A + P_B$$

If solute (component B) is non-volatile then

$$P = P_A = P_A^\circ X_A$$

$$P = P_A^\circ (1 - X_B)$$

$$P = P_A^\circ - P_A^\circ X_B$$

$$P_A^\circ X_B = P_A^\circ - P$$

$$\frac{P_A^\circ - P}{P_A^\circ} = X_B$$

$$(\because X_A + X_B = 1)$$

Thus, relative lowering of vapour pressure is equal to the mole fraction of non-volatile solute.

for dilute solutions, $n_B \ll n_A$. Hence,

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_A}$$

or

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{W_B \times M_A}{M_B \times W_A}$$

2. Elevation in boilingpoint

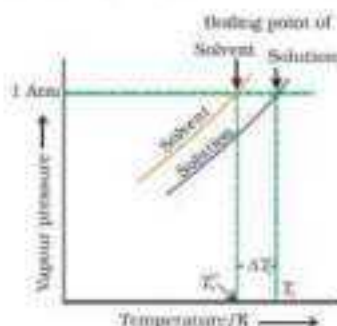
The vapour pressure of the solvent is depressed by the presence of a non-volatile solute. So it must be heated to a higher temperature to make the vapour pressure equal 1 atm

$$\Delta T_b = K_b m = K_b \times W_B \times 1000 / M_B \times W_A$$

K_b – Molal elevation constant

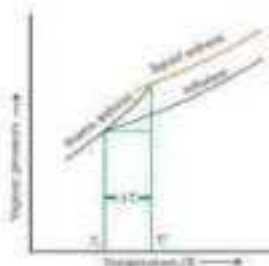
$$T_b = T_b^0 + \Delta T_b$$

T_b – b.pt of the solution, T_b^0 – b.pt of pure solvent, ΔT_b – Elevation in b.pt



3. Depression in freezingpoint

A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent. When a non-volatile solid is added to the solvent its vapour pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.



$$\Delta T_f = K_f m = K_f \times W_B \times 1000 / M_B \times W_A$$

K_f – Molal depression constant

$$T_f = T_f^0 - \Delta T_f$$

T_f - f.pt of the solution,
 T_f^0 - f.pt of pure solvent, ΔT_f - depression in f.pt

4. Osmotic pressure (π)

When solvent & solution are separated by a semipermeable membrane, solvent molecules flow through the membrane from pure solvent to the solution. This process is called osmosis.

The excess pressure applied to a solution that just stops the flow of solvent through a semipermeable membrane is called osmotic pressure.

$$\pi = C RT, \pi V = n_B RT, \pi V = W_B RT / M_B$$

Advantages of osmotic pressure method in determining molar mass of solutes:

- i) Osmotic pressure is measured at room temperature
- ii) Molarity is used instead of molality
- iii) Magnitude of osmotic pressure is large even for very dilute solutions.
- iv) This method is particularly used for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Isotonic solutions

Two solutions having same osmotic pressure at a given temperature separated by a semipermeable membrane are termed as isotonic solutions.

Hypertonic solution

A solution which has higher osmotic pressure than the other solution separated by a semipermeable membrane is called hypertonic solution.

Hypotonic solution

A solution which has lower osmotic pressure than the other solution separated by a semipermeable membrane is called hypotonic solution.

Reverse osmosis – If a pressure larger than osmotic pressure is applied to solution, then the direction of motion of solvent molecules is reversed. It now flows from solution to solvent.

Application: Reverse osmosis is used in desalination of sea water.

Abnormal molar masses are obtained whenever a solute undergoes dissociation or association.

In 1880 van't Hoff introduced a factor i , known as the van't Hoff factor, to account for the extent of dissociation or association.

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}} \\ = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

Modified Formulae for colligative properties of electrolytes

Relative lowering of vapour pressure, $\frac{P_1^0 - P_1}{P_1^0} = iX_2 = i \frac{n}{n+N}$

Osmotic pressure, $\pi = iCRT$

Elevation in boiling point, $\Delta T_b = i \cdot 1000 \times K_b \times \text{molality}$

Depression in freezing point, $\Delta T_f = i \cdot 1000 \times K_f \times \text{molality}$

Value of i

Solute undergoes neither dissociation nor association	Solute undergoes dissociation	Solute undergoes association
$i = 1$	$i > 1$	$i < 1$

Degree of dissociation	Degree of association
$\alpha = \frac{i-1}{n-1}$	$\alpha = \frac{i-1}{\frac{1}{n}-1}$
Value of n - NaCl -2 Al ₂ (SO ₄) ₃ -5	Value of n CH ₃ COOH in benzene -2

QUESTION BANK CHAPTER-SOLUTIONS

SECTION A

MULTIPLE CHOICE QUESTIONS (1 Marks Each)

1. A 5% solution of cane-sugar (molecular weight = 342) is isotonic with 1% solution of substance A. The molecular weight of X is

- (a) 342
- (b) 171.2
- (c) 68.4
- (d) 136.8

Answer: (c) 68.4

2. The law which indicates the relationship between solubility of a gas in liquid and pressure

- (a) Raoult's law
- (b) Henry's law
- (c) Lowering of vapour pressure
- (d) Van't Hoff law

Answer: (b) Henry's law

3. Which of the following solutions shows positive deviation from Raoult's law?

- (a) Acetone + Aniline
- (b) Acetone + Ethanol
- (c) Water + Nitric acid
- (d) Chloroform + Benzene

Answer: (b) Acetone + Ethanol

4. The system that forms maximum boiling azeotrope is

- (a) Acetone-chloroform
- (b) ethanol-acetone
- (c) n-hexane-n-heptane
- (d) carbon disulphide-acetone

Answer: (a) Acetone-chloroform

5. The relative lowering in vapour pressure is proportional to the ratio of number of

- (a) solute molecules to solvent molecules
- (b) solvent molecules to solute molecules
- (c) solute molecules to the total number of molecules in solution
- (d) solvent molecules to the total number of molecules in solution

Answer: (c) solute molecules to the total number of molecules in solution

6. The osmotic pressure of a solution can be increased by

- (a) increasing the volume
- (b) increasing the number of solute molecules
- (c) decreasing the temperature
- (d) removing semipermeable membrane

Answer: (b) increasing the number of solute molecules

7. For carrying reverse osmosis for desalination of water the material used for making semipermeable membrane is

- (a) potassium nitrate
- (b) parchment membrane
- (c) cellulose acetate
- (d) cell membrane

Answer: (c) cellulose acetate

8. At equilibrium the rate of dissociation of a solid solute in a volatile liquid solvent is

- (a) less than the rate of crystallisation
- (b) greater than the rate of crystallisation
- (c) equal to the rate of crystallisation
- (d) zero

Answer: (c) equal to the rate of crystallisation

9. Which of the following aqueous solutions should have the highest boiling point?

- (i) 1.0 M NaOH
- (ii) 1.0 M Na_2SO_4
- (iii) 1.0 M NH_4NO_3
- (iv) 1.0 M KNO_3

Answer : (ii) 1.0 M Na_2SO_4

10. The unit of ebullioscopic constant is _____.

- (i) K kg mol^{-1} or K (molality)^{-1}
- (ii) mol kg K^{-1} or $\text{K}^{-1}(\text{molality})$
- (iii) $\text{kg mol}^{-1} \text{K}^{-1}$ or $\text{K}^{-1}(\text{molality})^{-1}$
- (iv) K mol kg^{-1} or K (molality)

Answer : (i) K kg mol^{-1} or K (molality)^{-1}

ASSERTION REASONING QUESTIONS (1 Marks Each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are correct and the R is the correct explanation of A.
- (b) Both A and R are correct but R does not explain the A.
- (c) Assertion (A) is correct but Reason (R) is incorrect.
- (d) Assertion (A) is incorrect but Reason (R) is correct.

1. **Assertion:** Molarity of a solution in liquid state changes with temperature.

Reason: The volume of a solution changes with change in temperature.

Answer (a)

2. **Assertion:** When methyl alcohol is added to water, boiling point of water increases.

Reason: When a volatile solute is added to a volatile solvent elevation in boiling point is observed.

Answer (b)

3. **Assertion:** When NaCl is added to water a depression in freezing point is observed.

Reason: The lowering of vapour pressure of a solution causes depression in the freezing point.

Answer (a)

4. **Assertion:** When a solution is separated from the pure solvent by a semipermeable membrane, the solvent molecules pass through it from the pure solvent side the solution side.

Reason: Diffusion of solvent occurs from a region of high concentration solution to a region of low concentration solution.

Answer (b)

5. **Assertion:** If a liquid solute more volatile than the solvent is added to the solvent, the vapour pressure of the solution may increase i.e., $p_x > p_0$.

Reason: In the presence of a more volatile liquid solute, only the solute will form the vapours and solvent will not.

Answer (c)

SECTION B

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks Each)

1. What mass of ethylene glycol (molar mass = 62.0 g mol^{-1}) must be added to 5.50 kg of water to lower the freezing point of water from 0 to -10.0°C (k_f for water = $1.86 \text{ K kg mol}^{-1}$). (CBSE 2010).

Ans: $\Delta T_f = \frac{K_f \times 1000 \times w_B}{w_A \times M_B}$
 $K_f = 1.86 \text{ K kg mol}^{-1}$, $w_A = 5.50 \text{ kg} = 5500 \text{ g}$
 $w_B = ?$
 $M_B = 62.0 \text{ g/mol}$, $\Delta T_f = 0 - (-10) = 10^\circ\text{C}$
 $10 = \frac{1.86 \times 1000 \times w_B}{5500 \times 62}$
 $w_B = \frac{10 \times 5500 \times 62}{1.86 \times 1000} = 1833.3 \text{ g} = 1.833 \text{ kg}$

2. 15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at -0.34°C . What is the molar mass of this material? (k_f for water = $1.86 \text{ K kg mol}^{-1}$) (CBSE Delhi 2012)

Ans: Molecular mass, M_B is
 $M_B = \frac{K_f \times w_B \times 1000}{w_A \times \Delta T_f}$
 $\Delta T_f = 0 - (-0.34) = 0.34^\circ$
 $K_f = 1.86 \text{ K kg mol}^{-1}$, $w_B = 15.0 \text{ g}$, $w_A = 450 \text{ g}$
 $M_B = \frac{1.86 \times 15.0 \times 1000}{450 \times 0.34} = 182.3 \text{ g/mol}$

3. Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing (CBSE AI 2016)

- (i) 1.2% sodium chloride solution?
(ii) 0.4% sodium chloride solution?

Ans: (i) Water will flow out of the cell and they will shrink as 1.2% sodium chloride solution is hypertonic.

(ii) Water will flow into the cell and they will swell as 0.4% sodium chloride solution is hypotonic.

4. 18 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$ (molar mass = 180 g mol^{-1}), is dissolved in 1 kg of water in a saucepan. At what temperature will this solution boil? (CBSE Delhi 2013)

(K_b for water = $0.52 \text{ K kg mol}^{-1}$, boiling point of pure water = 373.15 K).

Ans: $\Delta T_b = \frac{K_b \times 1000 \times w_B}{w_A \times M_B}$
 $w_B = 18 \text{ g}$, $w_A = 1000 \text{ g}$, $M_B = 180 \text{ g/mol}$,
 $K_b = 0.52 \text{ K kg mol}^{-1}$
 $\therefore \Delta T_b = \frac{0.52 \times 1000 \times 18}{1000 \times 180} = 0.052 \text{ K}$
Boiling point of solution
 $= 373.15 + 0.052 = 373.202 \text{ K}$

5. A solution prepared by dissolving 1.25 g of oil of wintergreen (methyl salicylate) in 99.0 g of benzene has a boiling point of 80.31°C. Determine the molar mass of this compound. (B.P. of pure benzene = 80.10°C and K_b for benzene = 2.53 °C kg mol⁻¹) (CBSE Delhi 2010)

A

$$\Delta T_b = \frac{K_b \times 1000 \times w_B}{M_B \times w_A}$$

or $M_B = \frac{K_b \times 1000 \times w_B}{\Delta T_b \times w_A}$

$$K_b = 2.53^\circ\text{C kg mol}^{-1}$$

$$w_A = 99.0 \text{ g}, w_B = 1.25 \text{ g}$$

$$M_B = \frac{2.53 \times 1000 \times 1.25}{0.21 \times 99.0}$$

$$= 152.1 \text{ g mol}^{-1}$$

6. A solution containing 15 g urea (molar mass = 60 g mol⁻¹) per litre of solution in water has the same osmotic pressure (isotonic) as a solution of glucose (molar mass = 180 g mol⁻¹) in water. Calculate the mass of glucose present in one litre of its solution. (CBSE AI 2014)

Ans: For isotonic solutions, π (urea) = π (glucose)

$$\pi \text{ (urea)} = \frac{nRT}{V} = \frac{15}{60} \times \frac{RT}{1}$$

$$\pi \text{ (glucose)} = \frac{nRT}{V} = \frac{w}{180} \times \frac{RT}{1}$$

Now, $\frac{15}{60} RT = \frac{w}{180} RT$

$$\therefore w = \frac{15 \times 180}{60} = 45 \text{ g}$$

7. A 1.00 molal solution of trichloroacetic acid (CCl₃COOH) is heated to its boiling point. The solution has the boiling point of 100.18°C. Determine the van't Hoff factor for trichloroacetic acid (K_b for water = 0.512 K kg mol⁻¹).

(CBSE Delhi 2012)

Ans:

Observed boiling point elevation,

$$\Delta T_b = 100.18 - 100.0 = 0.18^\circ\text{C}$$

Molality of solution = 1.00 m

Calculated boiling point elevation,

$$\Delta T_b(\text{calc.}) = K_b \times m$$

$$= 0.512 \times 1 = 0.512$$

van't Hoff factor,

$$i = \frac{\text{Observed boiling point elevation}}{\text{Calculated boiling point elevation}}$$

$$= \frac{0.18}{0.512} = 0.351$$

8. 1.00 g of non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. Find the molar mass of the solute. (K_f for benzene = $5.12 \text{ K kg mol}^{-1}$). (CBSE AI 2013)

Ans:

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

$$= \frac{5.12 \times 1.0 \times 1000}{0.40 \times 50} = 256 \text{ g mol}^{-1}$$

9. Urea forms an ideal solution in water. Determine the vapour pressure of an aqueous solution containing 10% by mass of urea at 40°C . (Vapour pressure of water at 40°C = 55.3 mm of Hg). (CBSE AI 2006)

Ans: $w_A = 90 \text{ g}$, $w_B = 10 \text{ g}$

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{w_B \times M_A}{w_A \times M_B}$$

$$\frac{55.3 - p_A}{55.3} = \frac{10 \times 18}{90 \times 60} = 0.0333$$

$$55.3 - p_A = 1.84$$

$$\therefore p_A = 53.46 \text{ mm Hg}$$

10. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C ? The freezing point depression constant (K_f) for water is 1.86°C/m . Assume van't Hoff factor for NaCl is 1.87 (Molar mass of NaCl = 58.5 g mol^{-1}). (CBSE 2011)

Ans:

Lowering in freezing point,

$$\Delta T_f = 7.50^\circ\text{C}$$

$$K_f = 1.86^\circ\text{C/m}$$

Mass of water, $W_A = 65.0 \text{ g}$

Molar mass of NaCl, $M_B = 58.5 \text{ g}$

Mass of NaCl, $W_B = ?$

van't Hoff factor, $i = 1.87$

$$\Delta T_f = \frac{i K_f \times 1000 \times W_B}{W_A \times M_B}$$

$$\text{or } W_B = \frac{\Delta T_f \times W_A \times M_B}{i \times K_f \times 1000}$$

$$= \frac{7.50 \times 65.0 \times 58.5}{1.87 \times 1.86 \times 1000} = 8.20 \text{ g}$$

SECTION C
SHORT ANSWER TYPE QUESTIONS (3 Marks Each)

1. A solution of glucose (molar mass = 180 g mol^{-1}) in water is labelled as 10% by mass. What would be the molality and molarity of the solution? (Density of solution = 1.2 g mL^{-1}) (Delhi AI 2014)

(i) Calculation of molality

Mass of glucose = 10 g

Moles of glucose = $\frac{10}{180} = 0.0556$

(Molar mass of glucose = 180 g/mol)

Mass of water = 90 g

$$\therefore \text{Molality} = \frac{\text{Moles of glucose}}{\text{Mass of water}} \times 1000$$

$$= \frac{0.0556}{90} \times 1000$$

$$= 0.618 \text{ m}$$

(ii) Calculation of molarity

Moles of glucose = 0.0556 Mass

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}}$$

$$= \frac{100}{1.20} = 83.3 \text{ mL}$$

$$\text{Molarity} = \frac{\text{Moles of glucose}}{\text{Vol. of solution}} \times 1000$$

$$= \frac{0.0556}{83.3} \times 1000$$

$$= 0.667 \text{ M}$$

2. The vapour pressures of pure liquids A and B are 450 mm and 700 mm of Hg respectively at 350 K. Calculate the composition of liquid mixture if total vapour pressure is 600 mm of Hg. Also find the composition of the mixture in the vapour phase. (CBSE Sample Paper 2010)

Ans:

Let mole fraction of liquid A in solution = x_A

Mole fraction of liquid B in solution, $x_B = 1 - x_A$

$$P = P_A \cdot x_A + P_B \cdot x_B \text{ or } = P_A \cdot x_A + P_B (1 - x_A)$$

$$p = 600 \text{ mm Hg}$$

$$600 = 450 x_A + 700 (1 - x_A)$$

$$\text{Solving, } x_A = \frac{100}{250} = 0.4$$

$$\text{Mole fraction of liquid A} = 0.4$$

$$\text{Mole fraction of liquid B} = 1 - 0.4 = 0.6$$

Calculation of composition of vapour phase

$$p_A = P_A \cdot x_A = 450 \text{ mm} \times 0.4 = 180 \text{ mm}$$

$$p_B = P_B \cdot x_B = 700 \times 0.6 = 420 \text{ mm}$$

$$P_{\text{total}} = p_A + p_B = 180 + 420 = 600 \text{ mm}$$

$$y_A = \frac{p_A}{P_{\text{total}}} = \frac{180}{600} = 0.3$$

$$y_B = \frac{p_B}{P_{\text{total}}} = \frac{420}{600} = 0.7$$

3. Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene, 1 g of AB_2 lowers the freezing point by 2.3 K, whereas 1.0 g of AB_4 lowers it by 1.3 K. The molar depression constant for benzene is $5.1 \text{ K kg mol}^{-1}$. Calculate the atomic mass of A and B. (Delhi AI 2004)

Ans: Let us first calculate molar masses of AB_2 and AB_4 .

For AB_2 compound

$$M_2 = \frac{K_f \times W_2 \times 1000}{w_1 \times \Delta T_f}$$

$$\Delta T_f = 2.3 \text{ K}, W_2 = 1.0 \text{ g},$$

$$w_1 = 20.0 \text{ g}$$

$$K_f = 5.1 \text{ K kg mol}^{-1}$$

$$M_{AB_2} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 2.3}$$

$$\therefore M_{AB_2} = 110.87$$

For AB_4 compound

$$\Delta T_f = 1.3 \text{ K}, W_2 = 1.0 \text{ g},$$

$$w_1 = 20.0 \text{ g}$$

$$M_{AB_4} = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 1.3}$$

$$\therefore M_{AB_4} = 196.15$$

Let a be the atomic mass of A and b be the atomic mass of B, then

$$M_{AB_2} = a + 2b = 110.87 \dots (i)$$

$$M_{AB_4} = a + 4b = 196.15 \dots (ii)$$

Subtracting eqn. (ii) from eqn. (i)

$$-2b = -85.28$$

$$\therefore b = 42.64$$

Substituting the value of b in eqn. (i)

$$a + 2 \times 42.64 = 110.87$$

$$a = 110.87 - 85.28 = 25.59$$

Atomic mass of A = 25.59 g

Atomic mass of B = 42.64 g

4. 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated). (Given: Molar mass of benzoic acid = 122 g mol^{-1} , K_f for benzene = $4.9 \text{ K kg mol}^{-1}$) (CBSE Delhi 2015).

Ans: $\Delta T_f = i K_f \times m$

$$= \frac{i \times K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = 3.9 \text{ g}, W_1 = 49 \text{ g}, \Delta T_f = 1.62 \text{ K},$$

$$M_2 = 122 \text{ g mol}^{-1}$$

$$K_f = 4.9 \text{ K kg mol}^{-1}$$

$$1.62 = \frac{i \times 4.9 \times 3.9 \times 1000}{122 \times 49}$$

$$\text{or } i = \frac{1.62 \times 122 \times 49}{4.9 \times 3.9 \times 1000} = 0.506$$

Since i is less than 1, the solute is associated.

SECTION D
CASE STUDY BASED QUESTIONS (4 Marks Each)

PASSAGE 1

Read the passage given below and answer the following questions:

An ideal solution may be defined as the solution which obeys Raoult's law exactly over the entire range of the concentration. The solutions for which vapour pressure is either higher or lower than that predicted by Raoult's law are called non-ideal solutions. Non-ideal solutions can show either positive or negative deviations from Raoult's law depending on whether the A-B interactions in solution are stronger or weaker than A-A or B-B interactions.

(i) Which of the following solutions is/are ideal solution(s)?

- (I) Bromoethane and iodoethane
- (II) Acetone and chloroform
- (III) Benzene and acetone
- (IV) n-heptane and n-hexane

- (a) only I (b) I and II (c) II and III (d) I and IV

OR

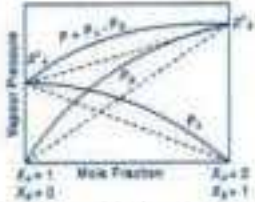
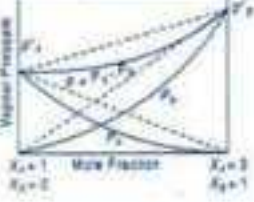
For which of the following solutions ΔH_{mix} and ΔV_{mix} is negative?

- (a) Acetone and aniline
- (b) Ethyl alcohol and cyclohexane
- (c) Acetone and CS₂
- (d) Benzene and toluene

(ii) Which of the following is not true for positive deviations?

- (a) The A-B interactions in solution are weaker than A-A and B-B interactions.
- (b) $P_A < P_A^0 x_A$ and $P_B < P_B^0 x_B$
- (c) Carbon tetrachloride and chloroform mixture is an example of positive deviations.
- (d) All of these.

(iii) For water and nitric acid mixture, which of the given graph is correct?

- (a)  (b)  (c) Both of these (d) None of these

(iv) Water HCl-mixture

- (I) shows positive deviations
- (II) forms minimum boiling azeotrope
- (III) shows negative deviations
- (IV) forms maximum boiling azeotrope

(a) I and II

(b) II and IV

(c) I and IV

(d) III and IV

PASSAGE 2

Read the passage given below and answer the following questions:

Few colligative properties are:

Relative lowering of vapour pressure: depends only on molar concentration of solute (mole fraction) and independent of its nature.

Depression of freezing point: it is proportional to molar concentration of solution.

Elevation of boiling point: it is proportional to molar concentration of solute.

Osmotic pressure: it is proportional to the molar concentration of solute.

A solution of glucose is prepared with 0.052g of glucose in 80.2g of water. ($K_f = 1.86 \text{ K kg mol}^{-1}$ and $K_b = 5.2 \text{ K kg mol}^{-1}$)

(i) Molality of the given solution is

(a) 0.0052 m

(b) 0.0036 m

(c) 0.0006 m

(d) 1.29 m

(ii) Boiling point for the solution will be

(a) 373.05 K

(b) 373.15 K

(c) 373.02 K

(d) 373.98 K

(iii) The depression in freezing point of solution will be

(a) 0.0187 K

(b) 0.035 K

(c) 0.082 K

(d) 0.067 K

(iv) Mole fraction of the solution in the given solution is

(a) 6.28×10^{-5}

(b) 1.23×10^{-4}

(c) 0.00625

(d) 0.00028

OR

If same amount of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) is taken instead of glucose then

(a) elevation of boiling point will be higher

(b) depression of freezing point will be higher

(c) depression in freezing point will be lower

(d) both (a) and (b)

ANSWERS

PASSAGE 1

(i) (d) OR (a)

(ii) (b)

(iii) (b)

(iv) (b)

PASSAGE 2

(i) (b)

(ii) (c)

(iii) (d)

(iv) (a) OR (c)

SECTION E
LONG ANSWER TYPE QUESTIONS (5 Marks Each)

1. (a) State Henry's law. Give its graphical representation.
(b) Mention some important applications and the Limitations of Henry's Law?
(c) The value of k_H for carbon dioxide at a temperature of 293 K is 1.6×10^3 atm.L.mol⁻¹. At what partial pressure would the gas have a solubility (in water) of 2×10^{-5} M?

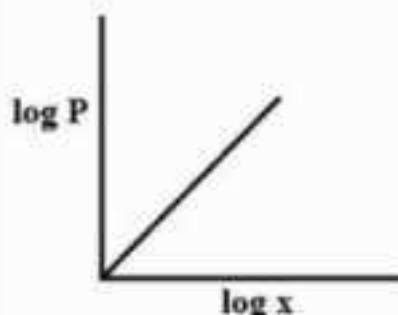
Ans: **Henry's Law** : Effect of pressure on solubility of gases in liquids at a particular temperature is given by Henry's law. "The mass of a gas dissolved in a given volume of the liquid at a constant temperature is directly proportional to the pressure of the gas present in equilibrium with the liquid."

Mathematically $m \propto p$
 $m = kp$

m = mass of the gas dissolved in a unit volume of the solvent

p = Pressure of the gas in equilibrium with the solvent

k = Constant called Henry's Law constant.



Graphical representation of Henry's Law:

Some important applications of Henry's law :

1. To increase the solubility of CO₂ in soft drinks and soda-water, the bottle is sealed under high pressure.
2. Deep sea divers use oxygen diluted with less soluble helium as breathing gas to minimise the painful effects accompanying the decompression.

The limitations of Henry's law are as follows:

1. The law is only valid when the molecules in the system are in equilibrium.
2. When the gases are under extremely high pressure, Henry's Law does not apply.
3. This law also does not apply when the solution and gas are involved in a chemical reaction with each other.

Substituting the given values $k_H = 1.6 \times 10^3$ atm.L.mol⁻¹ and $C = 2 \times 10^{-5}$ M into the Henry's law formula:

$$P = k_H \times C = (1.6 \times 10^3 \text{ atm.L.mol}^{-1}) \times (2 \times 10^{-5} \text{ mol.L}^{-1}) = 0.032 \text{ atm.}$$

2. (a) Define osmosis and osmotic pressure.
(b) What is an osmotic solution?
(c) How is osmosis different from diffusion?

Ans: **Osmosis** is a process by which the molecules of a solvent pass from a solution of low concentration to a solution of high concentration through a semipermeable membrane.

Osmotic pressure refers to the minimum pressure that must be applied to stop osmosis, i.e. the movement of particles from low concentration to high concentration through a semipermeable membrane.

$$\pi = iCRT$$

π = Osmotic Pressure

i = Vant Hoff factor

C = Molar concentration of the solute

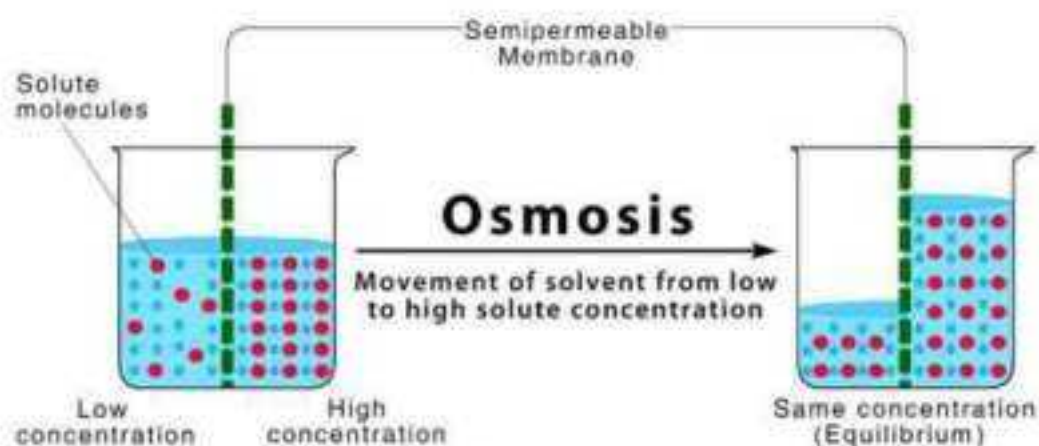
R = Gas Constant

T = Temperature.

A solution with the tendency and power to perform osmosis is known as an **osmotic solution**. We can classify osmotic solutions into three kinds.

1. Isotonic solution
2. Hypertonic Solution
3. Hypotonic Solution

Osmosis and diffusion are chemical phenomena occurring due to differences in concentration. The particles move from a higher concentration region to a low concentration region in diffusion. In contrast, in osmosis, the particles move from a lower concentration region to a high concentration region.



3. (a) What is the Van't Hoff Factor?
- (b) What will be its value for strong electrolytes?
- (c) How much molecular mass of NaCl is obtained experimentally using colligative properties?
- (d) Calculate the freezing point of a solution containing 0.5 g KCl (Molar mass = 74.5 g/mol) dissolved in 100 g water, assuming KCl to be 92% ionised. K_f of water = 1.86 K kg/mol.

Ans: **Van't Hoff factor (i)** is the ratio between the actual concentration of particles produced when the substance is dissolved and the concentration of a substance as calculated from its mass.

$$i = \frac{\text{observed molecular mass}}{\text{normal molecular mass}}$$

For strong electrolytes which dissociate completely, it is equal to the number of ions produced in the solution.

In case of association, two or more molecules associate to form a single molecule so the van't hoff factor will be less than 1.

In case of dissociation one molecule is forming two or more ions so the van't Hoff factor will be more than 1.



Van't Hoff Factor(i) = Calculated Molar Mass/Observed Molar Mass

So, Observed Molar Mass = Calculated Molar Mass/Van't Hoff Factor(i)

$$= (23 + 35.5)/2 = 29.25$$

Let us consider one mole of KCl whose degree of dissociation is α . The dissociation of KCl can be represented as:



$$1 - \alpha \quad \alpha \quad \alpha$$

Total number of moles after dissociation

$$= 1 - \alpha + \alpha + \alpha$$

$$= 1 + \alpha$$

$$\text{Hence } i = \frac{1 + \alpha}{1}$$

If the solute dissolves in the solvent giving n ions, then here $n = 2$.

$$i = 1 + (n - 1) \alpha$$

$$= 1 + (2 - 1) \alpha = 1 + \alpha$$

Now, $\Delta T_f = i K_f m$

$$= (1 + 0.92) \times 1.86 \times \frac{0.5 \times 1000}{74.5 \times 100}$$

$$\Delta T_f = 0.24$$

$$\Delta T_f = T_f^* - T_f = 0 - 0.24$$

$$T_f = -0.24^\circ\text{C}$$

CHAPTER-2-(ELECTROCHEMISTRY)

Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and inter-conversion of one form into another.

Oxidation is defined as a loss of electrons while **reduction** is defined as a gain of electrons.

In a **redox** reaction, both oxidation and reduction reaction take place simultaneously.

Direct redox reaction: In a direct redox reaction, both oxidation and reduction reactions take place in the same vessel. Chemical energy is converted to heat energy in a direct redox reaction.

Indirect redox reaction: In indirect redox reactions, oxidation and reduction take place in different vessels.

In an indirect redox reaction, chemical energy is converted into electrical energy. The device which converts chemical energy into electrical energy is known as an electrochemical cell.

An electrochemical cell consists of two metallic electrodes dipped in electrolytic solutions.

The cells are of two types:

- a) Electrolytic cells (b) Galvanic cells

In a Galvanic cell:

The half-cell in which oxidation takes place is known as **oxidation half-cell**

The half-cell in which reduction takes place is known as **reduction half-cell**.

Oxidation takes place at **anode** which is negatively charged and reduction takes place at **cathode** which is positively charged.

Transfer of electrons takes place from anode to cathode while electric current flows in the opposite direction.

An electrode is made by dipping the metal plate into the electrolytic solution of its soluble salt.

A **salt bridge** is a U-shaped tube containing an inert electrolyte in agar-agar and gelatin.

Salt bridge: A salt bridge maintains electrical neutrality and allows the flow of electric current by completing the electrical circuit.

Representation of an electrochemical cell:

Anode(s)/Anodic electrolyte(aq)//Cathodic electrolyte(aq)/Cathode(s)

Anode is written on the left while the cathode is written on the right.

Anode represents the oxidation half-cell and is written as:

Metal/Metal ion (Concentration).

Cathode represents the reduction half-cell and is written as:

Metal ion (Concentration)/Metal

Salt bridge is indicated by placing double vertical lines between the anode and the cathode.

Electrode potential E is the potential difference that develops between the electrode and its electrolyte. The separation of charges at the equilibrium state results in the potential difference between the metal and the solution of its ions. It is the measure of tendency of an electrode in the half cell to lose or gain electrons.

Standard electrode potential ($E^\ominus$): When the concentration of all the species involved in a half cell is unity, then the electrode potential is known as standard electrode potential.

Types of electrode potential: There are 2 types of electrode potentials namely,

Oxidation potential: It is the tendency of an electrode to lose electrons or get oxidized.

Reduction potential: It is the tendency of an electrode to gain electrons or get reduced. Oxidation potential is the reverse of reduction potential.

According to the present convention, standard reduction potential is called standard electrode potential.

The electrode having a higher reduction potential have higher tendency to gain electrons and so it acts as a cathode whereas the electrode having a lower reduction potential act as an anode.

The standard electrode potential of an electrode cannot be measured in isolation.

According to convention, the Standard Hydrogen Electrode is taken as a reference electrode and it is assigned a zero potential at all temperatures.

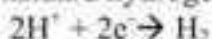
SHE: Standard hydrogen electrode consists of a platinum wire sealed in a glass tube and carrying a platinum foil at one end. The electrode is placed in a beaker containing an aqueous solution of an acid having 1 Molar concentration of hydrogen ions. Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at 298 K. The oxidation or reduction takes place at the Platinum foil.

The standard hydrogen electrode can act as both anode and cathode.

If the standard hydrogen electrode acts as an anode:



If the standard hydrogen electrode acts as a cathode:



The Standard Electrode Potential for any electrode dipped in an appropriate solution is defined with respect to standard electrode potential of hydrogen electrode taken as zero

In the electrochemical series, various elements are arranged as per their standard reduction potential values.

A substance with higher reduction potential value means that it has a higher tendency to get reduced. So, it acts as a **good oxidising agent**.

A substance with lower reduction potential value means that it has a higher tendency to get oxidised. So, it acts as a **good reducing agent**.

The electrode with **higher reduction potential acts as a cathode** while the electrode with a **lower reduction potential act as an anode**.

The potential difference between the 2 electrodes of a galvanic cell is called cell potential and is measured in Volts.

Standard cell potential is the difference between the standard reduction potential of cathode and anode.

The cell potential is the difference between the reduction potential of cathode and anode.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

Cell potential is called the electromotive force of the cell (EMF) when no current is drawn from the cell

Nernst equation: Nernst formulated a relationship between standard electrode potential E° and electrode potential E .

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}$$

$$E = E^{\circ} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \text{ (At 298K)}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Anode ion}]}{[\text{Cathode ion}]}$$



$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\text{At 298 K, } \frac{2.303RT}{nF} = \frac{0.0591}{n}$$

Then equation becomes

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Electrode potential increases with increase in the concentration of the electrolyte and decrease in temperature.

Nernst equation when applied to a cell, it helps in calculating the cell potential.

At equilibrium, cell potential E°_{cell} becomes zero.

Relationship between equilibrium constant K_c and standard cell potential E°_{cell} :

$$E^\circ_{\text{cell}} = \frac{0.059}{n} \log K_c (\text{At } 298\text{K})$$

Work done by an electrochemical cell is equal to the decrease in Gibb's energy

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

If E°_{cell} is positive, ΔG° would be negative and reaction would be spontaneous.

If E°_{cell} is negative, ΔG° would be positive and the reaction would be non-spontaneous.

CONDUCTIVITY AND MOLAR CONDUCTIVITY

The substances which allow the passage of electricity through them are known as conductors. Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.

The resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section A .

$$R = \rho l/a$$

where ρ is called specific resistance or resistivity. The SI unit of specific resistivity is ohm metre.

The inverse of resistance is known as conductance, C Unit of conductance is ohm^{-1} or mho. It is also expressed in Siemens denoted by S .

The inverse of resistivity is known as conductivity. It is represented by the symbol κ .

The SI unit of conductivity is Sm^{-1} . But it is also expressed in Scm^{-1}

$$\text{Conductivity} = \text{Conductance} \times \text{Cell constant}$$

Conductivity cell: For measuring the unknown resistance Wheatstone Bridge experiment can be done.

For measuring the resistance of an ionic solution, there are 2 problems:

1. Passing direct current changes the composition of the solution.

2. A solution cannot be connected to the bridge like a metallic wire or a solid conductor

This problem of measuring the resistance of an ionic solution can be resolved by using a **source of alternating current and the second problem is resolved by using a specially designed vessel called conductivity cell.**

Molar Conductivity: It is defined as the conducting power of all the ions produced by one gram mol of an electrolyte in a solution.

$$\lambda_m = \kappa C \quad \text{where } C = \text{concentration of solution in moles per litre (or Molarity)}$$

$$\lambda_m = \frac{\kappa \times 1000}{M} \quad (\text{if } \kappa = \text{Scm}^{-1})$$

$$\lambda_m = \frac{\kappa}{M \times 1000} \quad (\text{if } \kappa = \text{Sm}^{-1})$$

Where κ = Conductivity and M is the molarity Unit of Molar conductivity is $\text{Scm}^2 \text{mol}^{-1}$

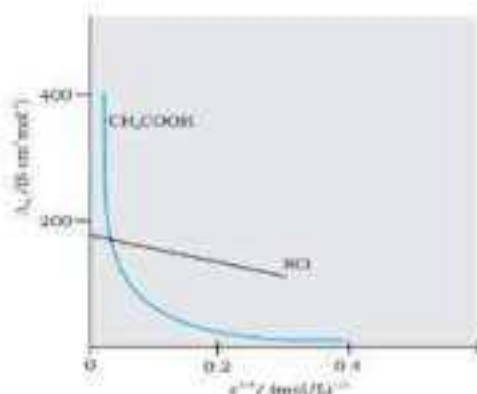
Conductivity of a solution decrease with dilution because Conductance of a solution is the conductance of ions present in a unit volume of the solution. On dilution the number of ions per unit volume decreases. So the conductivity decreases.

Molar conductivity increases with decrease in concentration. This is because the total volume, V , of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

Variation of molar conductivity with dilution (concentration is decreased)

A. **FOR STRONG ELECTROLYTES** molar conductivity increases slowly with dilution because in strong electrolytes the dissociation of the electrolyte into ions is almost complete however interionic forces are quite strong. **Upon dilution ionic attractions are reduced. This leads to increase in ionic mobility thus molar conductivity increases with dilution(or decrease in concentration)**

B. **FOR WEAK ELECTROLYTES** molar conductivity increases steeply with dilution because in weak electrolytes the dissociation of electrolyte into ions is comparatively less. **Dilution helps in dissociation of electrolyte.** As a result more ions are formed and corresponding value of conductivity also increases. This increase quite large.



Kohlrausch's Law of independent migration of ions: According to this law, molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.

If the limiting molar conductivity of the cations is denoted by λ_+^0 and that of the anions by λ_-^0 , then the limiting molar conductivity of electrolyte is:

Molar conductivity,

$$\Lambda_m^0 = v_+ \lambda_+^0 + v_- \lambda_-^0$$

Where v_+ and v_- are the number of cations and anions per formula of electrolyte

Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution. It is denoted by,

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^0}$$

Dissociation constant:

$$K_a = \frac{ca^2}{1-a}$$

Where K_a is acid dissociation constant, 'c' is concentration of electrolyte, α is degree of ionization.

Faraday constant: It is equal to charge on 1 mol of electrons. It is equal to 96487 C mol⁻¹ or approximately equal to 96500 C mol⁻¹.

Faraday's first law of electrolysis: The amount of substance deposited during electrolysis is directly proportional to quantity of electricity passed.

$$Q = nF$$

$$Q = ZIt$$

Faraday's second law of electrolysis: If same charge is passed through different electrolytes, the mass of substance deposited will be proportional to their equivalent weights.

PRODUCTS OF ELETROLYSIS

S. No	Electrolysis of	CATHODE	ANODE
1	Aqueous solution of AgNO ₃ with silver electrodes	Ag metal (Ag ⁺ are discharged compared to H ⁺ , E° is higher)	Ag ⁺ ions (Ag electrode being reactive dissolves to produce

			Ag ⁺ ions)
2	Aqueous solution of AgNO ₃ with platinum electrodes	Ag metal (Ag ⁺ are discharged compared to H ⁺ as its E ^o is higher)	O ₂ gas (OH ⁻ discharged compared to NO ₃ ⁻ as its E ^o is Lower)
3	Aqueous solution of CuCl ₂ with platinum electrodes	Copper metal	Cl ₂ gas
4	Aqueous solution of CuCl ₂ with Cu electrodes	Copper metal	Cu ²⁺ ions
5	Molten NaCl	Sodium metal	Cl ₂ gas
6	Aqueous sodium chloride solution	H ₂ gas	Cl ₂ gas
7	Dilute Sulphuric acid with Pt electrodes	H ₂ gas	O ₂ gas
8	Copper sulphate using inert electrodes (Pt)	Copper metal	O ₂ gas
9	Aqueous sodium bromide	H ₂ gas	Br ₂ gas

BATTERIES AND CORROSION

Primary Cell : In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused again. The most familiar example of this type is the dry cell

Dry Cell : The cell consists of a **zinc container that also acts as anode** and the **cathode is a carbon (graphite) rod** surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of ammonium chloride (NH₄Cl) and zinc chloride (ZnCl₂). The electrode reactions are complex, but they can be written approximately as follows :



It is **used** commonly in our **transistors and clocks**.

Ammonia produced in the reaction forms a complex with Zn²⁺ to give [Zn(NH₃)₄]²⁺.

Mercury Cell : It consists zinc-mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH & ZnO. Cathode: $\text{HgO} + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Hg(l)} + 2\text{OH}^-$

Anode: $\text{Zn(Hg)} + 2\text{OH}^- \rightarrow \text{ZnO(s)} + \text{H}_2\text{O} + 2\text{e}^-$

Overall reaction $\text{Zn(Hg)} + \text{HgO(s)} \rightarrow \text{ZnO} + \text{Hg(l)}$ Zn
Mercury cell suitable for low current devices like hearing aids, watches, etc

Secondary Batteries A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again. e.g. lead storage batteries, Nickel – cadmium storage batteries.

Lead Storage Battery : It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution of sulphuric acid is used as an electrolyte

Anode $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$

Cathode $\text{PbO}_{2(\text{s})} + \text{SO}_4^{2-} + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

Overall Reaction $\text{Pb(s)} + \text{PbO}_{2(\text{s})} + 2\text{H}_2\text{SO}_4(\text{aq}) \rightarrow 2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$

On charging the battery the reaction is reversed and $\text{PbSO}_4(\text{s})$ on anode and cathode is converted into Pb and PbO_2 , respectively.

$2\text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)} \rightarrow \text{Pb(s)} + \text{PbO}_{2(\text{s})} + 2\text{H}_2\text{SO}_4(\text{aq})$

Nickel cadmium cell is a secondary cell which has longer life than the lead storage cell but more expensive to manufacture. The overall reaction during discharge is: $\text{Cd(s)} + 2\text{Ni(OH)}_3(\text{s}) \rightarrow \text{CdO(s)} + 2\text{Ni(OH)}_2(\text{s}) + \text{H}_2\text{O(l)}$

Fuel Cell : Chemical energy of fossil fuels (coal, gas or oil) is first used for converting water into high pressure steam. This is then used to run turbine to produce electricity. The cells used to convert the energy of combustion of fuels like methane directly into electrical energy are called fuel cells e.g. Hydrogen with oxygen to form water. In the cell, hydrogen and oxygen are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalysts like finely divided platinum or palladium metal are incorporated into the electrodes for increasing the rate of electrode reactions.

Cathode : $\text{O}_2(\text{g}) + 2\text{H}_2\text{O(l)} + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

Anode : $2\text{H} + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$

Overall Reaction:

$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(l)}$

Fuel cells are pollution free.

Corrosion : The slow process of eating away of metals when exposed to the atmosphere is called corrosion. It is electro-chemical phenomenon in which metal is oxidized by loss of electrons to form metal oxide.

Mechanism of Corrosion : **Oxidⁿ** : $\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^{-}$

Redⁿ : $\text{O}_2(\text{g}) + 4\text{H}^{+}(\text{aq}) + 4e^{-} \rightarrow 2\text{H}_2\text{O}(\text{l})$

Atmospheric Oxidation

Rusting : Corrosion of iron is called rusting formula of rust $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

Prevention of Corrosion : (1). Barrier Protection, (2). Sacrificial Protection (Zn & Mg are used for the purpose), (3). Electrical Protection, (4). Using anti-rust solute

QUESTION BANK –CHAPTER- ELECTROCHEMISTRY

SECTION A

MULTIPLE CHOICE QUESTIONS (1 Marks Each)

1. Conductivity of aqueous solution of an electrolyte depends on:

- a) molecular mass of the electrolyte
- b) boiling point of solvent
- c) degree of ionization
- d) volume of the solvent

Answer: c

2. Which is not true for a standard hydrogen electrode ?

- a) The hydrogen ion concentration is 1 M
- b) Temperature is 25°C
- c) Pressure of hydrogen is 1 atmosphere
- d) It contains a metallic conductor which does not absorb hydrogen

Answer: d

3. In an electrochemical cell, anode and cathode are :

- a) positively and negatively charged ions
- b) positively and negatively charged electrodes
- c) negatively and positively charged electrodes
- d) negatively and negatively charged ions

Answer: c

4. More electronegative elements have :

- a) negative reduction potential
- b) tendency to lose electrons
- c) positive reduction potential
- d) positive oxidation potential

Answer: c

5. The strong oxidizing agent has :

- a) high value of reduction potential
- b) high value of oxidation potential
- c) low value of reduction potential
- d) high tendency to lose electrons

Answer: a

6. The passage of electricity in the Daniell cell when Zn and Cu electrodes are connected is from :

- a) Cu to Zn in the cell
- b) Cu to Zn outside the cell
- c) Zn to Cu outside the cell
- d) Zn to Cu in the cell

Answer: b

7. The highest electrical conductivity of the following aqueous solutions is of :

- a) 0.1 M acetic acid
- b) 0.1 M chloroacetic acid
- c) 0.1 M fluoroacetic acid
- d) 0.1 M difluoroacetic acid

Answer: d

8. On diluting the solution of an electrolyte

- a) both $\wedge$ and k increase
- b) both $\wedge$ and k decrease
- c) $\wedge$ increase and k decrease
- d) $\wedge$ decrease and k increase

Answer: c

9. If 96500 coulomb electricity is passed through CuSO_4 solution, it will liberate

- a) 63.5 g of Cu
- b) 31.75 g of Cu
- c) 127 g of Cu
- d) 100 g of Cu

Answer: b

10. The charge required for reducing 1 mole of MnO_4^- to Mn^{2+} is

- a) $1.93 \times 10^5 \text{ C}$
- b) $2.895 \times 10^5 \text{ C}$
- c) $4.28 \times 10^5 \text{ C}$

d) $4.825 \times 10^5 \text{ C}$

Answer: d

ASSERTION REASONING QUESTIONS (1 Marks Each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are correct and the R is the correct explanation of A.
- (b) Both A and R are correct but R does not explain the A.
- (c) Assertion (A) is correct but Reason (R) is incorrect.
- (d) Assertion (A) is incorrect but Reason (R) is correct.
- (e) Assertion (A) is incorrect but Reason (R) is incorrect.

1. Assertion: Emf and potential difference are same for cell.

Reason: Both give the difference in electrode potential under any condition

Answer: e

2. Assertion: In an electrochemical cell anode and cathode are respectively negative and positive electrodes.

Reason: At anode oxidation takes place and at cathode reduction takes place.

Answer: a

3. Assertion: An electrochemical cell can be set up only if the redox reaction is spontaneous.

Reason: A reaction is spontaneous if free energy change is negative.

Answer: a

4. Assertion: Identification of cathode and anode is done by the use of a thermometer.

Reason: Higher is the value of reduction potential, greater would be its reducing power.

Answer: d

5. Assertion: Zinc displaces copper from copper sulphate solution.

Reason: The E° of zinc is -0.76 V and that of copper is $+0.34 \text{ V}$.

Answer: a

6. Assertion: Galvanic cells containing hydrogen, methane, methanol etc. as fuels are called fuel cells.

Reason: They are designed to convert the energy of combustion of fuels directly into electrical energy.

Answer: a

7. Assertion: A negative value of standard reduction potential means that reduction takes place on this electrode with reference to standard hydrogen electrode.
Reason: The standard electrode potential of a half cell has a fixed value.
Answer: d
8. Assertion: For a cell reaction $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$; at the equilibrium, voltmeter gives zero reading.
Reason: At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.
Answer: a
9. Assertion: One coulomb of electric charge deposits weight equal to the electrochemical equivalent of the substance.
Reason: One Faraday deposits one mole of the substance.
Answer: b
10. Assertion: Electrical conductivity of copper increases with increase in temperature.
Reason: The electrical conductivity of metals is due to the motion of electrons.
Answer: d
11. Assertion: Equivalent conductance of all electrolytes decreases with the increases in concentration.
Reason: Lesser number of ions are available per gram equivalent at higher concentration.
Answer: a
12. Assertion: In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.
Reason: The molecular weights of silver and copper are different.
Answer: b
13. Assertion: Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.
Reason: The nature of the cathode can affect the order of discharge of ions.
Answer: a

SECTION B

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks Each)

1. Two half-reactions of an electrochemical cell are given below :



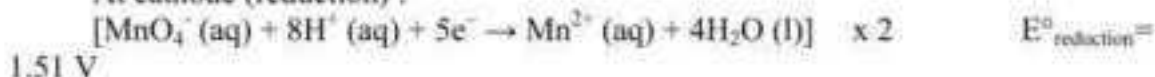
Construct the redox reaction equation from the two half-reactions and calculate the cell potential from the standard potentials and predict if the reaction is reactant or product favored.

Answer: The reactions can be represented at anode and at cathode in the following ways

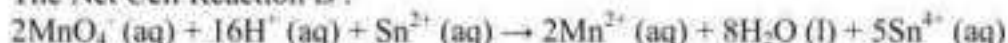
At anode (oxidation) :



At cathode (reduction) :



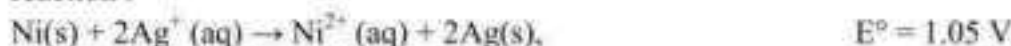
The Net Cell Reaction is :



$$\begin{aligned} \text{Now } E^\circ_{\text{cell}} &= E^\circ_{\text{reduction}} + E^\circ_{\text{oxidation}} \\ &= 1.51 + 0.15 = +1.66 \text{ V} \end{aligned}$$

$\therefore$ Positive value of E°_{cell} favors formation of product.

2. Determine the values of equilibrium constant (K_c) and ΔG° for the following reaction :



Answer: According to the formula

$$\Delta G^\circ = -nFE^\circ = -2 \times 96500 \times 1.05$$

$$\Delta G^\circ = -202650 \text{ J/mol} = -202.65 \text{ KJ/mol}$$

$$\Delta G^\circ \Rightarrow -202650 \text{ J/mol}$$

$$E^\circ = \frac{0.0591}{n} \log K_c$$

$$\log K_c = \frac{E^\circ \times n}{0.0591} = \frac{1.05 \times 2}{0.0591} = 35.533$$

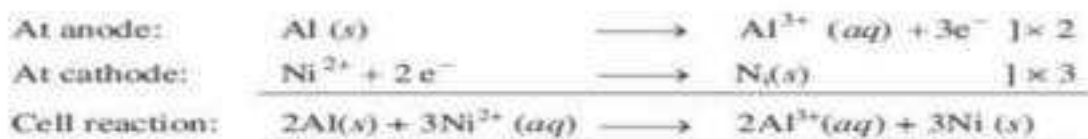
$$K_c = 3.412 \times 10^{35}$$

3. A voltaic cell is set up at 25°C with the following half cells :



Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential. $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25\text{V}$ and $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66\text{V}$

Answer:



Applying Nerst equation to the above cell reaction

Here, $E_{\text{cell}}^0 = E_{\text{Ni}^{2+}/\text{Ni}}^0 - E_{\text{Al}^{3+}/\text{Al}}^0 = -0.25 \text{ V} - (-1.66\text{V}) = 1.41\text{V}$, $n = 6$

$\therefore [\text{Al}^{3+}] = 1 \times 10^{-3} \text{M}$, $[\text{Ni}^{2+}] = 0.5 \text{ M}$

$$\begin{aligned}
 E_{\text{cell}} &= 1.41 \text{ V} - \frac{0.0591}{6} \log \frac{(10^{-3})^2}{(0.5)^3} = 1.41 \text{ V} - \frac{0.0591}{6} \log (8 \times 10^{-6}) \\
 &= 1.41 \text{ V} - \frac{0.0591}{6} (\log 2^3 + \log 10^{-6}) \\
 &= 1.41 \text{ V} - \frac{0.0591}{6} [3 \times \log 2 + (-67) \log 10] \\
 &= 1.41 \text{ V} - \frac{0.0591}{6} [3 \times 0.3010 - 6] \\
 &= 1.41 \text{ V} + 0.050 \text{ V} \\
 E_{\text{cell}} &= 1.46 \text{ V}
 \end{aligned}$$

4. Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (Λ_m) is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$. Given: $\lambda^\circ(\text{H}^+) = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ(\text{CH}_3\text{COO}^-) = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$

Answer: $\Lambda_m^\circ(\text{HAC}) = \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{AC}^-}$
 $= \lambda^\circ_{\text{CH}_3\text{COOH}} = \lambda^\circ_{\text{H}^+} + \lambda^\circ_{\text{CH}_3\text{COO}^-}$
 $= 349.6 \text{ S cm}^2 \text{ mol}^{-1} + 40.9 \text{ S cm}^2 \text{ mol}^{-1}$
 $= 390.5 \text{ S cm}^2 \text{ mol}^{-1}$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{39.05 \text{ cm}^2 \text{ mol}^{-1}}{390.05 \text{ cm}^2 \text{ mol}^{-1}} = 0.1$$

5. Calculate t _____ en a current of 2 amperes was passed through a solution of AgNO_3 for 15 minutes.

Answer: According to Faraday's First Law of Electrolysis:

$$W = \frac{ZIt}{n \times F} = \text{Mol. Wt} \times \frac{I \times t}{1 \times 96500} = \frac{108 \times 2 \times 15 \times 60}{1 \times 96500} = 2.0145 \text{ g}$$

SECTION C
SHORT ANSWER TYPE QUESTIONS (3 Marks Each)

1. Conductivity of 0.00241 M acetic acid is $7.896 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$. What is the dissociation constant? Answer: Molar conductivity, $\Lambda_m = 32.76 \text{ S cm}^2 \text{ mol}^{-1}$

Answer: Given, $K = 7.896 \times 10^{-5} \text{ S m}^{-1}$

$$c = 0.00241 \text{ mol L}^{-1}$$

Then, molar conductivity, $\Lambda_m = K/c$

$$= \frac{7.896 \times 10^{-5} \text{ S cm}^{-1}}{0.00241 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}}$$

$$= 32.76 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Again, } \Lambda_m^0 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\text{Now, } \alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{32.76 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}}$$

$$= 0.084$$

$$\text{Dissociation constant, } K_a = \frac{c\alpha^2}{(1-\alpha)}$$

$$= (0.00241 \text{ mol L}^{-1})(0.084)^2 / (1-0.084)$$

$$= 1.86 \times 10^{-5} \text{ mol L}^{-1}$$

2. Explain the following:

- How much charge is required for 1 mol of MnO_4^- to Mn^{2+}
- How much electricity is required in coulomb for the oxidation of 1 mol of H_2O to O_2
- How much electricity in terms of Faraday is required to produce 40g of Al from molten Al_2O_3

Answer: a) Charge for reduction of 1 mol of MnO_4^- to Mn^{2+}



Change in O.S. = 5

Charge required = $5 \times 96485 \text{ C}$

$$= 4.82 \times 10^5 \text{ C}$$

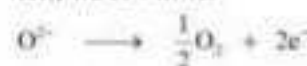
1 mole contains 6.022×10^{23} molecules

$$1 \text{ molecule} = \frac{1}{6.022 \times 10^{23}} \text{ mole}$$

$$\text{Charge required for 1mole} = 4.82 \times 10^5$$



Now, we can write:



Electricity required for the oxidation of 1 mol of H_2O to $\text{O}_2 = 2\text{ F}$

$$= 2 \times 96487\text{ C}$$

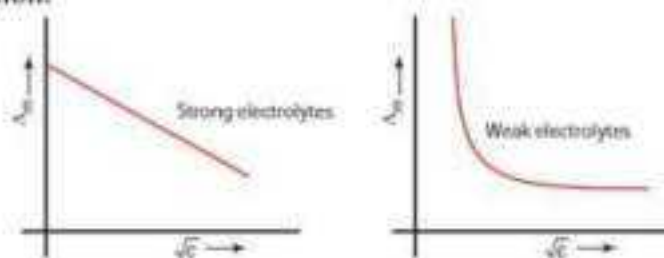
$$= 192974\text{ C}$$



27 gram of Al require electricity = 3F

$$\begin{aligned} 40\text{ gram of Al require electricity} &= \frac{3\text{F}}{27} \times 40 \\ &= 4.44\text{ F} \end{aligned}$$

3. Following two figures show the behavior of strong and weak electrolytes with change of concentration.



- What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte?
- What is meant by limiting molar conductivity?
- Which equation relates molar conductivity and concentration of a strong electrolyte?

Answer:

- When concentration of weak electrolyte becomes very low its degree of ionization rises sharply, there is a sharp increase in the ions in the solution hence the molar conductivity of a weak electrolyte rises steeply at low concentration.
- The molar conductivity of a solution at infinite dilution is known as limiting molar conductivity. In other words, When the concentration of the electrolyte approaches zero, the molar conductivity is known as limiting molar conductivity.
- Debye-Huckel-Onsager equation, $\Lambda = \Lambda^\circ - A\sqrt{c}$ in which Λ is the molar conductance at concentration c , Λ° is the molar conductance at infinite dilution and A is a constant.

SECTION D
CASE STUDY BASED QUESTIONS (4 Marks Each)

PARAGRAPH 1

Electrolysis is the process by which electric current is passed through a substance to effect a chemical change. The chemical change is one in which the substance loses or gains an electron (oxidation or reduction). The process is carried out in an electrolytic cell, an apparatus consisting of positive and negative electrodes held apart and dipped into a solution containing positively and negatively charged ions. The substance to be transformed may form the electrode, may constitute the solution, or may be dissolved in the solution. Electric current (i.e., electrons) enters through the negatively charged electrode (cathode); positively charged components of the solution travel to this electrode, combine with the electrons, and are transformed to neutral elements or molecules. The negatively charged components of the solution travel to the other electrode (anode), give up their electrons, and are transformed into neutral elements or molecules. If the substance to be transformed is the electrode, the reaction is generally one in which the electrode dissolves by giving up electrons.

Q.1. Faraday's law of electrolysis is related to

- | | |
|-----------------------------|--------------------------------------|
| (a) Atomic number of cation | (b) Speed of cation |
| (c) Speed of anion | (d) Equivalent weight of electrolyte |

Answer: d

Q.2. How long would it take to deposit 50 g of Al from an electrolytic cell containing Al_2O_3 using a current of 105 ampere

- | | |
|------------|------------|
| (a) 1.54 h | (b) 1.42 h |
| (c) 1.32 h | (d) 2.15 h |

Answer: b

Q.3. How much electricity in terms of Faraday is required to produce 100g of Ca from molten CaCl_2 ?

- | | |
|--------|--------|
| (a) 1F | (b) 2F |
| (c) 3F | (d) 5F |

Answer: d

Q.4. If a current of 1.5 ampere flows through a metallic wire for 3 hours, then how many electrons would flow through the wire?

- | | |
|-------------------------------------|-------------------------------------|
| (a) 2.25×10^{27} electrons | (b) 1.13×10^{23} electrons |
| (c) 1.01×10^{23} electrons | (d) 4.5×10^{23} electrons |

Answer: c

Q.5. How many coulombs of electricity is required to reduce 1 mole of $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium?

- | | |
|------------------------|------------------------|
| (a) 4×96500 C | (b) 6×96500 C |
| (c) 2×96500 C | (d) 1×96500 C |

Answer: b

PARAGRAPH 2

All chemical reaction involves interaction of atoms and molecules. A large number of atoms/ molecules are present in a few grams of any chemical compound varying with their atomic/molecular masses. To handle such large numbers conveniently, the mole concept was introduced. All electrochemical cell reactions are also based on mole concept. For example, a 4.0 molar aqueous solution of NaCl is prepared and 500 ml of this solution is electrolyzed. This leads to the evolution of chlorine gas at one of the electrodes. The amount of products formed can be calculated by using mole concept. (Molar weights of Na= 23 g/mol, Cl= 35.5 g/mol and Hg= 200 g/mol)

Q.1. The total number of moles of chlorine gas evolved is

- (a) 0.5 (b) 1.0 (c) 1.5 (d) 1.9

Answer: b

Q.2. If cathode is a Hg electrode, then the maximum weight of amalgam formed from this solution is

- (a) 300g (b) 446g (c) 396g (d) 256g

Answer: b

Q.3. The total charge (coulomb) required for complete electrolysis is

- (a) 186000 (b) 24125 (c) 48296 (d) 193000

Answer: d

Q.4. In the electrolytes, the number of moles of electrons involved are

- (a) 2 (b) 1 (c) 3 (d) 4

Answer: a

Q.5. In electrolysis of aqueous NaCl solution when Pt electrode is taken, then which gas is liberated at cathode?

- (a) H_2 (b) Cl_2 (c) O_2 (d) None of these

Answer: a

SECTION E
LONG ANSWER TYPE QUESTIONS (5 Marks Each)

1. Answer the following questions based on Electrochemistry:
- Why on dilution the Λ_m of CH_3COOH increases drastically while that of CH_3COONa increases gradually?
 - Solutions of two electrolytes 'A' and 'B' are diluted. The limiting molar conductivity of 'B' increases 1.5 times while that of 'A' increases 25 times. Which of the two is a strong electrolyte? Justify your answer.
 - The products of electrolysis of aqueous NaCl at the respective electrodes are: Cathode: H_2 and Anode: Cl_2 and not O_2 . Explain.
 - Why is alternating current used for measuring resistance of an electrolytic solution?
 - What is the necessity to use a salt bridge in a Galvanic cell?

Answer:

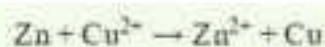
- In the case of CH_3COOH , which is a weak electrolyte, the number of ions increases on dilution due to an increase in degree of dissociation.
$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$$
 - 'B' is a strong electrolyte because a strong electrolyte is already dissociated into ions, but on dilution inter ionic forces are overcome, ions are free to move. So, there is a slight increase in molar conductivity on dilution.
 - On anode water should get oxidized to produce O_2 in preference to Cl^- but due to overvoltage/over potential Cl^- is oxidized to Cl_2 in preference to water.
 - Alternating current is used to prevent electrolysis so that concentration of ions in the solution remains constant.
 - To complete the inner circuit and to maintain the electrical neutrality of the electrolytic solutions of the half-cells we use a salt bridge in a Galvanic cell.
2. Answer the following questions based on electrochemical cells:
- What will be the sign of ΔG for an electrochemical cell and an electrolytic cell?
 - Standard electrode potentials of three metals X, Y and Z are 0.52V, -2.87 V and -0.44 V respectively. What will be the order of reducing power of these metals?
 - The standard electrode potential for a Daniel cell is 1.1V. Calculate the Standard Gibbs Energy for the reaction: $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
 - Calculate emf of the following cell at 25°C :
$$\text{Fe} | \text{Fe}^{2+} (0.001 \text{ M}) || \text{H}^+ (0.01 \text{ M}) | \text{H}_2(\text{g}) (1 \text{ bar}) | \text{Pt(s)}$$

 $E^\circ(\text{Fe}^{2+} | \text{Fe}) = -0.44 \text{ V}$ and $E^\circ(\text{H}^+ | \text{H}_2) = 0.00 \text{ V}$

Answer:

- ΔG for an electrochemical cell is -ve and ΔG for an electrolytic cell is +ve.
- $Y > Z > X$

c.



$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$= -2 \times 96487 \times 1.1$$

$$= -212271.4 \text{ Joules.}$$

d.

For the given cell representation, the cell reaction will be



The standard emf of the cell will be

$$E_{\text{cell}}^\circ = E_{\text{H}^+/\text{H}_2}^\circ - E_{\text{Fe}^{2+}/\text{Fe}}^\circ$$

$$E_{\text{cell}}^\circ = 0 - (-0.44) = 0.44\text{V}$$

The Nernst equation for the cell reaction at 25°C will be

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

$$= 0.44 - \frac{0.0591}{2} \log \frac{0.001}{(0.01)^2}$$

$$= 0.44 - \frac{0.0591}{2} \log 10$$

$$= 0.44 - \frac{0.0591}{2}$$

$$E_{\text{cell}} = 0.4105\text{V} \approx 0.41\text{V}$$

CHAPTER- 3 (CHEMICAL KINETICS)

Chemical Kinetics the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

Rate of a Chemical Reaction: the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. It can be expressed in terms of:

- (i) The rate of decrease in concentration of any one of the reactants.
- (ii) The rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, R

$\rightarrow P$

One mole of the reactant R produces one mole of the product P . If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then, $\Delta t = t_2 - t_1$, $\Delta[R] = [R]_2 - [R]_1$

$$\Delta[P] = [P]_2 - [P]_1$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \text{Decrease in concentration of } R / \text{Time taken} = -R/t$$

(1)

Rate of appearance of P

$$= \text{Increase in concentration of } P / \text{Time taken} = P/t \quad (2)$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.

Equations (1) and (2) given above represent the average rate of a reaction, r_{av} .

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur. (Ref. ncert Fig. 4.1)

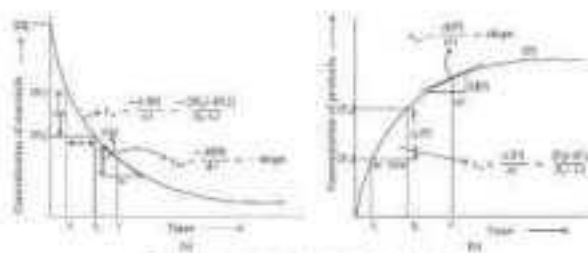


Fig. 4.1 Concentration and average rate of reaction

Units of rate of a reaction: The units will be $\text{mol L}^{-1}\text{s}^{-1}$.

In gaseous reactions, the units of the rate equation will be atm s^{-1} .

Factors affecting rate of reaction: The important factors are:

1. Concentration of the reacting species.
2. Temperature of the system.
3. Nature of reactant and products.
4. Presence of a catalyst.
5. Surface area.

6. Exposure to radiation.

Rate Law and Rate Constant:

Consider a general reaction: $aA + bB \rightarrow cC + dD$

Where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is $\text{Rate} = k[A]^x[B]^y$

Where exponents x and y may or may not be equal to the stoichiometric coefficients (a & b) of the reactants. Above equation can also be written as

$$\text{Rate} = k[A]^x[B]^y$$

$$-d[R]/dt = k[A]^x[B]^y$$

This form of equation is known as differential rate equation, where k is a proportionality constant called **rate constant**.

The equation, $\text{Rate} = k[A]^x[B]^y$ which relates the rate of a reaction to concentration of reactants is called rate law or rate expression.

Rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

For example:



$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

$$-d[R]/dt = k[\text{NO}]^2[\text{O}_2]$$

Order of reaction:

$$\text{Rate} = k[A]^x[B]^y$$

x and y indicate the rate is to the change in concentration of A and B.

Sum of these exponents, i.e., x + y in above equation gives the overall order of a reaction, whereas x and y represent the order with respect to the reactants A and B respectively.

Order of reaction is defined as the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction.

A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.

Units of rate constant:

Zero order rate of reaction:

$$\text{mol L}^{-1} \text{s}^{-1}$$

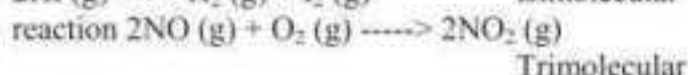
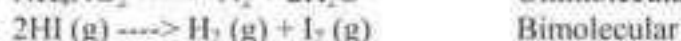
First order rate of reaction:

$$\text{s}^{-1}$$

$$\text{Second order rate of reaction: } \text{L mol}^{-1} \text{s}^{-1}$$

Molecularity of a reaction: The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

For examples:



reaction

Important points of distinction between order and molecularity

S.No.	Order	Molecularity
1	Order is the sum of powers of the concentration terms in the rate law expression.	Molecularity is the number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
2	Order of a reaction is determined experimentally.	Molecularity is a theoretical concept.
3	Order of a reaction can be zero.	Molecularity of a reaction cannot be zero.

Integrated rate equations:

Zero order reaction: Zero order reaction means that the rate of the reaction is proportional to zero power of the concentration of reactants.

Consider

the

reaction, R

$\rightarrow \text{P}$

Rate

$$-d[\text{R}] / dt = k$$

$$[\text{R}]^0$$

Rate

$$-d[\text{R}] / dt = k \times$$

$$1 \quad d[\text{R}] = -k \, dt$$

Integrating both sides

$$[\text{R}] = -k \, t + I \quad (1)$$

Where, I is the constant of integration

At $t = 0$ the concentration of reactant

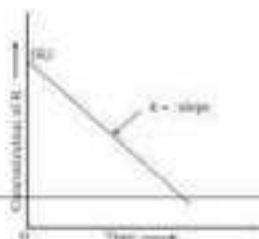
$[\text{R}] = [\text{R}]_0$ Where $[\text{R}]_0$ is the initial concentration of reactant.

$[\text{R}]_0 = -k \times 0 + I = I$, Substituting the value of I in the equation (1)

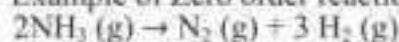
$$[\text{R}] = -k \, t + [\text{R}]_0$$

$$k = \{[\text{R}]_0 - [\text{R}]\} / t$$

Variation in the concentration Vs time plot for a zero-order reaction



Example of Zero order reaction is the decomposition of gaseous ammonia.



$$\text{Rate} = k[\text{NH}_3]^0 = k$$

the rate of the reaction is proportional to the

First Order Reactions: The rate of the reaction is proportional to the first power of the concentration of the reactant R.

For example:



$$\text{Rate} = -d[\text{R}]/dt = k[\text{R}]$$

$$d[\text{R}]/[\text{R}] = -k dt, \text{ integrating this}$$

$$\text{equation and we get } \ln [\text{R}] = -kt + I \quad (1)$$

$$\text{At } t = 0, \ln [\text{R}] = -k \times 0 + I,$$

$$I = \ln [\text{R}]_0. \text{ Substituting the value of } I \text{ in the}$$

$$\text{equation (1) } \ln [\text{R}] = -kt + \ln [\text{R}]_0$$

$$k = \{\ln [\text{R}]_0 - \ln [\text{R}]\} / t \text{ Remember that, } (\log a - \log b = \log(a/b))$$

$$k = (1/t) \ln \{[\text{R}]_0/[\text{R}]\}$$

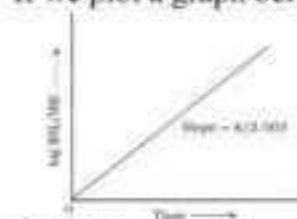
$$\ln \{[\text{R}]/[\text{R}]_0\} = -kt, \text{ taking antilog both sides.}$$

$$[\text{R}] = [\text{R}]_0 e^{-kt}$$

$$\text{We know that, } \ln a = 2.303 \log a$$

$$k = (2.303/t) \log \{[\text{R}]_0/[\text{R}]\}$$

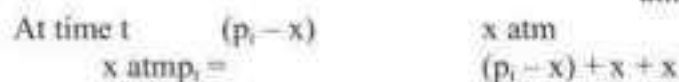
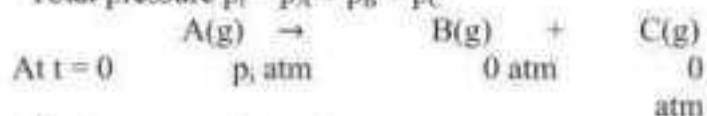
If we plot a graph between $\log [\text{R}]_0/[\text{R}]$ Vs t , the slope is $k/2.303$ for first order



reaction



$$\text{Total pressure } p_t = p_A + p_B + p_C$$



$$= p_i + x$$

$$x = (p_i - p_t)$$

$$p_A = p_i - x = p_i - (p_i - p_t)$$

$$= 2p_t - p_i$$

$$k = (2.303/t) \log [p_i/p_A]$$

$$k = (2.303/t) \log [p_i/(2p_t - p_i)]$$

Half-life of a reaction: The half-life of a reaction is the time in which the concentration of reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.

For a zero order reaction, rate constant is

$$k = \{[R]_0 - [R]\} / t$$

$$\text{At } t = t_{1/2}, [R] = [R]_0 / 2$$

$$k = \{[R]_0 - [R]_0 / 2\} / t_{1/2} = [R]_0 / 2 t_{1/2}$$

$$t_{1/2} = [R]_0 / 2 k$$

For a first order reaction, rate constant is

$$k = (2.303/t) \log \{[R]_0/[R]\}$$

$$\text{At } t = t_{1/2}, [R] = [R]_0 / 2$$

$$k = (2.303/t_{1/2}) \log \{[R]_0/[R]_0 / 2\}$$

[CHEMICAL KINETICS](#)

SECTION A

MULTIPLE CHOICE QUESTIONS (1 Marks Each)

1. Which of the following is the right temperature coefficient (n) expression?

- a) $n = \text{Rate constant at } T + 10^\circ / \text{Rate constant at } T^\circ$
- b) $n = \text{Rate constant at } T + 20^\circ / \text{Rate constant at } T^\circ$
- c) $n = \text{Rate constant at } T + 30^\circ / \text{Rate constant at } T^\circ$
- d) $n = \text{Rate constant at } T + 40^\circ / \text{Rate constant at } T^\circ$

Answer: a

2. A reaction in which reactants (R) are converted into products (P) follows second order kinetics. If concentration of R is increased by four times, what will be the increase in the rate of formation of P?

- (a) 9 times
- (b) 4 times
- (c) 16 times
- (d) 8 times

Answer: c

3. For a reaction $X \rightarrow Y$ the rate of reaction becomes twenty-seven times when the concentration of X is increased three times. What is the order of the reaction?

- (a) 2
- (b) 1
- (c) 3
- (d) 0

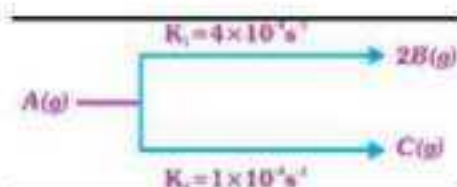
Answer: c

4. The rate constant (k') of one reaction is double of the rate constant (k'') of another reaction. Then the relationship between the corresponding activation energies of the two reactions (E_a' and E_a'') will be

- (a) $E_a' > E_a''$
- (b) $E_a' = E_a''$
- (c) $E_a' < E_a''$
- (d) $E_a' = 4E_a''$

Answer: c

5. A decomposes as
The rate of disappearance of B,
taking 4M concentration of A is equal to



- (a) $1.6 \times 10^{-3} \text{ Ms}^{-1}$
- (b) $6.4 \times 10^{-3} \text{ Ms}^{-1}$
- (c) $3.2 \times 10^{-3} \text{ Ms}^{-1}$
- (d) insufficient to calculate

Answer: b

6. The ΔH value of the reaction $\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$ is -44.12 kcal . If E_1 is the activation energy of the reactants and E_2 is the activation energy of the products, then for the above reaction

- (a) $E_1 > E_2$
- (b) $E_1 < E_2$
- (c) $E_1 = E_2$
- (d) ΔH is not related to E_1 and E_2

Answer: a

7. Which of the following statements regarding the molecularity of a reaction are correct?

- (a) It is the number of molecules of the reactants taking part in the elementary step
- (b) It is calculated from reaction mechanism
- (c) It depends on the rate determining step in the reaction
- (d) It's always a whole number

Answer: a and d

8. In a certain reaction, 10% of the reactant decomposes in 1 h, 20% in 2 h, 30% in 3 h, and so on. The dimensions of the rate constant is:

- (a) s^{-1}
- (b) $\text{mol L}^{-1} \text{ s}^{-1}$
- (c) $\text{mol}^{-1} \text{ L s}^{-1}$
- (d) mol s^{-1}

Answer: b

9. In a first-order reaction, the reacting substance has a half-life period of 10 min. What fraction of the substance will be left after an hour the reaction has occurred?

- (a) $1/6$ of initial concentration
- (b) $1/64$ of initial concentration
- (c) $1/12$ of initial concentration
- (d) $1/32$ of initial concentration

Answer: b

10. Time required for completion of ionic reactions in comparison to molecular reactions is

- (a) Maximum
- (b) Minimum
- (c) Equal
- (d) None

Answer: b

ASSERTION REASONING QUESTIONS (1 Marks Each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are correct and the R is the correct explanation of A.
- (b) Both A and R are correct but R does not explain the A.
- (c) Assertion (A) is correct but Reason (R) is incorrect.
- (d) Assertion (A) is incorrect but Reason (R) is correct.

1. **Assertion:** Order of the reaction can be zero or fractional.

Reason: We cannot determine order from a balanced chemical equation.

Answer: b

2. **Assertion:** Order and molecularity are same.

Reason: Order is determined experimentally and molecularity is the sum of the Stoichiometric coefficient of rate determining elementary step.

Answer: d

3. **Assertion:** The enthalpy of reaction remains constant in the presence of a catalyst.

Reason: A catalyst participating in the reaction, forms different activated complex and lowers down the activation energy but the difference in energy of reactant and product remains the same.

Answer: a

4. Assertion: All collisions of reactant molecules lead to product formation.

Reason: Only those collisions in which molecules have correct orientation and sufficient kinetic energy leads to compound formation.

Answer: d

5. Assertion: Rate constants determined from Arrhenius equation are fairly accurate for Simple as well as complex molecules.

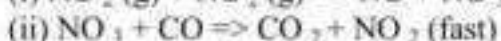
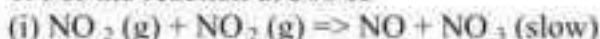
Reason: Reactant molecules undergo chemical change irrespective of their orientation during a collision.

Answer: c

SECTION B

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks Each)

1. For the reaction at 500 K



What is the rate law for the reaction? GIVE REASON.

Answer.

The slow step of the reaction mechanism is:



Hence, the rate of reaction is,

$$\text{Rate} = k [\text{NO}_2] [\text{NO}_2]$$

$$\text{Or rate} = k [\text{NO}_2]^2$$

Slowest step of the mechanism decides the rate of the reaction.

2. A first order reaction takes 69.3 minutes for 50% completion. How much time will be needed for 80% completion?

Answer:

$$t_{1/2} = 69.3 \text{ minutes}$$

$$k = 0.693/69.3 = 10^{-2} \text{ min}^{-1}$$

$$\text{Now } t = (2.303/k) \log a/(a-x)$$

$$= (2.303/10^{-2}) \times \log 100/(100-80)$$

$$= (2.303/10^{-2}) \times \log 5$$

$$= (2.303/10^{-2}) \times 0.6990 = 160.9 \text{ minutes.}$$

3. Define each of the following:

(i) Specific rate of a reaction

(ii) Activation energy of a reaction

Answer:

(i) Specific rate of a reaction: When the molar concentration of each of the reactants is

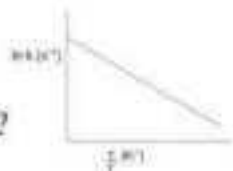
equal to 1, the rate of reaction is called the specific rate of reaction.

(ii) Activation energy of a reaction: The activation energy is the minimum extra amount of energy absorbed by the reactant molecules to acquire the threshold value. The addition of a catalyst reduces the reaction's activation energy.

4. Arrhenius equation can be represented graphically as follows:

(i) What will be the intercept and slope for the graph?

(ii) In the Arrhenius Equation, what does the factor $e^{-E_a/RT}$ correspond to?



Answer:

Exponential Form of Arrhenius Equation is $k = Ae^{-E_a/RT}$

k = Rate constant; A = Frequency factor

E_a = Activation energy; R = Gas constant; T = temperature

(i) Intercept is $\ln A$ and Slope is $-E_a/R$

(ii) $e^{-E_a/RT}$ corresponds to the fraction of molecules having kinetic energy greater than E_a .

SECTION C

SHORT ANSWER TYPE QUESTIONS (3 Marks Each)

1. What is activation energy? The rate constant of a first order reaction becomes 5 times when the temperature is raised from 350 K to 400K. Calculate the activation energy of the reaction.

Answer:

Activation energy is the minimum energy which must be supplied to the reactant molecule so that the collision between the reactant molecules is effective and can produce the chemical change.

From Arrhenius equation

$$\log k_2/k_1 = E_a / 2.303 R [1/T_1 - 1/T_2]$$

$$\log 5 = E_a / (2.303 \times 8.314) \times [1/350 - 1/400]$$

$$\log 5 = E_a / (2.303 \times 8.314) [50 / (350 \times 400)]$$

$$E_a = (\log 5 \times 2.303 \times 8.314 \times 350 \times 400) / 50$$

$$= 37480 \text{ J/mol}$$

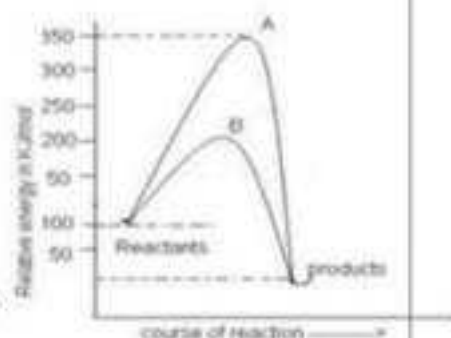
$$= 37.480 \text{ KJ/mol}$$

2. From the fig.

(a) Calculate activation energy for forward reaction.

(b) Identify the curve for catalyzed reaction.

(c) What is the activation energy in the presence of a catalyst?



Answer:

(a) From the figure-

Energy of reactants = 100 KJ/Mol and Energy of products = 50 KJ/Mol

Change in energy = 50 - 100 = -100 KJ/Mol and Threshold energy = 350 KJ/Mol

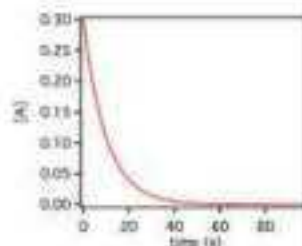
Activation energy = 350 - 100 = 250 KJ/Mol.

(b) The curve B is for catalyzed reaction.

(c) In the presence of catalysts,
 Threshold energy = 200 KJ/Mol
 Activation energy = 200-100 = 100 KJ/Mol.

3. Study the graph given and answer the following questions:

- Identify the order of the reaction from the graph.
- What will be the rate constant if the half-life period is 6 min.
- Give an example for zero order reaction and first order reaction.



Answer:

- First order reaction
- Half Life Period and Rate Constant for a first order reaction is related to each other as

$$t_{1/2} = 0.693/k$$

$$k = 0.693/6 = 0.115 \text{ min}^{-1}$$

- Zero order reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$
 First order reaction $2\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2} \text{O}_2$

SECTION D

CASE STUDY BASED QUESTIONS (4 Marks Each)

PASSAGE 1

The rate of a chemical reaction is expressed either in terms of decrease in the concentration of reactant per unit time or increase in the concentration of products per unit time. Rate of a reaction depends upon the nature of the reactants, surface area of the reactants, concentration of the reactants, temperature and presence of a catalyst. Rate of reaction is directly related to concentration of reactants. Rate Law states that the rate of a reaction depends upon the concentration terms on which the rate of a reaction actually depends as observed experimentally. The sum of powers of the concentration of reactants in the rate law expression is called order of the reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about the chemical reaction is called molecularity of the reaction.

Consider the decomposition of ammonia: $2\text{NH}_3(\text{g}) \longrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

- Express rate of the above-mentioned reaction in terms of reactants and products.
- Write the rate law expression for the above reaction if it follows zero order kinetics. What will be its molecularity?
- What is the difference between rate of reaction (dx/dt) and specific reaction rate (k)?
- Why are the reactions usually fast with finely divided reactants?
- How does a catalyst affect the rate of a chemical reaction?
- If the rate constant for the above reaction is $2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$ at what rate ammonia will disappear?

PASSAGE 2

Observe the table given showing volume of CO_2 obtained by reaction of CaCO_3 and dilute HCl after every minute. Answer the questions that follow:

Time/min	Volume of CO_2/cm^3
0	0
1	24 cm^3
2	34 cm^3
3	38 cm^3
4	40 cm^3
5	40 cm^3
6	40 cm^3

1. What happens to the rate of reaction with time for the above reaction?
2. How the rate of reaction is affected when powdered CaCO_3 is used instead of marble chips?
3. What happens to the rate of reaction when conc. HCl is used instead of dil. HCl ?
4. Express the rate of reaction in terms of reactants and products for the above reaction.
5. Why does the rate of reaction almost doubles for every 10°C rise in temperature?
6. Write two important factors necessary for fruitful collisions.

PASSAGE 1

1. For reaction, $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

$$\text{Rate} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = -\frac{d[\text{N}_2]}{dt}$$

2. $\text{Rate} = k [\text{NH}_3]^0 = k$ and Molecularity = 2

3. Rate of a reaction is defined as the change in the concentration of a reactant or product in unit time whereas Rate Constant is equal to rate of reaction when the concentration of each reactant is taken as unity in a reaction.

The rate of reaction depends upon the concentration of reactants, catalyst, and temperature whereas Rate Constant is independent of the concentration of the reactant and depends on temperature.

4. A finely divided solid has more surface area available for reaction than does one large piece of the same substance. Greater surface area faster will be the reaction.

5. Catalysts typically speed up a reaction by reducing the activation energy or changing the reaction mechanism.

6. $\frac{dx}{dt} = \text{rate} = k [\text{NH}_3]^0 = k = 2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$

Rate of Disappearance of Ammonia = 2 x rate of the reaction = $5 \times 10^{-3} \text{ mol L}^{-1} \text{ sec}^{-1}$

PASSAGE 2

1. The rate of the reaction first decreases and then becomes constant with time.
2. The rate of reaction increases as the surface area of the reactant increases.
3. The rate of reaction increases with increasing the concentration of the reactant.
4. Express the rate of reaction in terms of reactants and products for the above reaction.
5. $\text{Rate} = -\frac{d[\text{CaCO}_3]}{dt} = -\frac{1}{2}\frac{d[\text{HCl}]}{dt} = \frac{d[\text{CaCl}_2]}{dt} = \frac{d[\text{CO}_2]}{dt} = \frac{d[\text{H}_2\text{O}]}{dt}$
6. Two Factors responsible for Effective Collisions are proper orientation of reactant molecules and activation energy.

SECTION E

LONG ANSWER TYPE QUESTIONS (5 Marks Each)

1. Temperature is an important factor affecting the rate of reaction.
 - (i) What is the effect of temperature on the rate constant of a reaction?
 - (ii) How can this effect of temperature on rate constant be represented quantitatively?
 - (iii) The activation energy for the reaction $2\text{HI(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$ is 209.5 KJ/mol at 518 K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer:

- (i) With increase in temperature, the rate of the reaction and the rate constant increases. As a generalization, the rate of the reaction (and the rate constant) becomes almost double for every 10° rise in temperature. This is also called temperature coefficient. It is the ratio of rate constants of the reaction at two temperatures differing by 10° .

Thus, Temperature coefficient = $\frac{\text{Rate constant at } T^\circ\text{C}}{\text{Rate constant at } (T+10^\circ\text{C})}$

- (ii) The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation $k = Ae^{-E_a/RT}$

- (iii) We have

Activation energy = 209.5 KJ/mol

Temperature = 581 K

R = 8.314 J/mol/K

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as

$$x = e^{-E_a/RT}$$

taking log both sides we get

$$\log x = -E_a/(2.303RT)$$

$$\log x = -209500 / (2.303 \times 8.314 \times 581)$$

$$\log x = -18.832$$

$$x = \text{antilog}(-18.832) = \text{antilog}(-18.832 + 19 - 19) = \text{antilog}(0.1678 - 19)$$

$$x = 1.471 \times 10^{-19}$$

2. Concentration of reactants play an important role in deciding the rate of reaction.

(i) Give an expression for the dependence of rate of reaction on conc. of reactants.

(ii) How is the order of a reaction different from molecularity?

(iii) The following results have been obtained during the kinetic studies of the reaction:

$2A + B \rightarrow C + D$. Determine the rate law and the rate constant for the reaction.

Experiment	[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate of formation of D/mol L ⁻¹ min ⁻¹
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

Answer:

(i) The equation that describes mathematically the dependence of the rate of reaction on the concentration terms of reactants is the Rate equation. $\text{Rate} = k[A]^x[B]^y$

(ii) Order of a reaction is the sum of the coefficients of the reacting species involved in the rate equation. Molecularity is the number of reacting species involved in simultaneous collisions in an elementary or simplest reaction.

(iii) Let assume the rate of reaction wrt A is x and wrt B is y. So, the rate of reaction is expressed as-

$$\text{Rate} = k[A]^x[B]^y$$

$$r_1 = 6 \times 10^{-3} = k[0.1]^x[0.1]^y \quad -1$$

$$r_2 = 7.2 \times 10^{-2} = k[0.3]^x[0.2]^y \quad -2$$

$$r_3 = 2.88 \times 10^{-2} = k[0.3]^x[0.4]^y \quad -3$$

$$r_4 = 2.4 \times 10^{-2} = k[0.4]^x[0.1]^y \quad -4$$

$$\text{Divide Eqn 4 by 1} \quad 4 = (0.4/0.1)^x$$

$$\text{On Calculation we get} \quad x = 1$$

$$\text{Divide Eqn 3 by 2} \quad 4 = (0.4/0.2)^y$$

$$\text{On Calculation we get} \quad y = 1$$

$$\text{Rate} = k[A]^x[B]^y$$

Substituting values from Eqn 1

$$r_1 = 6 \times 10^{-3} = k[0.1]^x[0.1]^y$$

$$r_1 = 6 \times 10^{-3} = k[0.1]^1[0.1]^1$$

$$k = 6 \times 10^{-3} / ([0.1]^1[0.1]^1) = 6 \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$$

$$k = (2.303/t_{1/2}) \log 2$$

$$k = (2.303/t_{1/2}) 0.3010$$

$$t_{1/2} = 0.693/k$$

For zero order reaction $t_{1/2} \propto [R]_0$.

For first order reaction $t_{1/2}$ is independent of $[R]$

Concept of Activation energy: The excess energy (over and above the average energy of the reactants) which must be supplied to the reactants to undergo chemical reactions is called activation energy.

It is equal to the difference between the threshold energy needed for the reaction and the average kinetic energy of all the reacting molecules. That is,

Activation energy

= Threshold energy - Average kinetic energy of the reacting molecules

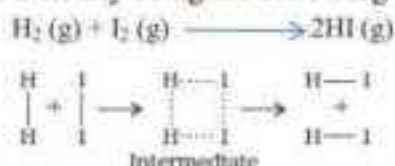
$E_a = E_a(\text{threshold}) - E_a$

(reactants) Low Activation

energy: Fast reactions High

Activation energy: Slow reactions

It can be understood clearly using the following simple reaction:



According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate. The energy

$$k = A e^{-E_a/RT}$$

required to form this intermediate, called **activated complex**, is known as **activation energy (E_a)**.

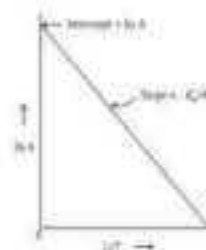
Taking logarithm both side

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The plot of $\ln k$ Vs $1/T$ gives a straight line.

Slope = $-E_a/R$ and intercept = $\ln A$.

So we can calculate E_a and A using these values.



$$\ln k = -\frac{E_a}{RT} + \ln A$$

Converting to common logarithm

$$\ln X = 2.303 \log X$$

$$= 2.303 \log A - E_a/RT$$

$$\log k = \log A - E_a/2.303 RT$$

Let k_1 and k_2 are the rate constants for the reaction at two different temperatures T_1 and T_2 respectively.

$$\log k_1 = \log A - E_a/2.303 RT_1$$

... (i)

$$\log k_2 = \log A - E_a/2.303 RT_2$$

... (ii) Subtracting eq. (i)

from (ii)

$$\log k_2 - \log k_1 = E_a/2.303 R [1/T_1 - 1/T_2]$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

CHAPTER-4- The d - and f- BLOCK ELEMENTS

TRANSITION ELEMENTS:

Transition elements include elements from group 3 to 12. These elements have properties which are intermediate between those of s and p block elements.

A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states. These are placed in the middle part (between s and p) of the periodic table.

There are four series of elements.

I- 3d series -From Sc to Zn

II- 4d series – From Y to Cd

III- 5d series- From La to Hg

IV- 6d series-From Ac to Cn

CONFIGURATIONS OF d BLOCK ELEMENTS:

General electronic configuration of d block elements is $[NG] (n-1) d^{1-10} ns^{1-2}$. The inner d orbital is being filled with increase in atomic number.

Special configuration of **Cr and Cu is due to the extra stability of half- filled and fully filled orbitals (d^5 and d^{10})**. Also the energy difference between the 3d and 4s is not very large.

GENERAL CHARACTERISTICS:

Almost all transition elements show typical metallic properties, high tensile strength, ductility, malleability, high thermal and electrical conductivity and metallic lustre.

Zn, Cd and Hg is considered as **non-transition elements** as these elements have completely filled d orbitals (d^{10} configuration)

METALLIC CHARACTER:

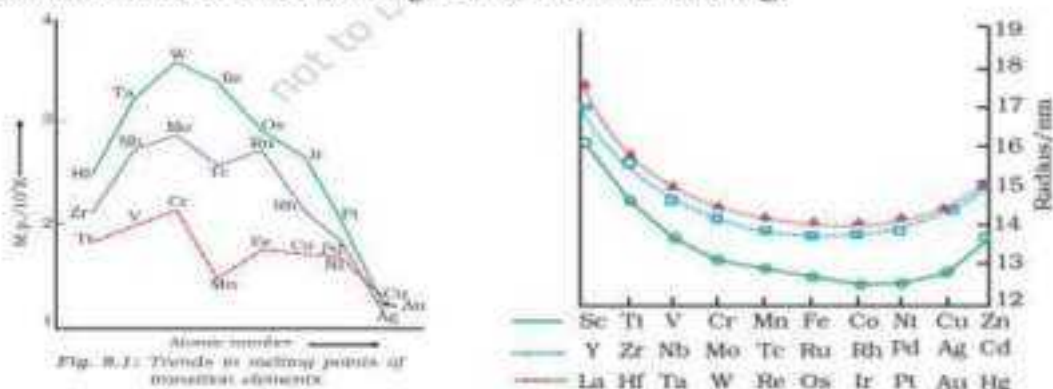
Except Hg which is a liquid, all transition elements have typical metallic structure. Metallic character is **due to their relatively low ionization enthalpy and one or two electrons in the outermost orbit**. These elements are electropositive.

MELTING POINT AND BOILING POINTS:

Melting and boiling points of transition elements **depends on the number of unpaired electrons**. Greater the number of unpaired electrons stronger is the metallic bonding and hence high melting points.

In a particular series; melting point increases up to the middle and then decreases with decrease in number of unpaired electrons. So **Zn, Cd and Hg have low melting and boiling points**.

There is a **dip** in the melting points of **Mn and Tc** in the figure. **Mn has stable configuration and electrons are more tightly held by the Mn atoms**. This reduces the delocalization of electrons resulting weaker metallic bonding.



ATOMIC SIZE AND IONIC SIZE:

Size of transition elements are intermediate between s and p block elements.

The atomic size first decreases with increase in atomic number due to increase in nuclear charge but low shielding effect.

Atomic size become almost **steady towards the middle of the series because of filling of d orbitals which screens outer shell of electrons**. So increase in nuclear charge is partly cancelled by increase in screening effect.

Towards the end of the series, there is slight increase in size due to the increased repulsion between the electrons in the same orbitals.

Atomic size of second transition series are found to be larger than first series.

Ionic size of lanthanoids also follow the same order as that of atomic size. Ionic radii are different in different oxidation states **due to increase in effective nuclear charge**. So M^{3+} cations are smaller than M^{2+} .

Atomic sizes of third transition series are found to be almost same as that of second series. This is explained on the basis of **lanthanoid contraction**.

DENSITY:

Density of transition elements increase along the series due to decrease in atomic size and increase in nuclear charge. (Atomic volume decreases and atomic mass increases).

IONISATION and ATOMISATION ENTHALPIES:

The first ionization enthalpy of d – block elements are higher than s and p block elements. This is due to **increase in nuclear charge and poor shielding effect of 'd' electrons**.

Increase in ionization enthalpy is not regular. This is because removal of one electron alters the relative energies of 4s and 3d orbitals, so there is reorganization of energy accompanying ionization.

First ionization enthalpy of Zn is very high because the electron has to be removed from 4s orbital of stable configuration ($3d^{10} 4s^2$).

Second ionization of Zn is found to be lower. This is because after the removal of one electron from Zn^+ it attains stable $3d^{10}$ configuration.

Cr and Cu have exceptionally high IE 2 (second IE) than the neighbouring elements due to the stability of half- filled and fully filled configuration respectively. ($3d^5$ and $3d^{10}$)

Third IE of Zn^{2+} and Mn^{2+} is very high due to stability of $3d^{10}$ and $3d^5$ configuration. Third IE of Fe (Fe^{+2} to Fe^{+3}) is low because loss of 3^{rd} electron gives stable $3d^5$ configuration.

Very high values of third IE of Cu, Zn, Ni indicate that it is difficult to show +3 oxidation state for these elements.

The first IE of third transition series is very high. This is due to the poor shielding effect of 4f electrons. So outer electrons are attracted by the nucleus with a greater force.

Ni^{+2} compounds are well-known but Pt^{+2} compounds are rare. This is because the first two ionization enthalpies of Ni are lower than Platinum. ($\text{IE}_1 + \text{IE}_2$)

Pt^{+4} compounds are well-known but Ni^{+4} compounds are rare. This is because the first four IEs ($\text{IE}_1 + \text{IE}_2$, $\text{IE}_3 + \text{IE}_4$) of Pt are lower than that of Ni. That is, $\text{K}_2 [\text{PtCl}_6]$ is available but $\text{K}_2 [\text{NiCl}_6]$ is not known.

Transition elements have high **enthalpy of atomization** due to the overlap of unpaired electrons between the atoms resulting strong metallic bonding.

Zn, Cd and Hg have low enthalpies of atomization as there is no unpaired electrons.

OXIDATION STATES:

Transition elements exhibit variable oxidation state, **due to the participation of electrons in the ns and (n-1) level which are of almost same energy**. Also incomplete d orbitals. Both ns and (n-1) d orbitals involve in bonding.

Out of fluorides and oxides, stability of higher oxidation states of oxides are more than fluorides due to **multiple bond formation** of oxygen with metals (oxo anions).

So highest fluorides of Mn is MnF_4 but oxide is Mn_2O_7 .

Maximum number of oxidation states are shown by elements which are present almost middle of the series.

Transitions elements show oxidation states from +1 to +7. +8 is shown by Os.

Except Sc all other elements from the first transition series show +2 oxidation state.

Sc is the element which shows only one oxidation state i.e. +3 and is the stable oxidation state.

The lowest oxidation states correspond to the number of ns electrons. Eg; Cu. It shows +1 oxidation state. For others it is +2.

The highest oxidation state is equal to the sum of ns and (n-1) electrons.

In the first series highest oxidation state and maximum number of oxidation states are shown by Mn. The highest oxidation state is +7 and others +2, +3, +4, +5, +6.

Ti^{+4} is more stable than Ti^{+2} and Ti^{+3} because Ti^{+4} is $3d^0 4s^0$. For Zn, Zn^{+2} is the most stable oxidation state. Zn^{+2} is $3d^{10} 4s^0$.

Some elements show zero oxidation state in compounds eg Ni, Fe; $[\text{Ni}(\text{CO})_4]$, $[\text{Fe}(\text{CO})_5]$

For transition elements heavier elements show more stable higher oxidation state. Eg: Mo^{+6} , W^{+6} etc. are more stable than Cr^{+6} . So, Cr^{+6} **act as oxidizing agent**. Eg: $\text{K}_2\text{Cr}_2\text{O}_7$ is a powerful oxidizing agent. But WO_3 and MoO_3 are not oxidizing agents.

+2 and +3 oxidation states are shown generally by ionic compounds and in higher oxidation states the compounds are covalent in nature.

STANDARD ELECTRODE POTENTIALS AND TRENDS IN OXIDATION STATES:

The stability of a particular oxidation state in aqueous solution depends on ionization enthalpy (IE), sublimation enthalpy (ΔH_{sub}) and enthalpy of hydration (ΔH_{hyd})

$$\Delta H = \Delta H_{\text{sub}} + \text{IE} + \Delta_{\text{hyd}}H$$

Smaller the value of ΔH for a particular oxidation state, greater will be the stability of that oxidation state.

E^0 values of first row transition elements are irregular (M^{+2}/M). This is explained with the irregular variation in IE ($\text{IE}_1 + \text{IE}_2$) and sublimation enthalpies which are very less for Mn and V

TRENDS IN OXIDATION STATE (M^{+2}/M)

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
I^{st} ionisation enthalpy	631	656	650	652	717	762	758	736	745	905 kJ mol^{-1}
II^{nd} ionisation enthalpy	1245	1320	1376	1635	1513	1564	1648	1757	1962	1736
III^{rd} ionisation enthalpy	2451	2721	2874	2995	3258	2964	3238	3401	3561	3839
$E^0_{\text{M}^{+2}/\text{M}}$ in volts	-	-1.63V	-1.18V	-0.91V	-1.18V	-0.44V	-0.28V	-0.25V	+0.34V	-0.76V
$E^0_{\text{M}^{+3}/\text{M}^{+2}}$ in volts	-	-0.37V	-0.26V	-0.41V	+1.57V	+0.77V	+1.97V	-	-	-

The general trend towards **less negative E^0 values across the series is related to increase in sum of first and second ionization enthalpies ($\text{IE}_1 + \text{IE}_2$).**

E^0 of Mn and Ni, Zn are more filled negative than expected from the

general trend. For Mn and Zn it is related to the half-filled (d^5) and fully (d^{10}) state respectively. The exceptional behavior of Ni towards E^0 is due to its high negative ΔH_{hyd} .

Zn has low ΔH_a (atomization) and high ΔH_{hyd} . But it has low reduction potential due high IE ($IE_1 + IE_2$).

Cu has positive value of E^0 (+0.34V) shows that this is the least reactive metal among the elements of first series. This unique behavior ($+E^0$) is responsible for the inability of Cu to release hydrogen from acids. **The very high IE is not balanced by its high hydration enthalpy.**

E^0 of Mn and Ni, Zn are more negative than expected from the general trend. For Mn and Zn it is related to the half-filled (d^5) and fully filled (d^{10}) state respectively. **The exceptional behavior of Ni towards E^0 is due to its high negative ΔH_{hyd}**

TRENDS IN OXIDATION STATE (M^{+3}/M^{+2}).

Except Cu and Zn all elements show +3 oxidation state.

Very low value for $E^0 Sc^{3+}/Sc^{2+}$, shows that Sc^{3+} is highly stable.

Highest E^0 value of Zn is due to its stable configuration in Zn^{+2} state. It is difficult to remove electron from d^{10} configuration to change into +3 state.

High value of $E^0 Mn^{3+}/Mn^{2+}$ is due to half-filled stability of Mn^{2+} (d^5)

Comparatively low value of $E^0 Fe^{3+}/Fe^{2+}$ is due to the extra stability of d^5 state. It has low value of third ionization enthalpy.

Low value of $E^0 V^{+3}/V^{+2}$ is related to half-filled t_{2g}^3 configuration

CHEMICAL REACTIVITY AND ELECTRODE POTENTIALS

Transition elements vary widely in their chemical reactivity. Some metals are highly electropositive and dissolve in acids. But some are noble metals which are not affected by acids.

First row transition elements (except Cu) are more reactive than the other series. These metals oxidized by acids. But Ti and V are passive to non-oxidizing acids.

E^0 values show that Mn^{+3} and Co^{+3} are the strongest oxidizing agents in aqueous solution whereas Ti^{+2} , V^{+2} , Cr^{+2} are the strongest reducing agents and liberate hydrogen from dilute acids.

STABILITY OF HIGHER OXIDATION STATES:

METAL HALIDES:

The reactivity order of halogens with metal is $F > Cl > Br > I$.

Transition metals show highest oxidation state in fluorides as it has high lattice enthalpy, electronegativity or due to high bond enthalpies.

CoF_3 is stable due to its high lattice enthalpy. But VF_5 and CrF_6 are stable due to high bond enthalpies

The highest oxidation state in halides vary from +4 to +6. For Ti, it is Ti^{+4} , for V, it is V^{+5} and for Cr, it is Cr^{+6} . Mn does not show simple oxidation state with +7 in halides. But in MnO_3F is available with +7

In first transition series, beyond Mn, no element shows oxidation state more than +3. Fe and Co form trihalides $FeCl_3$ and CoF_3

V shows +5 only in VF_5 but other halides undergo hydrolysis to give Oxo halides (VOX_3) in which V is in +5 state.

In lower oxidation states fluorides are unstable. Cu^{+2} halides are known, but +1 are unstable as it disproportionate to Cu^{+2} and Cu. $2 Cu^{+1} \rightarrow Cu^{+2} + Cu$
 CuI_2 is not known as Cu^{+2} oxidises iodide to iodine (I^- to I_2)

Cu^{+2} is more stable than Cu^{+1} . This due to much **more negative ΔH hydration** for Cu^{+2} than Cu^{+1} which compensates the high second ionization enthalpy of Cu

METAL OXIDES:

The ability of oxygen to stabilize highest oxidation state is more than fluorine as it can form multiple bonds with metals.

The highest oxidation state is same as that of group number up to group 7. Beyond group 7 maximum oxidation state is +3.

Higher oxidation states are seen in oxo cations and oxo anions. Eg: VO^{2+} , TiO^{2+} , MnO_4^- , CrO_4^{2-} , $Cr_2O_7^{2-}$ etc

Among halides, highest halides are with oxidation number +4. But in oxides +7 state is

found in Mn. Eg: Highest fluoride of Mn in MnF_4 whereas highest oxide is Mn_2O_7 .

The order of increasing oxidation power in the first series $\text{VO}^{2+} < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ are explained with the increasing stability of the lower species to which it is reduced.

MAGNETIC PROPERTIES

Paramagnetic substances are substances which are attracted in the magnetic field. These are having one or more unpaired electrons. Most of the transition elements are paramagnetic in nature and are attracted in the magnetic field. This is **due to the presence of unpaired electrons in their metal ions and in their compounds.**

Magnetic properties are expressed in terms of magnetic moments in Bohr Magneton units (BM) Formula for calculating spin only **Magnetic moment $\mu = \sqrt{n(n+2)}$ BM** where 'n' is the number of unpaired electrons.

FORMATION OF COLOURED COMPOUNDS

Most of the transition metal compounds are coloured both in solid state as well as in aqueous state. Colour is due to the presence of **incomplete d orbitals** with one or more **unpaired electrons**. Transition of electron from the lower energy d orbital to high energy d orbital

(d-d transition) occur and the energy of excitation corresponds to the frequency of light. This frequency lies in the visible region. The colour observed corresponds to the complementary colour of light absorbed.

Sc^{+3} is colourless $\text{Sc}^{+3} - [\text{Ar}] 3d^0 4s^0$ No unpaired electrons

Zn^{+2} , Cd^{+2} and Hg^{+2} are also colourless. All are having d^{10} configuration

Ti^{+3} is purple coloured $\text{Ti}^{+3} - [\text{Ar}] 3d^1 4s^0$

Cu^+ salts are colourless but Cu^{+2} salts are coloured

$\text{Cu}^{+2} [\text{Ar}] 3d^9 4s^0$ One unpaired electron in 3d orbital.

FORMATION OF COMPLEX COMPOUNDS

Most of the transition elements form complex compounds **due to small size and high ionic charges** of the metal ions and **availability** of **d orbitals** of suitable energy to accept electron pairs Eg: $\text{K}_4[\text{Fe}(\text{CN})_6]$

CATALYTIC PROPERTIES

Most of the transition elements are used as catalysts. This is because the ability of transition elements to **adopt multiple oxidation states** and to form **complexes or intermediate compounds of variable oxidation state**. Most of these metals are in solid state and hence it can provide enough surface area for intermediate formation.

FORMATION OF INTERSTITIAL COMPOUNDS

Transition elements can trap some smaller atoms like **carbon, hydrogen or nitrogen** inside the crystal lattices of metals. These compounds are non-stoichiometric in nature. These compounds are chemically inert, hard, have high melting point, retain metallic conductivity.

ALLOY FORMATION:

Transition elements form homogeneous solid solutions or alloys as these metals have **similarity in size and characteristics**. So substitution of one metal by the other in its crystal lattice become easier. Eg: Brass, Bronze, alloy steels, stainless steels etc.

PREPARATION OF $K_2Cr_2O_7$

1. Conversion of Chromite ore(GREEN) into Sodium Chromate(YELLOW)



2. Conversion of Sodium Chromate into Sodium dichromate(ORANGE)

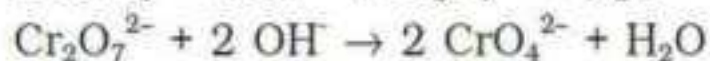


3. Conversion of Sodium dichromate into Potassium dichromate(ORANGE)



PROPERTIES: CHANGE IN pH

Yellow to orange upon adding acid



Orange to yellow upon adding base

OXIDISING ACTION: Potassium dichromate acts as a strong oxidizing agent in acidic medium and oxidises

1. Ferrous to Ferric
2. Stannous to Stannic
3. Sulphide to Sulphur
4. Iodide to Iodine, and itself gets reduced to Cr^{3+}

(Students to write the reactions on their own and refer book in case of difficulty)

PREPARATION OF KMnO_4

1. Conversion of MnO_2 - Pyrolusite (Black) into Potassium manganate
2. Conversion of Potassium manganate(green) into Potassium permanganate (dark purple)



CHEMICAL PROPERTIES OF KMnO_4

- Action of heat



- Oxidising action-

a) Acidic medium: Ferrous to Ferric, oxalate ions to CO_2 , KI to iodine

b) Basic medium : KI TO KIO_3 , thiosulphate to sulphate, Mn^{2+} to MnO_2

NOTE: In acidic medium MnO_4^- ions are reduced to Mn^{2+} , while in basic and neutral medium it gets reduced to MnO_2

(Students to write the reactions on their own and refer book in case of difficulty)

KMnO_4 is coloured due to Ligand-metal bond

INNER TRANSITION ELEMENTS:

These are f-block elements which includes lanthanoids and actinoids. These are called inner transition elements as the last electron enter into the (n-1) f-orbital. Fourteen elements comes after lanthanum (At No 58 to 71) are called lanthanoids and fourteen elements comes after Actinium (At No 90 to 103) are called Actinoids.

General configuration of these elements are $(n-2) f^{1-14} (n-1) d^{0-1} n s^2$

Lanthanoid Contraction

The atomic size or the ionic radii of tri positive lanthanide ions decrease steadily from La to Lu due to increasing nuclear charge and electrons entering the inner (n-2) f orbital. This gradual decrease in the size with an increasing atomic number is called **lanthanide contraction**.

CAUSE: The cause of lanthanide contraction is **the poor shielding effect of the 4f orbital** due to which the electrons in the s orbital attract more towards the nucleus which leads to the decrease in size of the atom. ... As the nuclear charge increases, the valence shell is pulled slightly towards the nucleus of the atom.

CONSEQUENCES

Atomic size: The size of the atom of the third transition series is closely the same as that of the atom of the second transition series.

Difficulty in the separation of lanthanides: As there is only a minute change in the ionic radii of Lanthanides, their chemical properties are similar. This makes the separation of elements in the pure state challenging.

Effect on the basic strength of hydroxides: The size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases.

DIFFERENCES BETWEEN LANTHANOIDS AND ACTINOIDS

CHARACTERISTICS	LANTHANOIDS	ACTINOIDS
Configuration	[Xe] 4f(1-14), 5d(0-1), 6s ²	[Rn] 5f(1-14), 6d(0-1), 7s ²
Oxidation State	+2, +3, +4 Most common (+3)	+3, +4, +5, +6, +7
Atomic size	Decreases from La to Lu due to Lanthanoid Contraction	Decreases from Ac to Lr due to Actinoid Contraction
Chemical Reactivity	High but with increasing atomic no. they behave like Aluminium	Very high radioactive metals

USES OF d- & f- BLOCK ELEMENTS:

Transition elements are used for making wide varieties of alloys, Misch metal is lanthanoid alloy used for making bullets, shells and lighter flints.

Many metals and compound are used as catalysts, some complexes are used as catalysts and in medical field. Eg Cis-Platin is used in cancer chemotherapy, ⁶⁰Co is used in radiation therapy.

QUESTION BANK-CHAPTER-d and f - BLOCK ELEMENTS

SECTION A

MULTIPLE CHOICE QUESTIONS (1 Marks Each)

1. The general outer electronic configuration of transition elements is _____.
- (a) $(n-1) d^{1-10} ns^2$ (b) $(n-1) d^{1-10} ns^{1-2}$
(c) $(n-1) d^{1-10} ns^{0-2}$ (d) $(n-1) d^{1-10} ns^1$

Answer: c

2. Which metal has the highest melting point?

(a) Pt (b) W (c) Pd (d) Au

Answer: b

3. Which metal has the highest density?

(a) Pt (b) Hg (c) Pd (d) Os

Answer: d

4. Which transition metal can show the highest oxidation state?

(a) Sc (b) Ti (c) Os (d) Zn

Answer: c

5. Which of the following would be paramagnetic?

(a) Zn^{2+} (b) Cu^+ (c) Sc^{3+} (d) Mn^{2+}

Answer: d

6. Which of the following is likely to form white salts?

(a) Cu^{2+} (b) Sc^{3+} (c) Ti^{3+} (d) Fe^{3+}

Answer: b

7. When $KMnO_4$ acts as oxidizing agent in alkaline medium, the oxidation number of Mn decreases by

(a) 1 (b) 2 (c) 3 (d) 5

Answer: c

8. The equivalent mass of $K_2Cr_2O_7$, when it acts as oxidizing agent in acidic medium, is equal to

(a) M (b) M/2 (c) M/6 (d) M/5

Answer: c

9. Which of the following oxides are acidic in nature?

(a) CrO (b) Cr_2O_3 (c) CrO_3 (d) CrO_2

Answer: c

10. The value of 'spin only' magnetic moment for one of the following configurations is 2.84 BM. The correct one is

- (a) d^4 (in strong ligand field)
- (b) d^4 (in weak ligand field)
- (c) d^3 (in weak as well as strong fields)
- (d) d^5 (in strong ligand field)

Answer: a

11. Which of the following factors may be regarded as the main cause of lanthanide contraction?

- (a) Poor shielding of 4f-electrons by 5d electrons.
- (b) Effective shielding 4f-electrons by 5d electrons.
- (c) Poorer shielding of 5d electrons by 4f electrons.
- (d) Greater shielding of 5d electrons by 4f electrons.

Answer: c

12. The electronic configuration of Cu(II) is $3d^9$ whereas that of Cu(I) is $3d^{10}$. Which of the following is correct?

- (a) Cu(II) is less stable
- (b) Cu(I) and Cu(II) are equally stable
- (c) Stability of Cu(I) and Cu(II) depends on nature of copper salts.
- (d) Cu(II) is more stable

Answer: d

13. Highest oxidation state of manganese in fluoride is +4 (MnF_4) but highest oxidation state in Oxides is +7 (Mn_2O_7) because

- (a) fluorine is more electronegative than oxygen.
- (b) fluorine does not possess d-orbitals.
- (c) fluorine stabilizes lower oxidation state.
- (d) in covalent compounds fluorine can form single bond only while oxygen forms double bond

Answer: d

ASSERTION REASONING QUESTIONS (1 Marks Each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

(a) Both A and R are correct and the R is the correct explanation of A.

(b) Both A and R are correct but R does not explain the A.

(c) Assertion (A) is correct but Reason (R) is incorrect.

(d) Assertion (A) is incorrect but Reason (R) is correct.

1. **Assertion :** All the members of actinide series are radioactive in nature.

Reason : The electrons are gradually accommodated in a 5f-energy subshell.

Ans. [B]

2. **Assertion :** TiCl_4 is a colorless compound.

Reason : Ti^{4+} ion has no unpaired electron.

Ans. [A]

3. **Assertion :** The highest oxidation state of a metal exhibited in its oxide or fluoride only.

Reason : Oxygen and Fluorine are small in size and are highly electronegative

Ans: [A]

4. **Assertion :** Cu cannot liberate hydrogen from acids.

Reason : Cu has positive electrode potential.

Ans: [A]

5. **Assertion :** Separation of Zr and Hf is difficult

Reason : Zr and Hf have almost similar atomic size due to lanthanoid contraction.

Ans:[A]

6. **Assertion :** The highest oxidation state of osmium is +8.

Reason : Osmium is a 5d-block element.

Ans : [B]

7. **Assertion :** E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is more positive than $\text{Cr}^{3+}/\text{Cr}^{2+}$

Reason : The third ionization energy of Mn is larger than that of Cr.

Ans : [B]

8. **Assertion :** Transition metals show variable valence.

Reason : Due to a large energy difference between the ns^2 and $(n-1)d$ electrons.

Ans : [D]

SECTION B

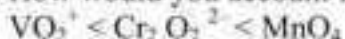
VERY SHORT ANSWER TYPE QUESTIONS (2 Marks Each)

1. Why is Cr^{2+} reducing and Mn^{3+} oxidizing when both have d^4 configuration?

Ans. Cr^{2+} is reducing as its configuration changes from d^4 to d^3 , the latter having a half-filled t_{2g} level. On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

2. (i) Explain why Cu^+ ion is not stable in aqueous solutions?

(ii) How would you account for the increasing oxidizing power in the series?



Ans. (i) This is because although energy is required to remove one electron from Cu^+ to Cu^{2+} , high hydration energy of Cu^{2+} compensates for it. Therefore, Cu^+ ion in an aqueous solution is unstable. It is disproportionate to give Cu^{2+} and Cu .

(ii) This is due to the increasing stability of the lower species to which they are

reduced, $\overset{\text{V}}{\text{VO}_2^+} \rightarrow \overset{\text{IV}}{\text{VO}^{2+}}, \overset{\text{VI}}{\text{Cr}_2\text{O}_7^{2-}} \rightarrow \overset{\text{III}}{\text{Cr}^{3+}} \rightarrow \overset{\text{VII}}{\text{MnO}_4^-} \rightarrow \overset{\text{II}}{\text{Mn}^{2+}}$

3. Why is the E^0 value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$? Explain.

Ans. Much larger third ionization energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

4. Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Ans. With atomic number 25, the divalent ion in aqueous solution will have d^5 configuration (five unpaired electrons). The magnetic moment, μ is $\mu = 5(5 + 2) = 5.92 \text{ BM}$

5. What is meant by disproportionation of an oxidation state? Give an example.

Ans. When a particular oxidation state becomes less stable relative to other oxidation states, one lower, one higher, it is said to undergo disproportionation. For example, manganese (VI) becomes unstable relative to manganese (VII) and manganese (IV) in acidic solution.



SECTION C

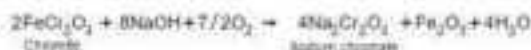
SHORT ANSWER TYPE QUESTIONS (3 Marks Each)

1. (i) Name a member of the lanthanoids series which is well known to exhibit +4 oxidation state.
(ii) Actinoids contraction is greater from element to element than lanthanoids contraction.
(iii) Which out of $\text{Lu}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ is more basic and why?
- Ans.** (i) Cerium ($Z = 58$)
(ii) This is because of poor shielding by 5f electrons in actinoids in comparison with shielding of 4f electrons in lanthanoids.
(iii) $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$ due to lanthanoids contraction.
2. (a) Indicate the steps in the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.
(b) What is the effect of increasing pH on a solution of potassium dichromate?
(c) Describe the oxidizing action of potassium dichromate and write the ionic equations for its reaction with:
(i) Iodide (ii) iron (II) solution (iii) H_2S

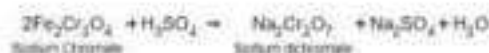
Ans. (a) Preparation of $K_2Cr_2O_7$ from chromite ore

The preparation of potassium dichromate from chromite involves the following main steps:

(ii) The climate is a dry ground and heated strongly with molten alkali in the presence of air.



(d) The solution of sodium chromate is filtered and acidified with glacial acetic acid so that sodium dichromate is obtained.



(9) A calculated quantity of potassium chloride is added to a hot concentrated solution of sodium dichromate. Potassium dichromate is less soluble therefore it crystallizes out first.



- (c) (i) $K_2Cr_2O_7$ oxidises iodide to iodine



(ii) $\text{K}_2\text{Cr}_2\text{O}_7$ oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.



(iii) $K_2Cr_2O_7$ oxidizes H_2S to sulphur



SECTION D
CASE STUDY BASED QUESTIONS (4 Marks Each)

PASSAGE-1

Within the 3d-series, Manganese exhibits oxidation states in aqueous solution from +2 to +7, ranging from Mn^{2+} (aq) to MnO_4^- (aq). Likewise, iron forms both Fe^{2+} (aq) and Fe^{3+} (aq) as well as the FeO_4^{2-} ion. Cr and Mn form oxyanions CrO_4^{2-} , MnO_4^- , owing to their willingness to form multiple bonds. The pattern with the early transition metals—in the 3d series up to Mn, and for the 4d, 5d metals up to Ru and Os is that the maximum oxidation state corresponds to the number of “outer shell” electrons. The highest oxidation states of the 3d-metals may depend upon complex formation (e.g., the stabilization of Co^{3+} by ammonia) or upon the pH (thus MnO_4^{2-} (aq) is prone to disproportionation in acidic solution). Within the 3d-series, there is considerable variation in relative stability of oxidation states, sometimes on moving from one metal to a neighbor; thus, for iron, Fe^{3+} is more stable than Fe^{2+} , especially in alkaline conditions, while the reverse is true for cobalt. The ability of transition metals to exhibit a wide range of oxidation states is marked with metals such as vanadium, where the standard potentials can be rather small, making a switch between states relatively easy. (Source: Cotton, S. A. (2011). Lanthanides: Comparison to 3d metals, Encyclopedia of inorganic and Bioinorganic Chemistry.) (Competency Based Question]

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices on the basis of the above passage.

Assertion and reason both are correct statements and reason is correct explanation for assertion.

Assertion and reason both are correct statements and reason is not correct explanation for assertion.

Assertion is a correct statement but the reason is incorrect.

Assertion is an incorrect statement but the reason is correct.

1. Assertion: Highest oxidation state is exhibited by transition metal lying in the middle of the series.
Reason: The highest oxidation state exhibited corresponds to the number of (n-1) d electrons.
2. Assertion: Fe^{3+} is more stable than Fe^{2+} .
Reason: Fe^{3+} has 3d⁵ configuration while Fe^{2+} has 3d⁶ configuration.
3. Assertion: Vanadium had the ability to exhibit a wide range of oxidation states.
Reason: The standard potentials vanadium are rather small, making a switch between oxidation states are relatively easy.
4. Assertion: Transition metals like Fe, Cr and Mn form oxyanions.
Reason: Oxygen is highly electronegative and has a tendency to form multiple bonds.
5. Assertion: The highest oxidation states of the 3d metals depend only on electronic configuration of the metal.
Reason: The number of electrons in the (n-1)d and ns subshells determine the

oxidation states exhibited by the metal.

PASSAGE-2

Potassium permanganate, (KMnO_4) is prepared by fusion of pyrolusite, MnO_2 , with KOH in the presence of an oxidizing agent like KNO_3 . This produces the dark green potassium manganate, K_2MnO_4 , which disproportionates in a neutral or acidic solution to give purple permanganate ions. Potassium permanganate is an important oxidizing agent in acidic, alkaline as well as neutral medium.

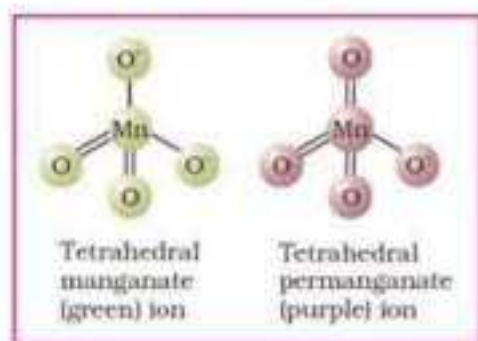
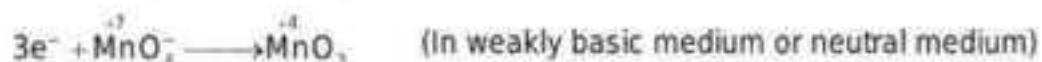
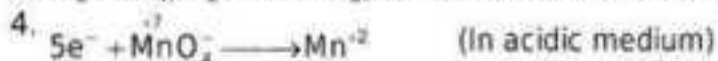
1. What is the state of hybridization of Mn in MnO_4^- ?
2. Write an application of potassium permanganate.
3. What are the products formed after heating potassium permanganate?
4. How many electrons are involved in oxidation by KMnO_4 , in different mediums?
5. Draw the structure of a permanganate and manganate ion.

PASSAGE-1

- 1.(c) 2.(a) 3.(a) 4.(b) 5.(d)

PASSAGE-2

1. sp^3
2. It is used for the estimation of hydrogen peroxide.
3. K_2MnO_4 , O_2 and MnO_2 , will be formed after heating of potassium permanganate.



SECTION E
LONG ANSWER TYPE QUESTIONS (5 Marks Each)

1. Explain giving reasons:
 - a. Transition metals and many of their compounds show paramagnetic behavior.
 - b. The enthalpies of atomization of the transition metals are high.
 - c. The transition metals generally form coloured compounds.
 - d. Transition metals and their many compounds act as good catalysts.
 - e. Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not?

Answer:

- a. Due to the presence of unpaired d- electrons.
 - b. Because of the large number of unpaired electrons in their atoms they have stronger interatomic interaction and hence stronger bonding between atoms resulting in higher enthalpies of atomization.
 - c. Due to unpaired d- electrons that undergo d-d transition.
 - d. Due to the presence of vacant orbitals or their tendency to form variable oxidation states.
 - e. On the basis of incompletely filled 3d orbitals in the case of scandium in its ground state ($3d^1$), it is regarded as a transition element. On the other hand, zinc has completely filled d orbitals ($3d^{10}$) in its ground state as well as in its oxidized state; hence it is not regarded as a transition element.
2. a. Define Lanthanoid Contraction.
 - b. Give its two consequences.
 - c. Tabulate the similarities and differences between actinoids and lanthanoids.

Answer:

- a. **Lanthanide contraction:**

The steady decrease in atomic and ionic sizes of lanthanide elements with increasing atomic number is called Lanthanide contraction.

Cause of Lanthanide contraction:

In the lanthanide series, as we move from one element to another, the nuclear charge increases by one unit and one electron is added. The new electrons are added to the same inner 4f- subshells. However, the shielding of one 4 f electron by another is less than one d electron by another with the increase in nuclear charge along the series. There is a regular decrease in the sizes with increasing atomic numbers.

- b. **Consequences of Lanthanide contraction:**

1. Resemblance of second and third transition series: As a result of Lanthanide contraction, the elements of second and third transition series resemble each other much more than the elements of first and second transition series.
2. Similarities among lanthanoids: Because of very small change in radii of lanthanoids, their chemical properties are quite similar. Thus, it is very difficult to separate the elements in a pure state.

c. Similarities between lanthanoids and actinoids:

1. Both exhibits +3 oxidation state.
2. Both involve the filling of f-orbitals.
3. Both having same number of unpaired electrons have quite similar spectra. In the absorption spectra of the elements of both the series, sharp lines like bands appear due to f-f transition.
4. Both are electropositive and have high reactivity.
5. Like lanthanoids contraction, there is actinoids contraction. These contractions are due to poor shielding of 5f and 4f electrons in lanthanoids and actinoids respectively.

d. Differences between lanthanoids and actinoids:

Sr. No.	Lanthanoids	Actinoids
i)	Besides +3 oxidation state, they show oxidation states of +2 and +4 also.	Besides +3 oxidation state, they show oxidation state of +4, +5, +6 and +7 also.
ii)	Most of their ions are colourless.	Most of their ions are coloured.
iii)	Lanthanoid compounds are less basic and less reactive.	Actinoid compounds are more basic and more reactive.
iv)	The general electronic configuration of lanthanoids is $[\text{Xe}]4f^{1-14} 5d^{0-1} 6s^2$	The general electronic configuration of actinoids is $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$.

CHAPTER-5-COORDINATION COMPOUNDS

Coordination compounds are a special class of compounds in which the central metal atom is surrounded by ions or molecules beyond their normal valency. Many biologically important compounds are Coordination compounds in which complicated organic species are bound to metal ions.

The common examples are:

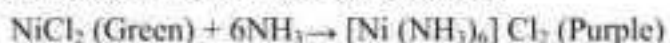
Hemoglobin which is a Coordination compound of **Iron**

Chlorophyll which is a Coordination compound of **Magnesium** and

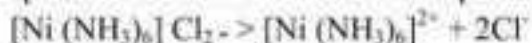
Vitamin B₁₂ which is a Coordination compound of **Cobalt** etc.

The Coordination compounds are also finding extensive applications in metallurgical processes, analytical chemistry, industrial catalysts, textile dyeing, electroplating and medicinal chemistry.

Coordination compounds are molecular compounds which are formed from the combination of two or more simple stable compounds and retain their identity in the solid as well as in the dissolved state.



When the compound $[\text{Ni} (\text{NH}_3)_6] \text{Cl}_2$ is dissolved in water it ionizes to give a new species. Such an ion is called complex ion $[\text{Ni} (\text{NH}_3)_6]^{2+}$.



Coordination compounds are the compounds in which the central metal atom is bound to a number of anions or neutral molecules by coordinate bonds.

Coordination entity and Coordination sphere:

Coordination entity: A coordination entity constitutes a central metal atom or ion bounded to a fix number of oppositely charged ions or neutral molecules.

For example, $[\text{Co Cl}_3 (\text{NH}_3)_3]$

Coordination sphere: The central metal atom or ion and the molecules or ions bonded to it are enclosed in a square bracket and a collectively called the

Coordination sphere.

For example: $[\text{Co} (\text{NH}_3)_6]^{3+}$

Central atom or ion and Ligands:

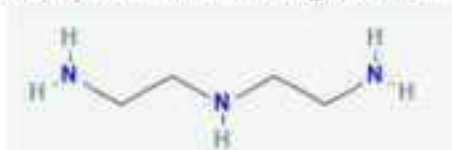
Central atom or ion: The atom or ion to which a fixed number of neutral molecules or ions are attached in the coordination entity is called **Central atom or ion**.

Ligands: The neutral molecules or ions bonded to the central atom or ion in the coordination entity are called **ligands**.

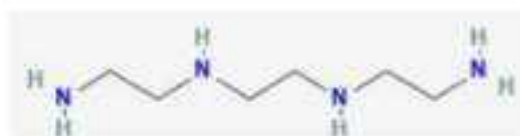
For example: $[\text{Ni} (\text{NH}_3)_6]^{2+}$: Central atom = Ni^{2+} , ligands = NH_3 molecules

Types of ligands:

- (i) **Unidentate or monodentate ligands:** When a ligand is bound to a metal ion through a single donor atom, as with Cl^- , H_2O or NH_3 , the ligand is said to be **Unidentate ligands**.
- (ii) **Didentate or Bidentate ligands:** When a ligand can bind through two donor atoms as in $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (ethane-1, 2-diamine) or $\text{C}_2\text{O}_4^{2-}$ (oxalate), the ligand is said to be **Didentate ligands**.
- (iii) **Polydentate ligands:** Ligands having more the two donor atoms present in the molecule, the ligands are said to be **Polydentate ligands**.
Diethylene triamine acts as **tridentate ligand** having three donor N atoms.



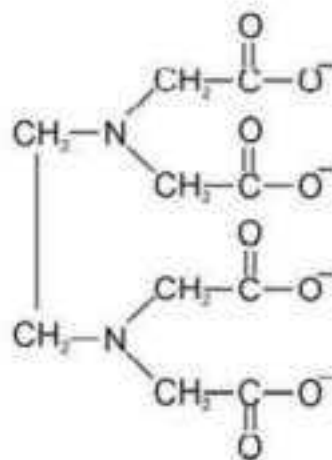
Triethylene tetra amine acts as **tetradentate ligand** having four donor N atoms.



Ethylenediamine triacetate ion acts as **Pentadentate ligand** having two N atoms and three O atoms.

Ethylenediaminetetraacetate ion (EDTA^{4-}) is an important **hexadentate**

ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.



Chelate ligand When a di- or Polydentate ligand uses its two or more donor atoms simultaneously to bind a single metal ion, it is said to be a **chelate ligand**. The number of such ligating groups is called the denticity of the ligand. Such complexes, called chelate complexes tend to be more stable than similar complexes containing Unidentate ligands.

Ambidentate ligand: Ligand which has two different donor atoms and either of the two ligates in the complex

Examples of such ligands are the NO_2^- and SCN^- ions.

NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal atom/ion.

Similarly, SCN^- ion can coordinate through the Sulphur or Nitrogen atom.

Coordination number: The total number of ligands attached to a central metal atom or ion is called the Coordination number of that metal atom or ion.

For example: $[\text{Ni}(\text{NH}_3)_4]^{2+}$: C.N. of $\text{Ni}^{2+} = 4$ $[\text{CoCl}_3(\text{NH}_3)_3]$: C.N. of $\text{Co}^{3+} = 6$

IUPAC nomenclature of coordination compounds: Write the IUPAC names of the following coordination compounds:

- | | |
|---|---|
| (a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$ | Diamminechloridonitrito-N-platinum (II) |
| (b) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$ | Potassium trioxalatochromate (III) |
| (c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ | Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride |
| (d) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$ | Pentaamminecarbonatocobalt (III) chloride |
| (e) $\text{Hg}[\text{Co}(\text{SCN})_4]$ | Mercury (I) tetrathiocyanato-S-cobaltate (III) |
| (f) $[\text{Cr}(\text{NH}_3)_3(\text{H}_2\text{O})_3]\text{Cl}_3$ | Triamminetriaquachromium (III) chloride |

- (g) $[\text{Co}(\text{en})_3]_2(\text{SO}_4)_3$ Tris (ethane-1,2-diamine)cobalt(III) sulphate
 (h) $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$ Diamminesilver (I) dicyanidoargentate (I)

Werner's theory: Werner proposed the concept of a primary valence and a secondary valence for a metal ion. Binary compounds such as CrCl_3 , CoCl_2 or PdCl_2 have primary valence of 3, 2 and 2 respectively.

In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess silver nitrate solution in cold but some remained in solution.

1 mol $\text{CoCl}_3 \cdot 6\text{NH}_3$ (Yellow) gave 3 mol AgCl

1 mol $\text{CoCl}_3 \cdot 5\text{NH}_3$ (Purple) gave 2 mol AgCl

1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Green) gave 1 mol AgCl 1 mol $\text{CoCl}_3 \cdot 4\text{NH}_3$ (Violet) gave 1 mol AgCl

Werner proposed the term secondary valence for the number of groups bound directly to the metal ion; in each of these examples the secondary valences are six.

Formulation of Cobalt (III) Chloride-Ammonia Complexes:

Colour	Formula	Solution conductivity corresponds to
Yellow	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$	1:3
Purple	$[\text{CoCl}(\text{NH}_3)_5]^{2+} 2\text{Cl}^-$	1:2
Green	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1
Violet	$[\text{CoCl}_2(\text{NH}_3)_4]^+ \text{Cl}^-$	1:1

The main postulates are:

1. In coordination compounds metals show two types of linkages (valences)-primary and secondary.
2. The primary valences are normally ionisable and are satisfied by negative ions.
3. The secondary valences are non ionisable. These are satisfied by neutral molecules or negative ions. The secondary valence is equal to the coordination number and is fixed for a metal.
4. The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements corresponding to different coordination numbers.

Valence Bond Theory (VBT) for bonding in Coordination Compounds:

The main assumptions of this theory are listed below:

1. The central metal ion in the complex makes available a number of empty

orbitals for the formation of coordination bonds with suitable ligands.

2. The number of empty orbitals made available for this purpose is equal to coordination number of the central metal ion. For example, if coordination number is 6, six empty orbitals are made available and if coordination number is 4, four empty orbitals are made available in the central metal ion.
3. The appropriate atomic orbitals (s, p and d) of the metal hybridize to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral and octahedral and so on.
4. The d-orbitals involved in the hybridization may be either inner d-orbitals i.e. (n-1) d or outer d-orbitals i.e. nd. For example, in case of octahedral hybridization. The orbitals may be two 3d, one 4s and three 4p (d^2sp^3) or one 4s, three 4p and two 4d (sp^3d^2).
5. Each ligand has at least one orbital (of donor atom) containing a lone pair of electrons.
6. The empty hybrid orbitals of metal ion overlap the filled orbitals of the ligand to form metal-ligand coordinate covalent bonds.

Number of Orbitals, Types of Hybridizations and Magnetic Properties of Coordination Compounds:

Coordination number	Type of hybridization	Complex/ Ion	Geometry	No. of unpaired electrons	Magnetic Character
4	sp^3	$[\text{NiCl}_4]^{2-}$	Tetrahedral	2	Paramagnetic
4	dsp^2	$[\text{Ni}(\text{CN})_4]^{2-}$	Square planar	0	Diamagnetic
6	sp^3d^2	$[\text{CoF}_6]^{3-}$	Octahedral	4	Paramagnetic
6	d^2sp^3	$[\text{Co}(\text{NH}_3)_6]^{3+}$	Octahedral	0	Diamagnetic

CRYSTAL FIELD THEORY (CFT): The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand.

Ligands are treated as point charges in case of anions or point dipoles in case of neutral molecules. The five *d* orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate.

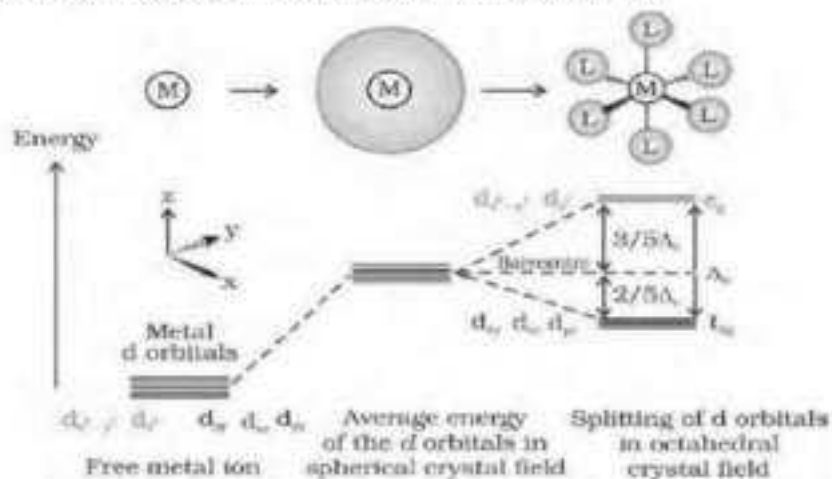
This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion.

However, when this negative field is due to ligands (either anions or the negative ends of dipolar molecules like NH_3 and H_2O) in a complex, it becomes asymmetrical and the degeneracy of the *d* orbitals is lifted.

It results in splitting of the *d* orbitals. The pattern of splitting depends upon the nature

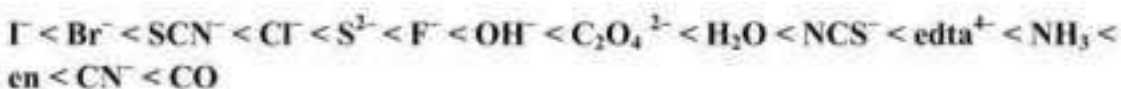
of the crystal field. The conversion of five degenerate d-orbitals of the metal ion into different sets of orbitals having different energies in the presence of electric field of ligand is called **crystal field splitting**.

(a) **Crystal field splitting in octahedral coordination entities:**



d orbital splitting in an octahedral crystal field

Spectrochemical series: ligands can be arranged in a series in the order of increasing fieldstrength as given below:



For d^4 ions, two possible patterns of electron distribution arise:

- The fourth electron could either enter the t_{2g} level and pair with an existing electron, or
- It could avoid paying the price of the pairing energy by occupying the e_g level.

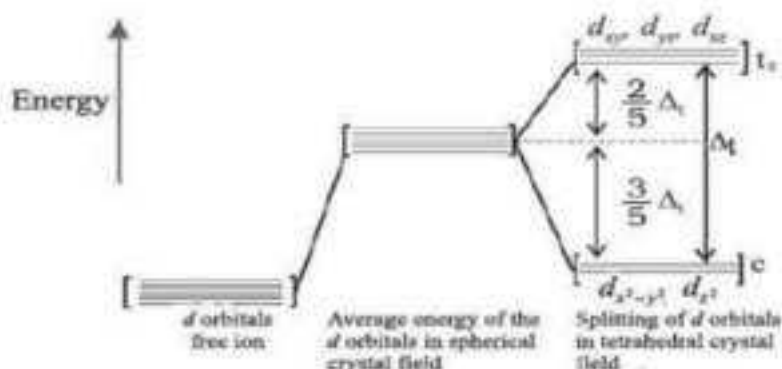
Which of these possibilities occurs, depends on the relative magnitude of the crystal field splitting, Δ_o and the pairing energy, P (P represents the energy required for electron pairing in a single orbital). The two options are:

- If $\Delta_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3 e_g^1$.

Ligands for which $\Delta_o < P$ are known as **weak field ligands** and form high spin complexes.

- If $\Delta_o > P$, it becomes more energetically favorable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^4 e_g^0$. Ligands which produce this effect are known as **strong field ligands** and form low spin complexes.

(b) Crystal field splitting in tetrahedral coordination entities:



d orbital splitting in a tetrahedral crystal field (fig.9.9 ncert)

In tetrahedral coordination entity formation, the d orbital splitting (Fig. 9.9) is inverted and is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = (4/9) \Delta_o$.

Colour in Coordination Compounds: The crystal field theory attributes the colour of the coordination compounds to $d-d$ transition of the electron.

Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities:

Coordination entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[\text{Co}(\text{CN})_6]^{3-}$	310	Violet	Pale Yellow
$[\text{Co}(\text{NH}_3)_6]^{3+}$	475	Blue	Yellow Orange
$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	500	Blue Green	Red
$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$	510	Blue Green	Purple
$[\text{CoCl}(\text{NH}_3)_5]^{2+}$	535	Yellow	Violet
$[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$	600	Red	Blue

Isomerism in Coordination Compounds:

Two or more compounds having the same molecular formula but different arrangement of atoms are called **isomers** and the phenomenon is called **Isomerism**.

Two types of isomerism are: (a) Structural isomerism (b) Stereoisomerism

Structural isomerism: The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers.

(a) Ionization isomerism: The compounds which have same molecular formula but

give differentiations in solution are called ionization isomers. For example:



(b) Solvate isomerism: The compounds which have same molecular formula but differ in the number of solvent molecules present as ligands and as free solvent molecules in the crystal lattice are called solvate isomers. This form of isomerism is known as hydrate isomerism in case where water is involved as a solvent.

For example: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet) and its solvate isomer $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (grey-green).

(c) Coordination isomerism: This type of isomerism arises from the interchange of ligands between cationic and anionic entities of different metal ions present in a complex. For example: $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which the NH_3 ligands are bound to Co^{3+} and the CN^- ligands to Cr^{3+} . In its coordination isomer $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$, the NH_3 ligands are bound to Cr^{3+} and the CN^- ligands to Co^{3+} .

(d) Linkage isomerism: The compounds which have same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers. Linkage isomerism arises in a coordination compound containing ambidentate ligand.

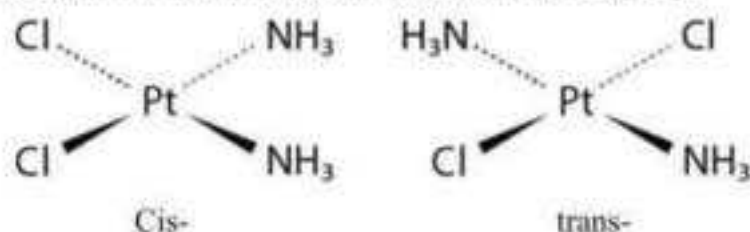
For example: $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ the ligand is bound through nitrogen ($-\text{NO}_2$).
 $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ the ligand is bound through oxygen ($-\text{ONO}$).

Stereoisomerism: Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangement of atoms.

Two types of isomerism are: **(a) Geometrical isomerism (b) Optical isomerism**

(a) Geometrical isomerism: This type of isomerism arises in heteroleptic complexes due to ligands occupying different positions around the central ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to cis- form (ligand occupy adjacent position) and trans- form (ligand occupy opposite position). For example:

Geometrical isomers (cis and trans) of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



(b) Optical isomerism: Optical isomers are mirror images that cannot be

superimposed on one another. These are called as enantiomers. The molecules or ions that cannot be superimposed are called chiral.

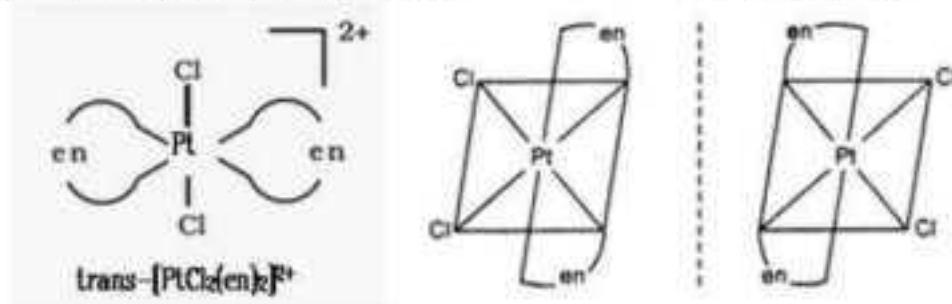
The two forms are called dextro (d) and laevo (l) depending upon the direction they rotate

the plane of polarized light in a polarimeter (d rotates to the right, l to the left).

Optical isomerism is common in octahedral complexes involving Didentate ligands.

Optical isomers of $[\text{PtCl}_2(\text{en})_2]^{2+}$

Only Cis isomer show optical isomerism.



Importance and Applications of Coordination Compounds:

- Coordination compounds find use in many qualitative and quantitative chemical analyses. Examples of such reagents include EDTA, DMG (dimethylglyoxime), etc.
- Ni^{2+} ions are detected by adding DMG (dimethylglyoxime) in the presence of NH_4OH to nickel salt solution, red precipitates are formed.
- Hardness of water is estimated by simple titration with Na_2EDTA . The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes.
- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[\text{Au}(\text{CN})_2]^-$ in aqueous solution.
- Purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds.
For example, impure nickel is converted to $[\text{Ni}(\text{CO})_4]$, which is decomposed to yield pure nickel.
- **Biological importance:** Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, **chlorophyll**, is a coordination compound of magnesium.

Haemoglobin, the red pigment of blood which acts as oxygen carrier is a coordination compound of iron.

Vitamin B12, cyanocobalamine, the anti-pernicious anaemia factor, is a coordination compound of cobalt.

- **In catalyst:** Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[\text{Rh}(\text{Ph}_3\text{P})_3\text{Cl}]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.
- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[\text{Ag}(\text{CN})_2]^-$ and $[\text{Au}(\text{CN})_2]^-$ than from a solution of simple metal ions.
- In black and white photography: The developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$.
- **In medicine:** Complexing agents are used for removal of metal poisoning. A platinum complex, $[\text{PtCl}_2(\text{NH}_3)_2]$ known as cis-platin has been used in cancer therapy.

ASSIGNMENTS:

Q1. Write the formulas for the following coordination compounds:

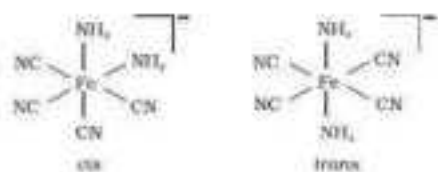
- (a) Tetraammineaquachloridocobalt (III) chloride
- (b) Potassium tetrahydroxidozincate (II)
- (c) Potassium trioxalatoaluminate (III)
- (d) Dichloridobis (ethane-1, 2-diamine) cobalt (III) ion
- (e) Tetracarbonylnickel (0)
- (f) Diamminechloridonitrito-N-platinum (II)
- (g) Potassium trioxalatochromate (III)
- (h) Dichloridobis (ethane-1, 2-diamine) cobalt (III) chloride
- (i) Pentaamminecarbonatocobalt (III) chloride
- (j) Mercury (I) tetrathiocyanato-S-cobaltate (III)

Q2. Write the IUPAC names of the following coordination compounds:

- (a) $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{NO}_2)]$
- (b) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
- (c) $[\text{CoCl}_2(\text{en})_2]\text{Cl}$
- (d) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
- (e) $\text{Hg}[\text{Co}(\text{SCN})_4]$
- (f) $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- (g) $\text{K}_2[\text{Zn}(\text{OH})_4]$
- (h) $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$
- (i) $[\text{CoCl}_2(\text{en})_2]^+$
- (j) $[\text{Ni}(\text{CO})_4]$

Q3. Draw structures of geometrical isomers of $[\text{Fe}(\text{NH}_3)_2(\text{CN})_4]^-$

Ans.



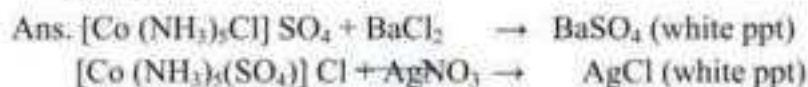
Q4. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

- (i) $\text{K}[\text{Cr}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$
- (ii) $[\text{Co}(\text{en})_3]\text{Cl}_3$
- (iii) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)](\text{NO}_3)_2$
- (iv) $[\text{Pt}(\text{NH}_3)(\text{H}_2\text{O})\text{Cl}_2]$

Ans.

- (i) Both geometrical (cis and trans) and optical isomers for cis.
- (ii) Two optical isomers
- (iii) Geometrical, ionization and linkage isomers.
- (iv) Geometrical (cis and trans)

Q5. Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ are ionization isomers.



Q6. The spin only magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?

Ans. Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridization) or square planar (dsp^2 hybridization). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the d orbitals.

Q7. Predict the number of unpaired electrons in the square planar $[\text{Pt}(\text{CN})_4]^{2-}$ ion.

Ans. $\text{Pt} = 5d^9 6s^1$

$\text{Pt (II)} = 5d^8$, square planar geometry and dsp^2 hybridization.

Q8. Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and the $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is

paramagnetic. Ans. $[\text{Ni}(\text{CN})_4]^{2-}$ square planar geometry and dsp^2 hybridization.
 $[\text{NiCl}_4]^{2-}$ Tetrahedral geometry and sp^3 hybridization.

Q9. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain.

Ans. In both the complexes, Fe is in +3 oxidation state.

CN^- is strong field ligand, inner d-orbitals are involved, d^2sp^3 hybridization, one unpaired electron, weakly paramagnetic.

H_2O is weak field ligand, outer d-orbitals are involved, sp^3d^2 hybridization, five unpaired electrons, strongly paramagnetic.

Q10. Explain $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

Ans. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex, d^2sp^3 hybridization. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex, sp^3d^2 hybridization.

QUESTION BANK-CHAPTER-COORDINATION COMPOUNDS

SECTION A

MULTIPLE CHOICE QUESTIONS (1 Marks Each)

1. The IUPAC name of the complex $[\text{Pt}(\text{NH}_3)_3\text{BrCl}(\text{NO}_2)]\text{Cl}$ is
- triamminechloridobromidonitrito-N-platinum(IV) chloride
 - triamminebromidonitrito-N-chloridoplatinum(IV) chloride
 - triamminebromidochloridonitrito-N-platinum(IV) chloride
 - triamminenitrito-N-chloridobromidoplatinum(IV) chloride

Answer: c

2. As per IUPAC nomenclature, the name of the complex $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_2$ is
- tetraaquadiamminecobalt(II) chloride
 - tetraaquadiamminecobalt(III) chloride
 - diamminetetraaquacobalt(II) chloride
 - diamminetetraaquacobalt(III) chloride

Answer: d

3. Which of the following represents the correct formula of dichloridobis(ethane-1,2-diamine)cobalt(III) ion?

- $[\text{CoCl}_2(\text{en})]^{2+}$
- $[\text{CoCl}_2(\text{en})_2]^{2+}$
- $[\text{CoCl}_2(\text{en})]^+$
- $[\text{CoCl}_2(\text{en})_2]^+$

Answer: d

4. Correct formula of pentaamminenitrito-O-cobalt(III) sulphate is

- a. $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{SO}_4$
- b. $[\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{SO}_4$
- c. $[\text{Co}(\text{NO}_2)(\text{NH}_3)_4](\text{SO}_4)_2$
- d. $[\text{Co}(\text{ONO})(\text{NH}_3)_4](\text{SO}_4)_2$

Answer: b

5. What is the oxidation state of metal in $[\text{Mn}_2(\text{CO})_{10}]$?

- (a) +1
- (b) -1
- (c) +2
- (d) 0

Answer: d

6. Ambidentate ligands like NO_2^- and SCN^- are-

- (a) Unidentate
- (b) bidentate
- (c) polydentate
- (d) has variable denticity

Answer: a

7. Which of the following species is not expected to be a ligand?

- (a) NO
- (b) NH_4^+
- (c) $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
- (d) CO

Answer: b

8. A chelating agent has two or more than two donor atoms to bind to a single metal ion. Which of the following is not a chelating agent?

- (a) Thiosulphato
- (b) Oxalato
- (c) Glycinato
- (d) Ethane-1,2-diamine

Answer: a

9. EDTA is a negative ligand having charge and denticity respectively

- (a) -2, 2
- (b) -1, 2
- (c) -1, 6
- (d) -2, 6

Answer: d

10. The correct IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is

- a. diamminedichloridoplatinum(II)
- b. diamminedichloridoplatinum(IV)
- c. diamminedichloridoplatinum(0)
- d. dichloridodiammineplatinum(IV)

Answer: a

11. The formula of the coordination compound tetraammineaquachloridocobalt(III)chloride is-

- a. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$
- b. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_3$
- c. $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$

d. $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}$

Answer: a

12. Due to the presence of ambidentate ligands coordination compounds show isomerism. Palladium complexes of the type $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{SCN})_2]$ and $[\text{Pd}(\text{C}_6\text{H}_5)_2(\text{NCS})_2]$ are

- a. Linkage isomers
- b. Coordination isomers
- c. Ionization isomers
- d. Geometrical isomers

Answer: a

13. $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ exhibits which of the following structural isomerism:

- a. Linkage isomerism
- b. Coordination isomerism
- c. Ionization isomerism
- d. Hydrate isomerism

Answer: b

14. Indicate the complex ion which shows geometrical isomerism-

- a. $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$
- b. $[\text{Pt}(\text{NH}_3)_3\text{Cl}]$
- c. $[\text{Co}(\text{NH}_3)_6]^{3+}$
- d. $[\text{Co}(\text{CN})_5(\text{NC})]^{3-}$

Answer: a

15. Atomic numbers of Mn, Fe and Co are 25, 26 and 27 respectively. Which of the following is an inner orbital octahedral complex ion that is diamagnetic?

- a. $[\text{Co}(\text{NH}_3)_6]^{3+}$
- b. $[\text{Ni}(\text{CN})_6]^{4-}$
- c. $[\text{Fe}(\text{H}_2\text{O})_6]^{4+}$
- d. $[\text{FeCl}_6]^{3-}$

Answer: a

16. On the basis of crystal field theory, electronic configuration of d^4 complex when $\Delta_o > P$ is

- a. $t_{2g}^3 e_g^1$
- b. $t_{2g}^2 e_g^2$
- c. $t_{2g}^1 e_g^3$
- d. $t_{2g}^4 e_g^0$

Answer: a

17. The complex used as an anticancer agent is

- a. $\text{trans}-[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
- b. $\text{cis}-[\text{PtCl}_2(\text{NH}_3)_2]$
- c. $\text{cis}-\text{K}_2[\text{PtCl}_2\text{Br}_2]$
- d. Na_2CO_3

Answer: b

18. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect

- a. Cyanocobalamin is B12 and contains cobalt.
- b. Hemoglobin is the red pigment of blood and contains iron.
- c. Chlorophylls are green pigments in plants and contain calcium.
- d. Carboxypeptidase-A is an enzyme and contains zinc.

Answer: c

ASSERTION REASONING QUESTIONS (1 Marks Each)

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct answer out of the following choices.

- (a) Both A and R are correct and the R is the correct explanation of A.
- (b) Both A and R are correct but R does not explain the A.
- (c) Assertion (A) is correct but Reason (R) is incorrect.
- (d) Assertion (A) is incorrect but Reason (R) is correct.

1. Assertion: Both $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ have the same magnetic moment. Reason: Number of unpaired electrons in Cr^{3+} and Fe^{3+} are the same

Answer: a

2. Assertion: $[\text{Co}(\text{en})_3]^{3+}$ is paramagnetic. Reason: It is an inner orbital complex.

Answer: d

3. Assertion: $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic complex. Reason: It involves dsp^2 hybridisation and there is no unpaired electron.

Answer: a

4. Assertion: Oxalate ion is a bidentate chelating ligand. Reason: Oxalate ion has two donor atoms

Answer: b

5. Assertion: The complex $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{SO}_4$ gives precipitate with AgNO_3 solution.

Reason: The given complex is non-ionisable.

Answer: d

SECTION B

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks Each)

1. Give evidence that $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Cl}$ are ionization isomers. **Ans.** $[\text{Co}(\text{NH}_3)_5\text{Cl}] \text{SO}_4 + \text{BaCl}_2 \longrightarrow \text{BaSO}_4$ (white ppt)
 $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)] \text{Cl} + \text{AgNO}_3 \longrightarrow \text{AgCl}$ (white ppt)
2. The spin only magnetic moment of $[\text{MnBr}_4]^{2-}$ is 5.9 BM. Predict the geometry of the complex ion?
Ans. Since the coordination number of Mn^{2+} ions in the complex ion is 4, it will be either tetrahedral (sp^3 hybridization) or square planar (dsp^2 hybridization). But the fact that the magnetic moment of the complex ion is 5.9 BM, it should be tetrahedral in shape rather than square planar because of the presence of five unpaired electrons in the d orbitals.

3. Explain on the basis of valence bond theory that $[\text{Ni}(\text{CN})_4]^{2-}$ ion with square planar structure is diamagnetic and the $[\text{NiCl}_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Ans. $[\text{Ni}(\text{CN})_4]^{2-}$ square planar geometry and dsp^2 hybridization.
 $[\text{NiCl}_4]^{2-}$ Tetrahedral geometry and sp^3 hybridization.

4. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is strongly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic. Explain.

Ans. In both the complexes, Fe is in +3 oxidation state.

CN^- is a strong field ligand, inner d-orbitals are involved, d^2sp^3 hybridization, one unpaired electron, weakly paramagnetic.

H_2O is weak field ligand, outer d-orbitals are involved, sp^3d^2 hybridization, five unpaired electrons, strongly paramagnetic.

5. Explain $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

Ans. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex, d^2sp^3 hybridization. $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex, sp^3d^2 hybridization.

SECTION C

SHORT ANSWER TYPE QUESTIONS (3 Marks Each)

1. Write the types of isomerism exhibited by the following complexes:

(i) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$

(ii) $[\text{Co}(\text{en})_3]^{3+}$

(iii) $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$

Answer:

(i) Ionization isomerism

(ii) Optical isomerism

(iii) Coordination isomerism

2. Answer the following questions:

(i) What type of isomerism is shown by $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$?

(ii) On the basis of CFT, write the electronic configuration for d^4 ion if $\Delta_o < P$.

(iii) Write the hybridization and shape of $[\text{Fe}(\text{CN})_6]^{3-}$. (Atomic number of Fe =

26)

Answer:

(i) Linkage isomerism

(ii) $t_{2g}^3 e_g^1$

(iii) d^2sp^3 , octahedral shape.

3. (a) Write the hybridization and shape of the following complexes:

(i) $[\text{CoF}_6]^{3-}$

(ii) $[\text{Ni}(\text{CN})_4]^{2-}$

(b) Out of NH_3 and CO , which ligand forms a more stable complex with a transition metal and why?

Answer:

(a) (i) sp^3d^2 , octahedral (ii) dsp^2 , square planar.

(b) CO can form a more stable complex than NH_3 because it is the strongest ligand and can form both a sigma as well as pi-bond (synergic bonding or back bonding).

4. What is meant by crystal field splitting energy? On the basis of crystal field theory, write the electronic configuration of d^6 in terms of t_{2g} and e_g in an octahedral field when

(i) $\Delta_o > P$ (ii) $\Delta_o < P$

Answer:

The difference between energies of two sets of d-orbitals t_{2g} and e_g is called crystal field splitting energy (Δ_o).

(i) If $\Delta_o > P$, the configuration will be $t_{2g}^6 e_g^0$. Ligands will produce a strong field and a low spin complex will be formed.

(ii) If $\Delta_o < P$, the configuration will be $t_{2g}^4 e_g^2$. Ligands will produce a weak field and a high spin complex will be formed.

SECTION D

CASE STUDY BASED QUESTIONS (4 Marks Each)

PASSAGE 1

Werner, a Swiss chemist in 1892 prepared and characterized a large number of coordination compounds and studied their physical and chemical behavior. He proposed that, in coordination compounds, metals possess two types of valencies, viz. primary; valencies, which are normally ionisable and secondary valencies which are non-ionisable. In a series of compounds of cobalt (III) chloride with ammonia, it was found that some of the chloride ions could be precipitated as AgCl on adding excess AgNO_3 solution in cold, but some remained in solution. The number of ions furnished by a complex in a solution can be determined by precipitation reactions. The measurement of molar conductance of solutions of coordination compounds helps to estimate the number of ions furnished by the compound in solution.

1. The primary and secondary valency of cobalt in $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ is
a. +3 and 3 b. +3 and 6 c. 0 and 3 d. 0 and 6
- Answer: b**
2. The formula of the complex that requires 2 mol of AgNO_3 to precipitate chloride ions is
a. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ b. $[\text{Co}(\text{NH}_3)_3\text{Cl}_2]\text{Cl}$
c. $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ d. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Answer: d

3. The ionic conductivity of which of the following complex will be maximum
 a. $K_4[Fe(CN)_6]$ b. $[Co(NH_3)_6]Cl_3$
 c. $[Cu(NH_3)_4]Cl_2$ d. $[Ni(CO)_4]$

Answer: a

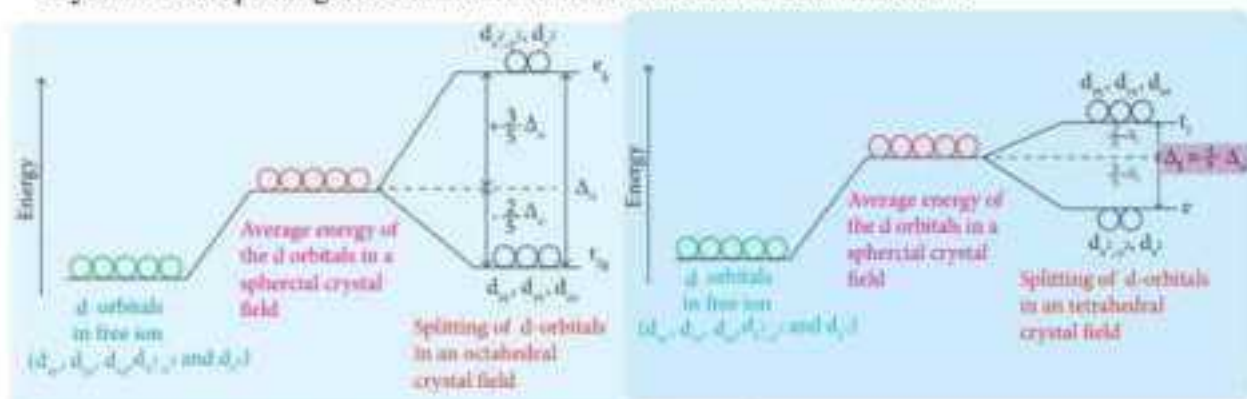
4. The aqueous solution of which complex will have least osmotic pressure
 a. $K_4[Fe(CN)_6]$ b. $[Co(NH_3)_6]Cl_3$
 c. $[Cu(NH_3)_4]Cl_2$ d. $[Ni(CO)_4]$

Answer: d

PASSAGE 2

Coordination compound consists of a metal atom or ion at the centre, surrounded by a number of oppositely charged ions or neutral molecules. A coordinate connection connects these ions or molecules to the metal atom or ion. When dissolved in water, they do not dissociate into simple ions. H. Bethe and V. Bleck proposed the crystal field theory (CFT). This theory describes metal complexes' bonding, characteristics, electronic spectra, and magnetism in greater detail. **Crystal field splitting is the conversion of five degenerate d-orbitals of a metal ion into different sets of orbitals with varying energies in the presence of a crystal field of ligands.** The type of the ligand determines the crystal field splitting. Weak field ligands are ligands that cause just a minor crystal field splitting. Strong field ligands are ligands that generate a high crystal field splitting. The **spectrochemical series** is the grouping of common ligands in ascending order of crystal field splitting (Δ).

Factors Affecting the Magnitude of Orbital Splitting Energy (Δ) are oxidation state and coordination number of central ion, nature of ligand and type of crystal field. The Crystal Field Splitting for Octahedral and Tetrahedral is shown below:



1. Crystal field stabilization energy for high spin d^4 octahedral complex is:
 a. $-1.8 \Delta_o$ b. $-1.6 \Delta_o$ c. $-1.2 \Delta_o$ d. $-0.6 \Delta_o$

Answer d. $-0.6 \Delta_o$

2. What will be CFSE for the d^6 high spin complex for both tetrahedral and octahedral complexes?
 a. 0.6, 0.6 b. 0.4, 0.4 c. 0.4, 0.6 d. 0.6, 0.4

Answer c. $-0.6, 0.6$

3. Strong field ligands such as CN^- :
- usually produce high spin complexes and small crystal field splittings.
 - usually produce low spin complexes and small crystal field splittings.
 - usually produce low spin complexes and high crystal field splittings.
 - usually produce high spin complexes and high crystal field splittings.

Answer c

4. According to crystal field theory which of the following is true:
- The order of increasing field strength of ligands is $\text{F}^- > \text{H}_2\text{O} > \text{NH}_3$.
 - If pairing energy exceeds the magnitude of crystal field splitting, then pairing occurs.
 - d^2 to d^7 coordination entities are more stable for the strong field than weak field cases.
 - Tetrahedral complexes have sufficiently large splitting energy to force pairing, and

Answer c

5. Which of the following compounds is paramagnetic?
- Hexa amine chromium (III) ion
 - Tetraamminezinc (II) ion
 - Tetracyanonickelate (II) ion
 - Diammine silver (I) ion

Answer a

SECTION E

LONG ANSWER TYPE QUESTIONS (5 Marks Each)

1. State a reason for each of the following situations:
- Co^{2+} is easily oxidized to Co^{3+} in presence of a strong ligand.
 - CO is a stronger complexing reagent than NH_3 .
 - The molecular shape of $\text{Ni}(\text{CO})_4$ is not the same as that of $[\text{Ni}(\text{CN})_4]^{2-}$.
 - Nickel (II) does not form low spin octahedral complexes.
 - $[\text{Fe}(\text{CN})_6]^{4-}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ are of different colors in dilute solutions.

Answer:

- Strong ligands provide energy which overcomes 3rd ionization enthalpy and Co^{2+} gets oxidized to Co^{3+} .
- CO can form a sigma as well as pi bond, therefore, it is a stronger ligand than NH_3 which can form only a sigma bond.
- $\text{Ni}(\text{CO})_4$ has sp^3 hybridization, tetrahedral shape, whereas $[\text{Ni}(\text{CN})_4]^{2-}$ has dsp^2 hybridization, therefore, it has a square planar shape.
- Ni^{2+} has unpaired electrons, therefore, forms a high spin complex as pairing of electrons does not take place because after pairing only one d-orbital will be left which cannot be used in an octahedral complex.
- They absorb different wavelengths from visible light, undergo d-d transitions and radiate complementary colour. CN^- is a stronger ligand than H_2O and causes more splitting of d-orbitals of central metal in the octahedral field.

2. For the complex $[\text{FeCl}_2(\text{en})_2]\text{Cl}$, identify the following:
- Oxidation Number and Coordination Number of Central Atom
 - Hybridization and Geometry of Complex
 - Magnetic behavior and Magnetic Moment of the complex.
 - Isomerism exhibited by the complex
 - IUPAC Name of the complex.

Answer:

(i) +3 and 6

(ii) d^2sp^3 , octahedral

(iii) paramagnetic and magnetic moment $= \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$

(iv) Geometrical and Optical Isomerism

(v) Dichloridobis-(ethane-1, 2-diamine)iron(III) chloride

3. Compare the following complexes with respect to hybridization, structural shapes and magnetic behavior : $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Ni}(\text{CO})_4]$
(At. Nos.: Co = 27, Cr = 24, Ni = 28)

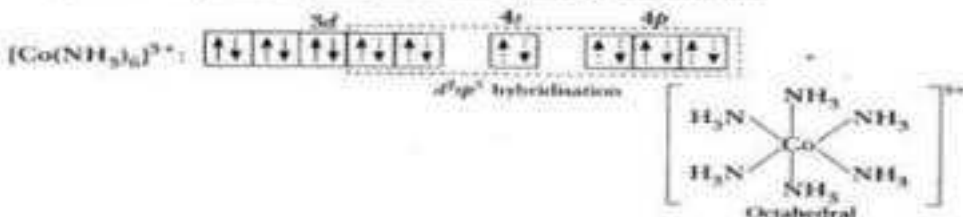
Answer

In $[\text{Co}(\text{NH}_3)_6]^{3+}$,

Electronic configuration of Co(27): $[\text{Ar}] 4s^2 3d^7$

Electronic configuration of Co^{3+} (27): $[\text{Ar}] 4s^0 3d^6$

NH_3 is a strong field ligand, will cause pairing of electrons.

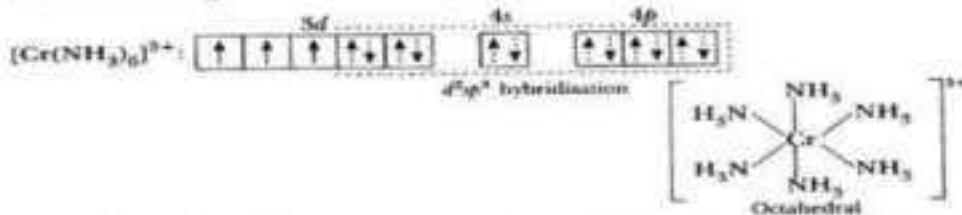


It has d^2sp^3 hybridisation, octahedral shape and diamagnetic in nature.

In $[\text{Cr}(\text{NH}_3)_6]^{3+}$,

Electronic configuration of Cr(24) : $[\text{Ar}] 4s^1 3d^5$

Electronic configuration of Cr^{3+} : $[\text{Ar}] 4s^0 3d^3$

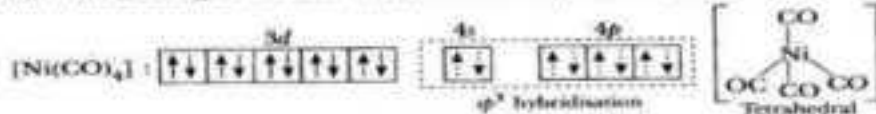


It has d^2sp^3 hybridisation, octahedral shape and paramagnetic in nature.

In $[\text{Ni}(\text{CO})_4]$,

Electronic configuration of Ni(28) in ground state : $[\text{Ar}] 4s^2 3d^8$

Electronic configuration of Ni(28) in exciting state : $[\text{Ar}] 4s^0 3d^{10}$



It has sp^3 hybridisation, tetrahedral shape and diamagnetic in nature.

CHAPTER-6-(HALOALKANES & HALOARENES)

PART – 1 (GENERAL INTRODUCTION)

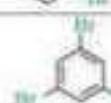
➤ Hydrogen atom of aliphatic or aromatic hydrocarbon is replaced by halogen atom.

➤ $R-X$ (Haloalkane) & C_6H_5-X (Haloarene)

❖ **CLASSIFICATION OF HALOALKANE:-** On the basis of number of halogen atoms.

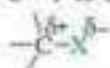
HALOALKANES			
Monohaloalkane		Dihaloalkane	Trihaloalkane
Polyhaloalkane	Primary	Secondary	Tertiary
ALLYLIC HALIDES	BENZYLIC HALIDE	VINYLIC HALIDES	ARYL HALIDES
The compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to carbon-carbon double bond ($C=C$) is called	The compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom next to an aromatic ring, is called	The compounds in which the halogen atom is bonded to an sp^2 -hybridised carbon atom of a carbon-carbon double bond ($C=C$) is called	The compounds in which the halogen atom is bonded to an sp^2 -hybridised carbon atom of an aromatic ring, is called.. (also called Haloarenes)
 		 	

❖ **COMMON AND IUPAC NAME OF SOME HALOALKANES AND ITS CLASSIFICATION:-**

S.	EXAMPLES	COMMON NAME	IUPAC NAME	TYPES
1	$CH_3CH_2CH_2Br$	n-Propyl bromide	1-Bromopropane	Alkylhalide, primary
2	$CH_3CH(Br)CH_3$	Iso-Propyl bromide	2-Bromopropane	Alkylhalide, secondary
3	$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane	Alkylhalide, secondary
4	$(CH_3)_2CHCH_2Cl$	Iso-butyl chloride	1-Chloro-2-methyl propane	Alkylhalide, Primary
5	$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane	Alkylhalide, Primary
6	$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane	Alkylhalide, Tertiary
7	$CH_2=CHCl$	Vinyl chloride	Chloroethene	Vinyl halide
8	$CH_2=CHCH_2Br$	Allyl bromide	3-Bromopropene	Allylic halide
9	CH_2Cl_2	Methylene chloride	Dichloromethane	Dihaloalkane
10	CH_3-CHCl_2	Ethylidene chloride	1,1-Dichloroethane	Gem dihalide
11	CH_2-CH_2 Cl Cl	Ethylene dichloride	1,2-Dichloroethane	Vic dihalide
12	$CHCl_3$	Chloroform	Trichloromethane	Trihaloalkane
13	CCl_4	Carbon tetrachloride	Tetrachloromethane	Tetrahaloalkane
14		Bromobenzene	Bromobenzene	Aryl halide
15		m-Dibromobenzene	1,3-Dibromobenzene	Aryl halide
16		Sym-Tribromobenzene	1,3,5-Tribromobenzene	Aryl halide

17		o-Chlorotoluene	1-Chloro-2-methylbenzene Or 2-Chlorotoluene	Aryl halide
18		Benzyl chloride	Chlorophenylmethane	Benzylic halide

- ♦ **NATURE OF C-X BOND:-** Since halogen atoms are more electronegative than carbon, the carbon—halogen bond of alkyl halide is polarised; the carbon atom bears a partial positive charge whereas the halogen atom bears a partial negative charge. Carbon—halogen bond length increases from C—F to C—I. Consequently Carbon—halogen bond enthalpy decreases from C—F to C—I.

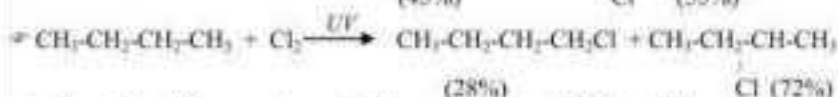
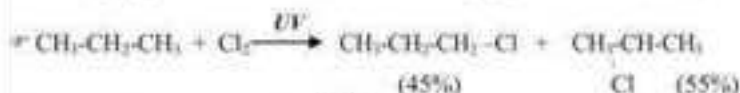
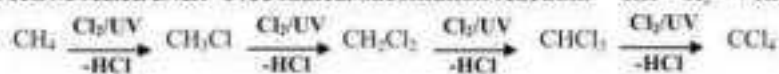


PART - 2 (NAME REACTION & CHEMICAL TEST)

1	WURTZ REACTION:- $2\text{RCl} + 2\text{Na} \rightarrow \text{RR} + 2\text{NaCl}$ WURTZ-FITTIG REACTION $\text{C}_6\text{H}_5\text{Cl} + 2\text{Na} + \text{RCl} \xrightarrow{\text{Dry Ether}} \text{C}_6\text{H}_5\text{R} + 2\text{NaCl}$ FITTIG REACTION:- $2\text{C}_6\text{H}_5\text{Cl} + 2\text{Na} \xrightarrow{\text{Dry Ether}} \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + 2\text{NaCl}$ FRANKLAND REACTION:- $2\text{RI} + \text{Zn} \rightarrow \text{RR} + \text{ZnI}_2$	
2	FINKELSTEIN REACTION:- $\text{R-X} + \text{NaI} \xrightarrow{\text{Dry Acetone}} \text{R-I} + \text{NaX}$ (Here X = Cl & Br) The reaction takes place by SN² mechanism. ➤ Sodium chloride and Sodium bromide being less soluble in acetone get precipitated from the solution & can be removed by filtration. SWARTS REACTION:- $\text{R-X} + \text{AgF} \rightarrow \text{R-F} + \text{AgX}$ (Here X = Cl & Br)	
3	DIAZOTIZATION:- $\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{0-5^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{NaCl} + 2\text{H}_2\text{O}$	
4	SANDMEYERS REACTION:- $\text{C}_6\text{H}_5\text{N}_2\text{X} + \text{HX} \xrightarrow{\text{Cu}_2\text{X}_2} \text{C}_6\text{H}_5\text{Cl} + \text{N}_2 + \text{HX}$ (X = Cl, Br) Noted:- If Cu powder is used instead of Cu_2X_2 then the reaction is called GATTERMAN REⁿ. BALZ-SCHIEHMANN REACTION:- $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{HBF}_4 \rightarrow \text{C}_6\text{H}_5\text{N}_2\text{BF}_4 \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{F} + \text{N}_2 + \text{BF}_3$	
5	HUNSDIECKER REACTION:- $\text{CH}_3\text{COOAg} + \text{Br}_2 \xrightarrow{\text{CCl}_4} \text{CH}_3\text{CH}_2\text{Br} + \text{AgBr} + \text{CO}_2$ The yield of halide is Primary > Secondary > Tertiary & bromine is generally used. ➤ Iodoalkanes cannot be prepared by this reaction b/c ester can be formed instead of iodoalkanes. $2\text{CH}_3\text{COOAg} + \text{I}_2 \xrightarrow{\text{CCl}_4} \text{CH}_3\text{COOCH}_3 + 2\text{AgI} + \text{CO}_2$ (Birbaum Simonini reaction)	

PART - 3A (PREPARATION OF HALOALKANES & HALOARENES)

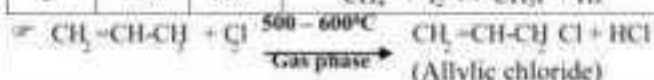
1 FROM ALKANE:- Free radical substitution reaction. $RH + X_2 \rightarrow RX + HX$



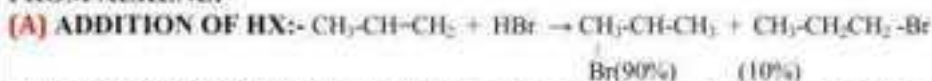
Therefore, halogenations of alkanes are not suitable for laboratory preparation of haloalkanes. This is mainly b/c a mixture of different isomeric mono & polyhaloalkanes are formed which are difficult to separate. Consequently, the yield of any one compound is low.

Note:- The relative amounts of these isomeric Haloalkanes depend upon the nature of the halogen (Cl_2 or Br_2) & the number & type of the hydrogen (1° , 2° or 3°) being substituted. The order of substitution of various hydrogen's are:- $3^\circ > 2^\circ > 1^\circ$

H Atom	X - Cl	X - Br	➤ Fluorination is highly exothermic & violent. This leads to polysubstitution & results into cleavage of C—C bonds. ➤ Iodination is reversible but it may be carried out in the presence of an oxidizing agent such as HIO_3 , HNO_3 etc. $CH_4 + I_2 \rightleftharpoons CH_3I + HI$ $5HI + HNO_3 \rightarrow 3I_2 + 3H_2O$
1°	1	1	
2°	3.8	82	
3°	5.0	1600	



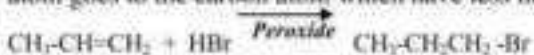
2 FROM ALKENE:-



MARKOVNIKOV'S RULE:- According to this rule, during the addition of halogen acid to unsymmetrical alkenes the hydrogen atom goes to the carbon atom which have more number of hydrogen atoms.

ANTIMARKOVNIKOV'S RULE/PEROXIDE EFFECT/KHARASCH EFFECT:- The addition of

HBr to unsymmetrical alkenes in the presence of peroxide ($C_6H_5CO-O-O-COC_6H_5$), the hydrogen atom goes to the carbon atom which have less number of hydrogen atoms.



Noted:- The anti Markovnikov's rule applies to the addition of HBr only and not to the addition of HI or HCl.

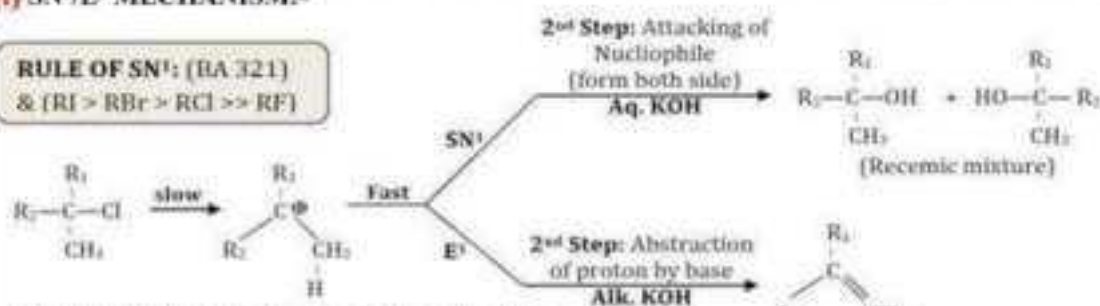


In this reaction, the brown colour of bromine gets discharged due to the formation of vic- dibromide, which is colourless. This is the important test for the detection of double bond.

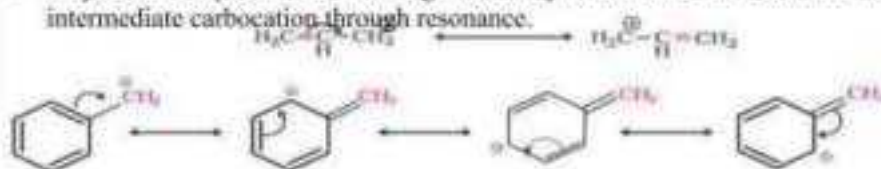
PART – 3B (CHEMICAL PROPERTIES OF HALOALKANES & HALOARENES)

A NUCLEOPHILIC SUBSTITUTION (SN¹, SN² & SNAR) AND ELIMINATION (E¹, E² & E¹CB):- (I) SN¹/E¹ MECHANISM:-

RULE OF SN¹: (BA 321)
 & {RI > RBr > RCl >> RF}

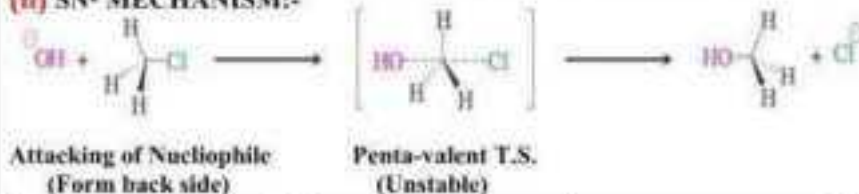


- Reactivity of alkyl halides towards SN¹ reaction:- The order of reactivity depends upon the stability of carbocation in the first step. Greater the stability of carbocation, greater will be its ease of formation from alkyl halide & faster will be the rate of the reaction.
- Benzylic halide > Allylic halide > tert. Halide > sec. halide > pri. Halide.
- EXAMPLES:- C₆H₅C(CH₃)(C₆H₅)Br > C₆H₅CH(C₆H₅)Br > C₆H₅CH(CH₃)Br > C₆H₅CH₂Br
- Allylic & Benzylic halide show high reactivity towards the SN¹ reaction due to stabilization of intermediate carbocation through resonance.



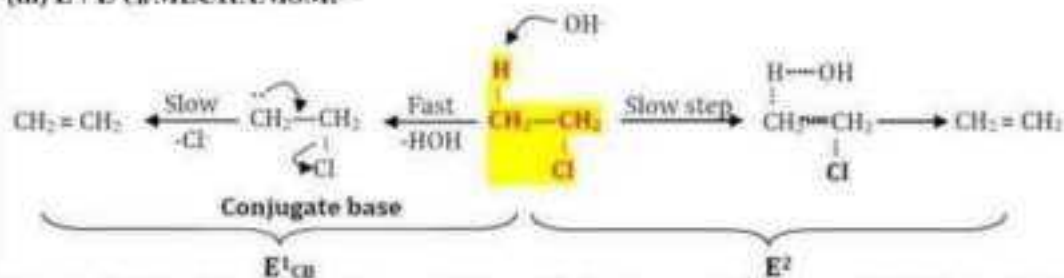
(Resonance stabilization of Allylic & Benzylic carbocation)

(II) SN² MECHANISM:-

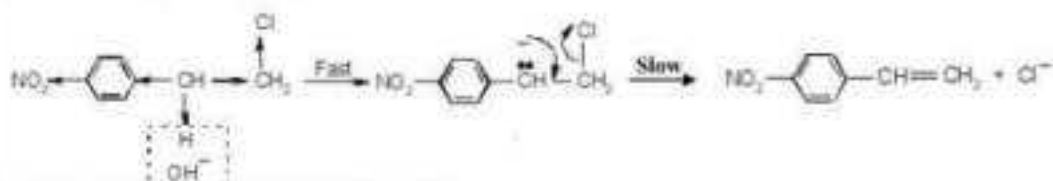


SN ¹ REACTION	SN ² REACTION
① Only one molecule is involved in rate determining step.	① Two molecules are involved in rate determining step.
② 3 ^o alkyl halide show SN ¹ reaction.	② 1 ^o alkyl halide show SN ¹ reaction.
③ Carbocation is formed as a intermediate.	③ Pentavalent T.S. is formed.
④ Nucleophile attack at the carbocation from both side.	④ Nucleophile attack from back side.
⑤ Racemic mixture is obtained.	⑤ Valden inversion is obtained.
⑥ The reaction is take place in polar medium.	⑥ take place in non polar medium.
⑦ SN ¹ reaction take place in two steps	⑦ SN ¹ reaction take place in one steps

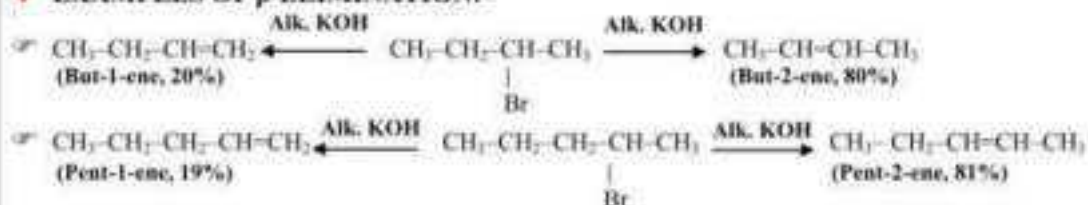
(iii) E^2/E^1_{CB} MECHANISM:-



Noted:- In E^1_{CB} Substrate must be containing acidic hydrogens & Presence of EWG (-m) at β -C. (EWG = $-\text{NO}_2$, $>\text{C}=\text{O}$, $-\text{CN}$)



❖ **EXAMPLES OF β -ELIMINATION:-**



SAYTZEFF RULE:- If there is of more than one possibility of formation alkene during dehydrohalogenation of Haloalkanes, the Alkene obtained as a major product which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

❖ **SOME IMPORTANT EXAMPLES OF NUCLEOPHILIC SUBSTITUTION REACTION:-**

- REACTION WITH KCN/NaCN & AgCN:-** $\text{R-X} + \text{KCN/NaCN} \rightarrow \text{R-CN}$ While $\text{R-X} + \text{AgCN} \rightarrow \text{R-NC}$. KCN is predominantly ionic and provides cyanide ions (act as an ambident nucleophile) in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom & not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.
- REACTION WITH $\text{KNO}_2/\text{NaNO}_2$ & AgNO_2 :-** $\text{R-X} + \text{KNO}_2 \rightarrow \text{R-O-N=O}$ & $\text{R-X} + \text{AgNO}_2 \rightarrow \text{R-NO}_2$
- REACTION WITH Aq. KOH/NaOH & ALK. KOH/NaOH:-** Aq. KOH produces hydroxide ions which act as strong nucleophiles. Hence undergo substitution to form alcohol. While alcoholic KOH gives alkoxide ion which is a strong base. It abstract β -hydrogen atom from Alkylhalide and give alkene.
- REACTION WITH RCOOAg :-** $\text{R-X} + \text{RCOOAg} \rightarrow \text{RCOOR} + \text{AgX}$
- REACTION WITH AMINES:-** $\text{R-X} + \text{NH}_3 \rightarrow \text{R-NH}_2 + \text{HX}$
- REACTION WITH NaOR:-** $\text{R-X} + \text{NaOR} \rightarrow \text{R-O-R} + \text{NaX}$

B NUCLEOPHILIC SUBSTITUTION REACTION IN HALO ARENES:-



Aryl & vinyl halides do not undergo $\text{S}_{\text{N}}1$ nucleophilic substitution due to the following reasons:-

① **Resonance effect:-** C—Cl bond in Haloarenes & vinyl halides acquires a partial double bond character due to resonance.



② **Difference in hybridization states of carbon atoms in C—X bond:-**



③ Phenyl cation not be stabilized by resonance.

④ **Repulsion between the electron rich attacking nucleophiles & electron rich arenes.**

⑤ Back-side attack required for $\text{S}_{\text{N}}2$ reaction is blocked in aryl halides

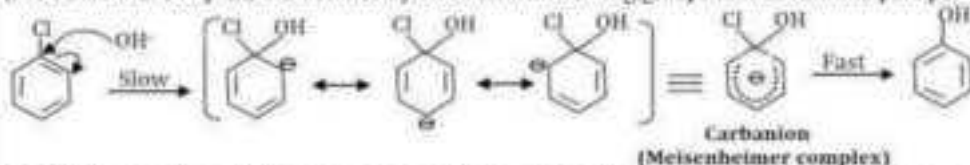


Noted:- However, under drastic conditions, Haloarenes undergo substitution reactions by $\text{S}_{\text{N}}1$, $\text{S}_{\text{N}}2$ & Benzyne mechanism.

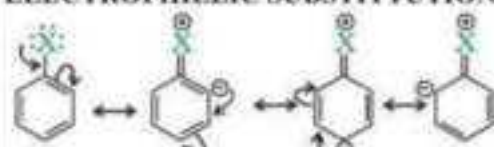
BIMOLECULAR SUBSTITUTION (Nucleophilic Aromatic Substitution by Addition-Elimination): The $\text{S}_{\text{N}}\text{Ar}$ Mechanism:- It is a I_{pso} substitution.



MECHANISM:- The reaction occurs through an addition-elimination mechanism. Intermediate carbanion (Meisenheimer complex) is stabilized by electron-withdrawing groups in the ortho and para positions

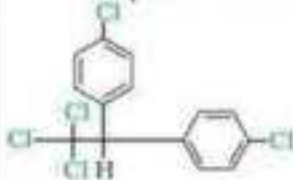


Noted:- In case of *m*-nitrobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the $-\text{NO}_2$ group. Therefore, the presence of nitro group at *meta*-position does not stabilize the negative charge & no effect on reactivity is observed by the presence of $-\text{NO}_2$ group at *meta*-position.

C	REACTION WITH METALS:- FORMATION OF ORGANO-METALLIC COMPOUNDS. Compounds having carbon-metal bonds are known as organo-metallic compounds. An important example of organo-metallic compound is alkyl magnesium halide (RMgX), prepared by Victor Grignard in 1900, and is also known as Grignard Reagents. $\text{CH}_3\text{CH}_2\text{I} + \text{Mg} \xrightarrow{\text{dry ether}} \text{CH}_3\text{CH}_2\text{MgI}$ Grignard reagents are highly reactive and react with active hydrogen containing compound (Like water, alcohol, ammonia, amine etc.) and give corresponding hydrocarbons. $\text{RMgX} + \text{H}_2\text{O} \longrightarrow \text{RH} + \text{Mg(OH)X}$
D	ELECTROPHILIC SUBSTITUTION REACTION IN HALOARENES:- 

PART – 4 : (PHYSICAL PROPERTIES & POLYHALOGEN COMPOUNDS)

	❖ PHYSICAL PROPERTIES 1. Alkyl halides are insoluble in water but soluble in organic solvents. 2. Decreasing order of their densities is: Iodide > Bromide > Chloride > Fluoride 3. Decreasing order of their boiling points for the same alkyl or aryl group is: Iodide > Bromide > Chloride > Fluoride 4. Their stability order is: $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$ (since C — X bond strength decreases in the same order.) 5. Alkyl halides are insoluble in water although it has polar nature.
	POLYHALOGEN COMPOUNDS
1	DICHLOROMETHANE (METHYLENE CHLORIDE):- It is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.
2	TRICHLOROMETHANE (CHLOROFORM):- It is used as a solvent for fats, alkaloids, iodine and other substances. It is also used in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform. Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out. $2\text{CHCl}_3 + \text{O}_2 \xrightarrow{\text{light}} 2\text{COCl}_2 + 2\text{HCl}$

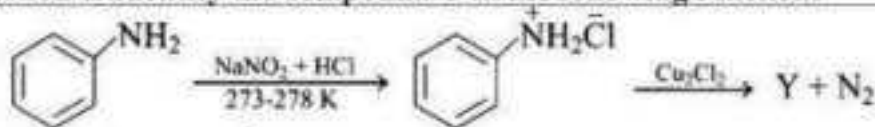
3	TRIODOMETHANE (IODOFORM):- It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.
4	TETRACHLOROMETHANE (CARBON TETRACHLORIDE):- It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl_4 can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer.
	Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.
5	FREONS:- The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon-12 (CCl_2F_2) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.
6	<i>p,p'</i>-DICHLORODIPHENYLTRICHLOROETHANE(DDT):- DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world. 

**QUESTION BANK : CHAPTER- HALOALKANE AND
HALOARENE HALOALKANE AND HALOARENE**

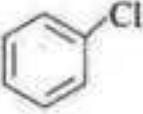
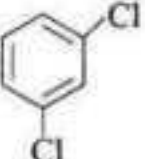
SECTION -A

MULTIPLE CHOICE QUESTIONS (1M each)

Question 1. Identify the compound Y in the following reaction:

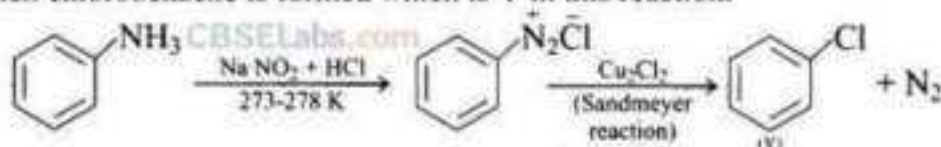


CBSE Labs.com

- (a)  (b)  (c)  (d) 

Solution: (a) When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid and treated with sodium nitrite, a diazonium salt is formed. When this freshly prepared diazonium salt is mixed with cuprous chloride, diazonium group is replaced by -Cl.

Then chlorobenzene is formed which is Y in this reaction.



Q2) Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

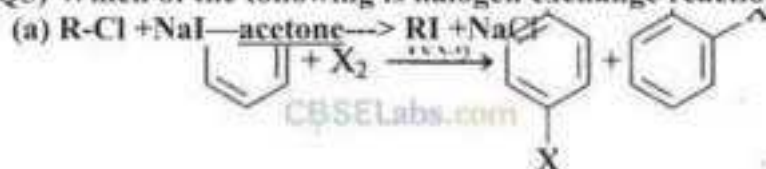
- (a) electrophilic elimination reaction
(b) electrophilic substitution reaction
(c) free radical addition reaction
(d) nucleophilic substitution reaction

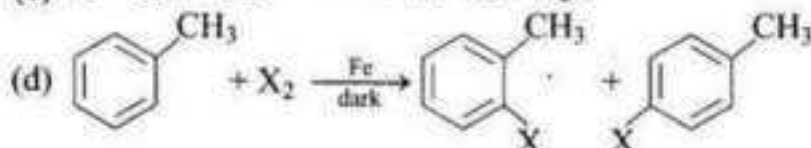
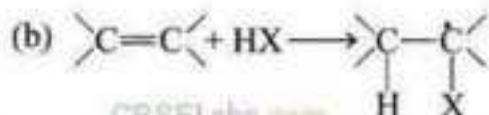
solution. (b)

This is an example of electrophilic substitution reaction.

10)

Q3) Which of the following is halogen exchange reaction?





Solution: (a) Halogen exchange reaction are those reactions in which one halide replaces another. This reaction is known as Finkelstein reaction.

In

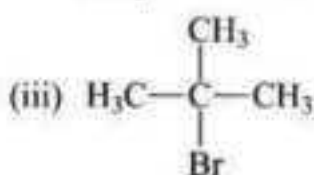
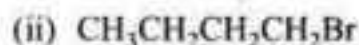
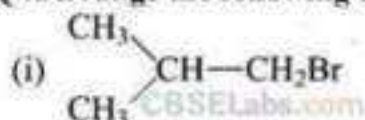
(a) Halogen (-X) is replaced by iodine

(b) Addition of hydrogen halide on alkene

(c) Halogen replaces alcoholic group

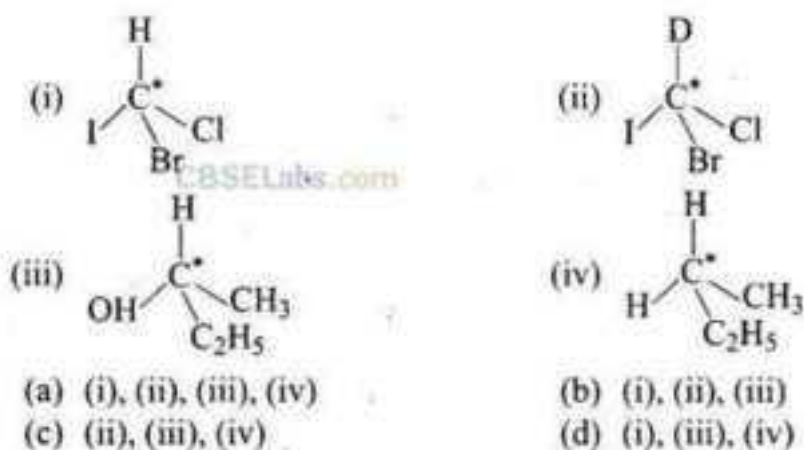
(d) Halogen replaces the hydrogen of benzoic ring

Q4. Arrange the following compounds in increasing order of their boiling points



Solution: (c) Boiling points of isomeric haloalkanes decrease with increase in branching as with increase in branching surface area decreases which leads to decrease in intermolecular forces.

Question 5. In which of the following molecules carbon atom marked with asterisk (*) is Asymmetric ?



Solution: (b) Asymmetric/chiral carbon atom is that in which all of its four valencies with four different groups or atoms.

In molecules (i), (ii) and (iii), all have asymmetric carbon as each carbon has satisfied all four valencies with four different groups or atoms.

In molecule (iv), carbon satisfies two of its valencies with two hydrogen atoms i.e., similar atom. So, it is not an asymmetric carbon atom.

Question 6. A primary alkyl halide would prefer to undergo.

- (a) S_N^1 reaction (b) S_N^2 reaction
(c) α -Elimination (d) Racemisation

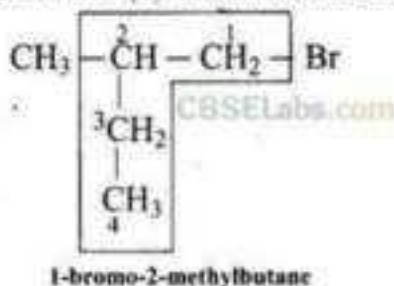
Solution: (b) S_N^2 reaction proceeds via formation of transition state which is formed easily in primary alkyl halide due to less steric hindrance

Question 7

Which is the correct IUPAC name of $\text{CH}_3-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_2-\text{Br}$?

- (a) 1-Bromo-2-ethylpropane
(b) 1-Bromo-2-ethyl-2-methylethane
(c) 1-Bromo-2-methylbutane
(d) 2-Methyl-1-bromobutane

Solution: (c) The correct IUPAC name of the given compound is

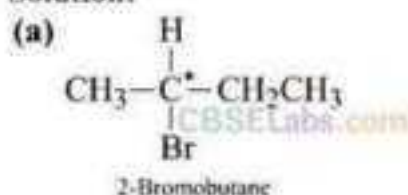


Q8) Molecules whose mirror image is non superimposable over them are known

as chiral. Which of the following molecule is chiral in nature?

- (a) 2-Bromobutane (b) 1-Bromobutane
(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

Solution:



Q 9. Reaction of $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ with aqueous sodium hydroxide follows

- (a) S_N^1 mechanism
(b) S_N^2 mechanism
(c) any of the above two depending upon the temperature of reaction
(d) Saytzeff rule

Solution: (a) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ will follow S_N^1 mechanism on reaction with aqueous sodium hydroxide since the carbocation formed $\text{C}_6\text{H}_5\text{CH}_2^+$ is a resonance stabilized cation.

Benzylic halides show high reactivity towards the S_N^1 reaction.

The carbocation thus formed gets stabilized through resonance as shown in the structure.



Q10 which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

- (i) $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \text{Br}$ (ii) $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\underset{|}{\overset{\text{Br}}{\text{C}}}} - \text{CH}_3$
(iii) $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \text{CH}_2\text{Br}$

- (a) (i) (b) (i), (ii), (iii) (c) (ii), (iii) (d) (i), (iii)

Solution:

(a) $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\underset{|}{\text{CH}}} - \text{Br}$ will give a racemic mixture on nucleophilic substitution

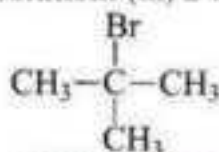
by OH^- ion since the alkyl halide has a chiral carbon atom. During the $\text{S}_\text{N}1$ reaction a mixture of enantiomers is formed which are present in equal proportions.

Q11. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

- (i) 1-Bromobutane (ii) 2-Bromobutane

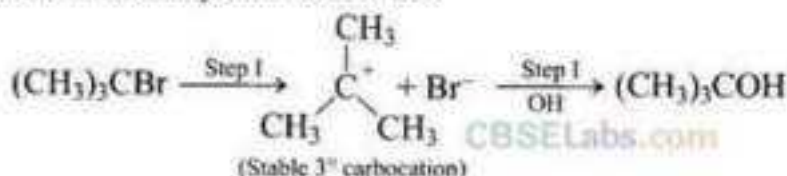
(iii) 2-Bromo-2-methylpropane (iv) 2-Chlorobutane

Solution: (iii) 2-Bromo-2-methylpropane



CBSE Labs.com

will react the aqueous KOH most easily because the carbocation formed during the reaction is tertiary and most stable.



CBSE Labs.com

ASSERTION-REASONING QUESTIONS

Directions: These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

Q.1. Assertion : SN^2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.

Reason : SN^2 reactions always proceed with inversion of configuration.

Answer (d) Assertion is false, because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. However Reason is true

Q2Assertion : Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.

Reason : Alkyl halides are less reactive than acyl halides.

Answer (c) Alkyl halides give polyalkylation products.

Q3Assertion : CHCl_3 is stored in dark bottles.

Reason : CHCl_3 is oxidised in dark.

Answer(c) CHCl_3 is stored in dark bottles to prevent oxidation of CHCl_3 in presence of sunlight. It forms a poisonous Phosgene gas COCl_2 .

Q4Assertion : Exposure of ultraviolet rays to human causes the skin cancer, disorder and disrupt the immune system.

Reason : Carbon tetrachloride is released into air it rises to atmosphere and deplets the ozone layer

Answer(b) Carbon tetrachloride rises to atmosphere and deplete the ozone layer. This depletion of ozone layer increases exposure of UV rays to human being which lead to increase of skin cancer, eye diseases and disorder with disruption of the immune system

Q5 Assertion: S_N2 reaction proceeds with inversion of configuration.

Reason: S_N2 reaction occurs in one step

Answer : A

Q6. Assertion: Treatment of chloroethane with a saturated solution of AgCN gives ethyl isocyanide as a major product.

Reason: Cyanide ion (CN^-) is an ambident nucleophile.

Answer : B

Q7) Assertion : Thionyl chloride are preferred over Hydrogen halides (HX) for the preparation of alkyl halides from alcohols .

Reason : Gaseous side products are formed in case of thionyl chloride

Answer : A

Q8) Assertion : S_N2 mechanism leads to inversion of configuration .

Reason : As in this mechanism optical activity is lost .

Answer : C Assertion is correct but reason is incorrect statement.

Q9) Assertion : Haloalkanes are sparingly soluble in water.

Reason : As haloalkanes do not form hydrogen bonds with water

Answer : B

Q10) Assertion : Propene reacts with HBr to form 2-bromo propane .

Reason : As intermediate formed carbocation is secondary which is more stable than primary .

Answer : A

Q11) Assertion : Grignard reagent should be prepared in dry ether.

Reason : Grignard reagent reacts with water to form R-H (Alkane)

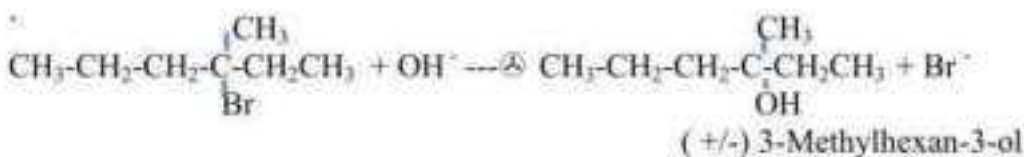
Answer : A

SECTION-B (Very short Answer type ques. 2M each.)

Q1) An optically active compound having molecular formula $C_7H_{15}Br$ react with aqueous KOH to give a racemic mixture of products. Write the mechanism in this reaction.

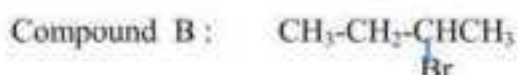
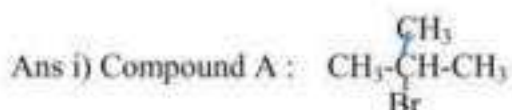
Answer : Since the optically active compound having $C_7H_{15}Br$ reacts with KOH from a racemic mixture , therefore must be tertiary alkyl halide and the reaction will follow

SN1 mechanism.



Q2) Compound 'A' with molecular formula C₄H₉Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

- i) Write down the structural formula of both compound ;A; ans B.
- ii) Out of these two compounds, which one will be converted to the product with inverted configuration?



(ii).A

Q3) Give reason.

a) n - Butyl bromide has higher boiling point than t- butyl bromide.

Ans: Its is because n- butyl bromide has more surface area than t- butyl bromide, therefore more van der Waal's forces of attraction, hence higher boiling point.

b) The presence of nitro group at ortho and para position increases the reactivity of haloarenes towards nucleophilic substitution reaction.

Ans: -NO₂ group stabilizes the negatively (-ve) charged ion formed during nucleophilic substitution reaction of haloarenes, therefore reactivity increases.

Q4) Write the main product when.

a) 2,4,6-Tri nitrochlorobenzene is subjected to hydrolysis.

Ans: Picric acid (2,4,6- Trinitro phenol)

b) Methyl chloride is treated with AgCN.

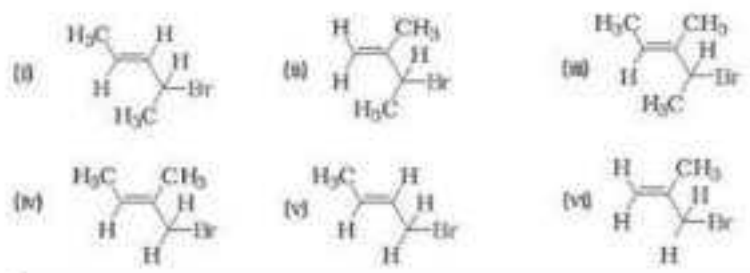
Ans: methyl isocyanide

Q5) Answer the following-Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH.and why ?

Ans: $C_6H_5CHClC_6H_5$ will get hydrolysed easily because carbocation formed will be stabilized more by resonance due to the presence of two phenyl groups.

SECTION -C (short answer type question 3M each)

Q2. Write IUPAC names of the following:



Ans.

- (i) 4-Bromopent-2-ene
- (ii) 3-Bromo-2-methylbut-1-ene
- (iii) 4-Bromo-3-methylpent-2-ene
- (iv) 1-Bromo-2-methylbut-2-ene
- (v) 1-Bromobut-2-ene
- (vi) 3-Bromo-2-methylpropene

1. Give reasons for the following:

- i) Benzyl chloride is highly reactive towards the S_N1 reaction.**
- ii) 2-bromobutane is optically active but 1-bromobutane is optically inactive.**
- iii) Electrophilic reactions in haloarenes occurs slowly.**

Ans.i) Benzyl chloride [$C_6H_5-CH_2-Cl$] undergoes S_N1 nucleophilic substitution via resonance stabilized benzyl carbocation. The carbocation thus formed is then attacked by nucleophile and hence undergoes substitution readily.

Ans.ii) Because 2-bromobutane has chiral carbon centre and form non-superimposable mirror images.

Ans.iii)

Halogen atom is <i>o, p</i> directing; therefore, further substitution occurs at <i>ortho</i> - and <i>para</i> positions with respect to the halogen atom.	Further, the halogen atom Because of its $-I$ effect [EWG] has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.
---	--

2. How do you convert?

- i) Chlorobenzene to toluene**
- ii) But-1-ene to But-2-ene**
- iii) Ethanol to Ethyl iodide**

Ans.i)- By Wurtz Fittig reaction

Ans. ii) - i) HBr (Markovnikov addition) ii) Alc. KOH

Ans. iii) - i) Ethanol into Chloromethane ii) Finkelstein reaction

3. What happens when?

i) n-butyl chloride is treated with alcoholic KOH.

ii) 2-chloropropane is treated with sodium in the presence of dry ether.

iii) Chlorobenzene is treated with CH_3Cl in the presence of anhydrous AlCl_3 .

Ans.i) But-1-ene is formed

Ans. ii) 2,3-Dimethylbutane is formed

Ans. iii) Friedal craft reaction(Hint)

4. The following compounds are given to you:

2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane

a) Write the compound which is most reactive towards $\text{S}_{\text{N}}2$ reaction.

b) Write the compound which is optically active.

c) Write the compound which is most reactive towards β -elimination reaction.

Ans. a) 1-Bromopentane

Ans.b) 2-Bromopentane

Ans.c) 2-Bromo-2-methylbutane

5. Give reasons for the following :

a) The presence of $-\text{NO}_2$ group at ortho or para position increases the reactivity of haloarenes toward nucleophilic substitution reactions.

b) p-dichlorobenzene has higher melting point than that of ortho or meta isomer.

c) Thionyl chloride method is preferred for preparing alkyl chloride from alcohols.

Ans. a) The presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by $-\text{NO}_2$ group.

Ans. b) The melting point of para isomer is quite higher than that of ortho or meta isomers. This is due to the fact that it has symmetrical structure and therefore, its molecules can easily pack closely in crystal lattice. As a result, intermolecular forces of attraction are stronger and therefore, greater energy is required to break its lattice and it melts at higher temperature.

Ans.c) SOCl_2 is preferred because in this case both the other products formed are gases (SO_2 and HCl) and escape readily leaving chloroethane.

SECTION-D (Case Study Based Questions 4 M each)

Read the passage given below and answer the following questions:

1. Nucleophilic substitution reactions are of two types; substitution nucleophilic bimolecular ($\text{S}_\text{N}2$) and substitution nucleophilic unimolecular ($\text{S}_\text{N}1$) depending on molecules taking part in determining the rate of reaction. The reactivity of alkyl halide towards $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ reactions depends on various factors such as steric hindrance, stability of intermediate or transition state, and polarity of the solvent. $\text{S}_\text{N}2$ reaction mechanism is favoured mostly by primary alkyl halide or transition state and polarity of the solvent, $\text{S}_\text{N}1$ reaction mechanism is favoured mostly by primary alkyl halide then secondary and then tertiary. This order is reversed in the case of $\text{S}_\text{N}1$ reactions.

(a) Which of the following is most reactive towards nucleophilic substitution reaction and why ?

(i) $\text{C}_6\text{H}_5\text{Cl}$ (ii) $\text{CH}_2=\text{CHCl}$ (iii) $\text{ClCH}_2\text{CH}=\text{CH}_2$ (iv) $\text{CH}_3\text{CH}=\text{CHCl}$

Ans. d) $\text{ClCH}_2-\text{CH}=\text{CH}_2$

Explanation: More the stability of the carbocation higher will be the reactivity of the parent chloride. Allyl chloride > Vinyl chloride > Chlorobenzene.

(b) Out of $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ by which mechanism Isopropyl chloride undergoes hydrolysis and why ?

Ans. Isopropyl chloride undergoes hydrolysis via both $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanisms.

Both of them yield the same result/ products. Since, isopropyl chloride is a secondary alkyl halide.

(c) Why does tertiary alkyl halides are practically inert to substitution by S_N2 mechanism ?

Ans. The repulsion between the alkyl or any other groups present on an carbon atom, if the distance between the two is less than vander waals radius, than it is said to be the steric hindrance. That is the reason why tertiary alkyl halides are practically inert to substitution by S_N2 mechanism as there is steric hindrance.

**(d) Arrange the following is the correct order of decreasing S_N2 reactivity?
 RCH_2X , R_3CX , R_2CHX**

Ans $RCH_2X > R_2CHX > R_3CX$

2. Haloalkanes are colourless (when pure), sweet smelling liquids. CH_3Cl , CH_3Br and C_2H_5Cl and freons are gases. Boiling point increases with increase in molecular weight and increase in carbon chain and decreases with branching. They are insoluble in water due to inability to form H-bonds with water. Dipole moment increases with polarity, density increases with increase in molar mass. They are non-inflammable, therefore, CCl_4 is used as fire extinguisher under the name pyrene. *p*-dichlorobenzene has zero dipole moment, higher melting point than *o*-dichloro benzene due to symmetry, fits into crystal lattice readily. Haloalkanes undergo nucleophilic substitution reaction by S_N2 mechanism, $1^\circ > 2^\circ > 3^\circ$, S_N1 if carbocation formed is stable. They also undergo nucleophilic elimination reactions with alcoholic KOH. Haloarenes are less reactive than haloalkanes towards nucleophilic substitution due to resonance. Haloarenes undergo electrophilic substitution reaction like nitration, sulphonation, Friedel Crafts alkylation, acylation. Chloroform is used as solvent, Freon is used as refrigerant, dichloromethane is used as paint remover. Iodoform is used as antiseptic. DDT is insecticide but non- biodegradable.

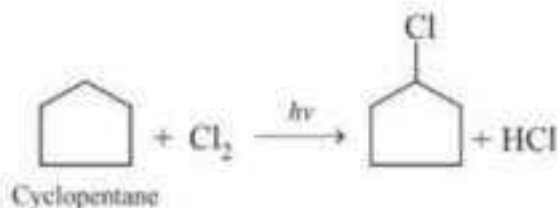
(a) Arrange $R-F$, $R-Br$, $R-I$, $R-Cl$ in increasing order of boiling point.

Ans. $R-F < R-Cl < R-Br < R-I$

(b) A hydrocarbon 'A' (C_5H_{10}) gives only one monochloro product on photo chlorination.

Identity 'A'.

Ans,

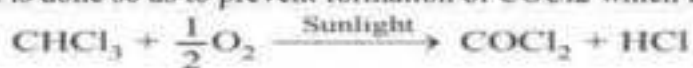


(c) Out of $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ which one undergoes $\text{S}_\text{N}1$ mechanism faster?

Ans. $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ because $\text{CH}_2=\text{CH}-\text{CH}_2^+$ is more stable due to resonance.

(d) Why is chloroform stored in dark coloured bottles?

Ans. It is done so as to prevent formation of COCl_2 which is poisonous.



3. The substitution reaction of alkyl halides occurs in $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ mechanism whatever mechanism alkyl halide follow for substitution reaction to occur, the polarity of the carbon-halogen bond is responsible for the substitution reaction. The rate of $\text{S}_\text{N}1$ reactions are governed by the stability of carbocation where as for $\text{S}_\text{N}2$ reactions steric factor is the deciding factor. If the starting material is a chiral compound, we may end up with an inverted product or racemic mixture depending upon the type of mechanism followed by alkyl halide. Cleavage of ethers with HI is also governed by steric factor and stability of carbocation which indicates that in organic chemistry, these two major factors help us in deciding the kind of product formed.

(a) Predict the stereochemistry of the product formed if optically active alkyl halide undergoes substitution reaction by $\text{S}_\text{N}1$ mechanism.

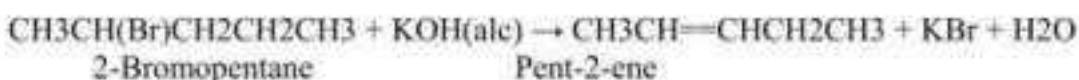
Ans. Racemic mixture will be formed.

(b) Name the instrument used for measuring the angle by which the plane polarised light is rotated.

Ans. Polarimeter

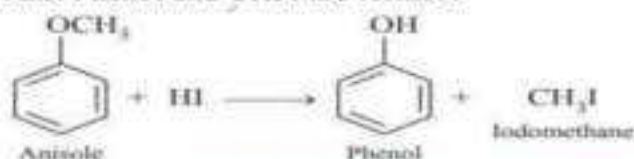
(c) Predict the major product formed when 2-bromopentane reacts with alcoholic KOH.

Ans. Pent-2-ene will be major product.



(d) Write the structure of the products formed when anisole is treated with HI.

Ans. Phenol and CH_3I are formed.

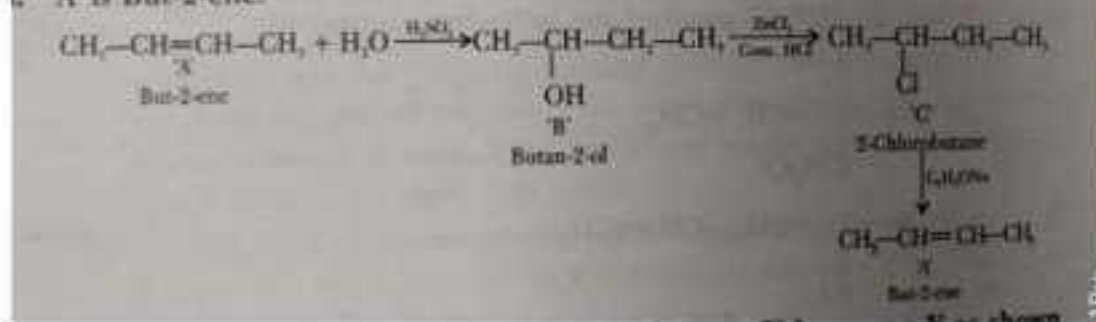


SECTION-E (LONG ANSWER TYPE QUES. 5MEach)

Q1) An organic compound 'A' having molecular formula C_4H_8 on treatment with $\text{dil. H}_2\text{SO}_4$ gives 'B'. However, 'B' on treatment with conc. HCl and anhydrous ZnCl_2 gives 'C' and on treatment with sodium ethoxide gives back 'A'. Identify the compounds 'A', 'B' and 'C'. Also write the equations involved.

Ans 'A' is But-2-ene

Q. 'A' is But-2-ene.



Q2) What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

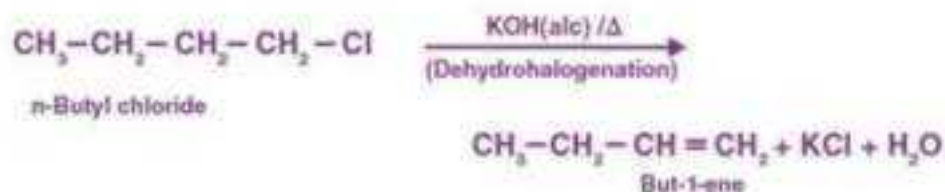
(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

Ans (i) When n-butyl chloride is treated with alcoholic KOH, the formation of but-1-ene takes place. This reaction is a dehydrohalogenation reaction.

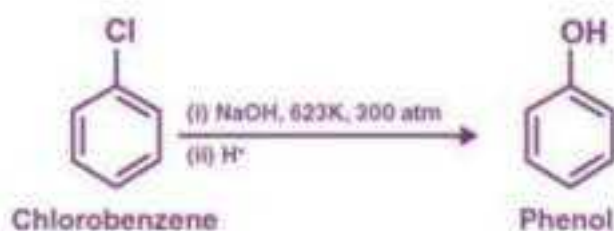


(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.

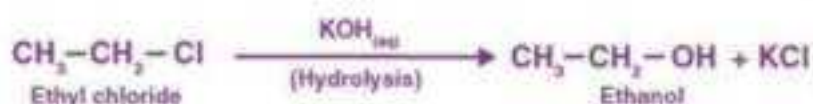


(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a

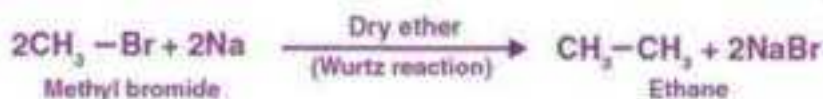
temperature of 623 K and a pressure of 300 atm to form phenol.



(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction



Q3) Answer the following questions.

a) Give one use of Iodoform.

Ans: Iodoform is used as an antiseptic because it liberates Iodine slowly.

b) Why chloroform is stored in closed dark coloured bottles completely filled?

ans: because chloroform is slowly oxidised by air in the presence of light to form an extremely poisonous gas called Carbonyl chloride or Phosgene.

c) Name two polyhalogens when released into air depletes ozone layer?

ans: Carbon tetra chloride, CCl_4 and Freons (CFC)

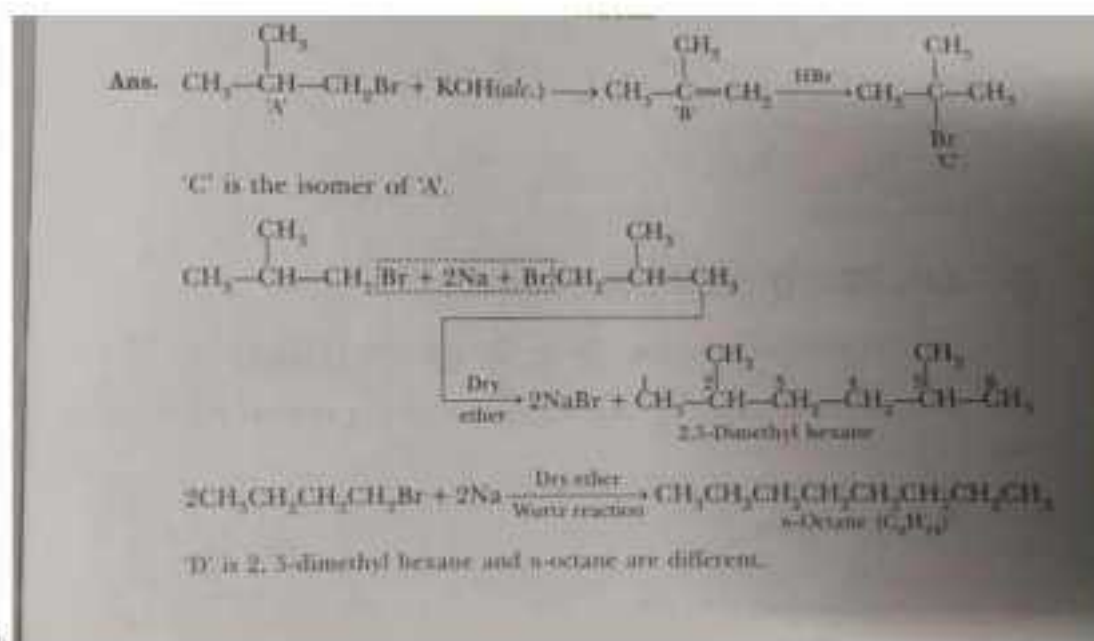
d) Why DDT was banned in different countries?

Ans: The chemical stability of DDT and its fat solubility was major problem, DDT was deposited and stored in the fatty tissues.

e) Give two uses of carbon tetrachloride.

Ans: CCl₄ is used as solvent. It is also used in fire extinguisher because its vapour are heavy and cut off supply of air.

Q4) Primary alkyl halide C₄H₉Br (A) reacted with alcoholic KOH to give compound (B). Compound (B) is reacted with HBr to give (C) which is an isomer of (A). When (A) is reacted with sodium metal it gives compound (D), C₈H₁₈ which is different from the compound formed when n-butyl bromide is reacted with sodium. Give structural formula of A, B C and write the reaction involved.



Ans

Q5) a) Write the mechanism of the following reaction

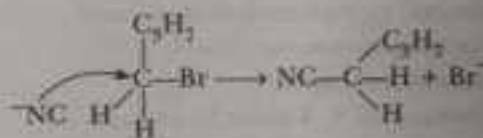


b) Why racemisation occurs in SN1 reaction?

Ans a) it is a nucleophilic substitution reaction in which stronger nucleophile CN⁻ is replacing weaker Br⁻. It will follow SN2 Mechanism.

Ans. It is nucleophilic substitution reaction in which stronger nucleophile CN^- is replacing weaker nucleophile Br^- . It will follow $\text{S}_\text{N}2$ mechanism.

Mechanism



$$\text{Rate} = k[\text{C}_2\text{H}_5\text{CH}_2\text{Br}][\text{CN}^-]$$

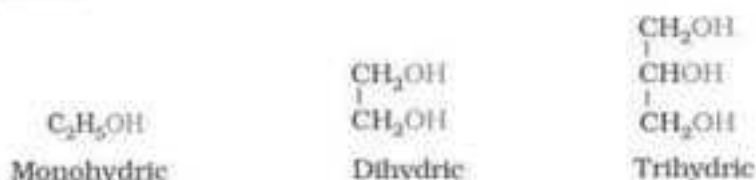
b) In $\text{S}_\text{N}1$ mechanism, intermediate carbocation is sp^2 hybridised and has planar structure, therefore there is equal probability of attacking nucleophile from either of the side, leading to the formation of equal amount of Dextro and Levo rotatory products and hence racemization occurs.

CHAPTER-7-ALCOHOLS, PHENOLS AND ETHERS

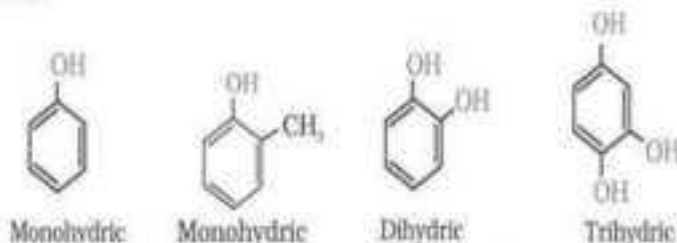
Alcohols and Phenols

Alcohols and phenols are formed when a hydrogen atom in hydrocarbon (aliphatic and aromatic) is replaced by hydroxyl group ($-\text{OH}$ group)

- Alcohols and phenols may be classified as monohydric, dihydric, trihydric or polyhydric according to number of hydroxyl groups they contain



- In phenols, $-\text{OH}$ group is attached to Sp^2 hybridized carbon. These may also be monohydric, dihydric, etc. The dihydric phenol be ortho, meta or para derivative.

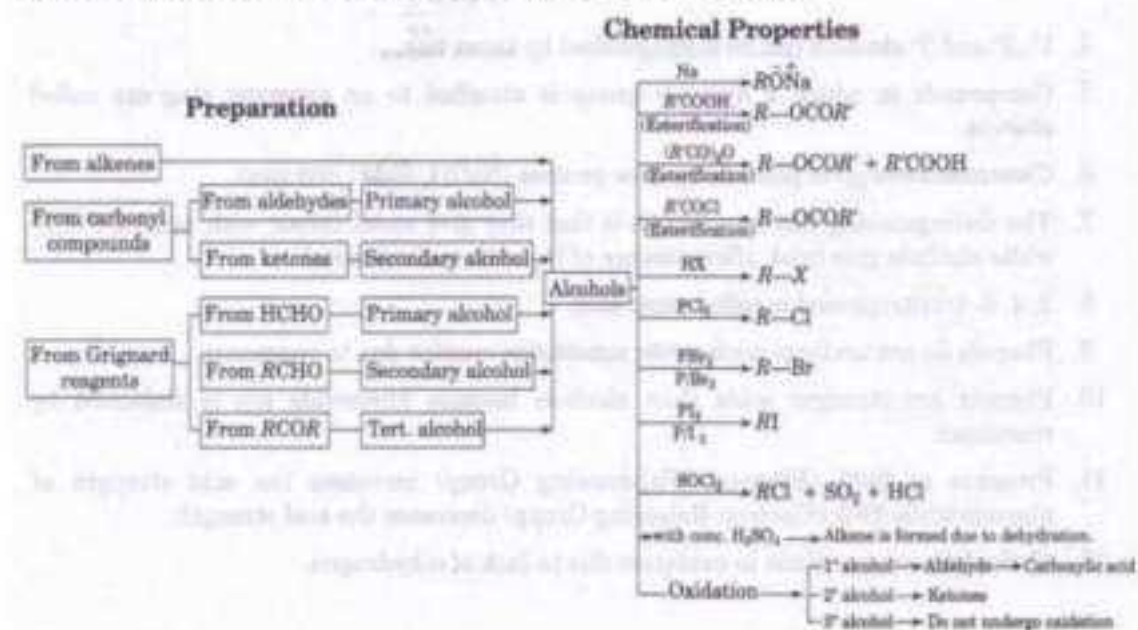


In Allylic alcohols, $-\text{OH}$ group is attached to sp^3 hybridized carbon but next to $>\text{C}=\text{C}<$ bond. e.g. $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$, Benzyl alcohol



They are suffixed by 'ol' while writing their IUPAC names

PREPARATION AND PROPERTIES OF ALCOHOLS:

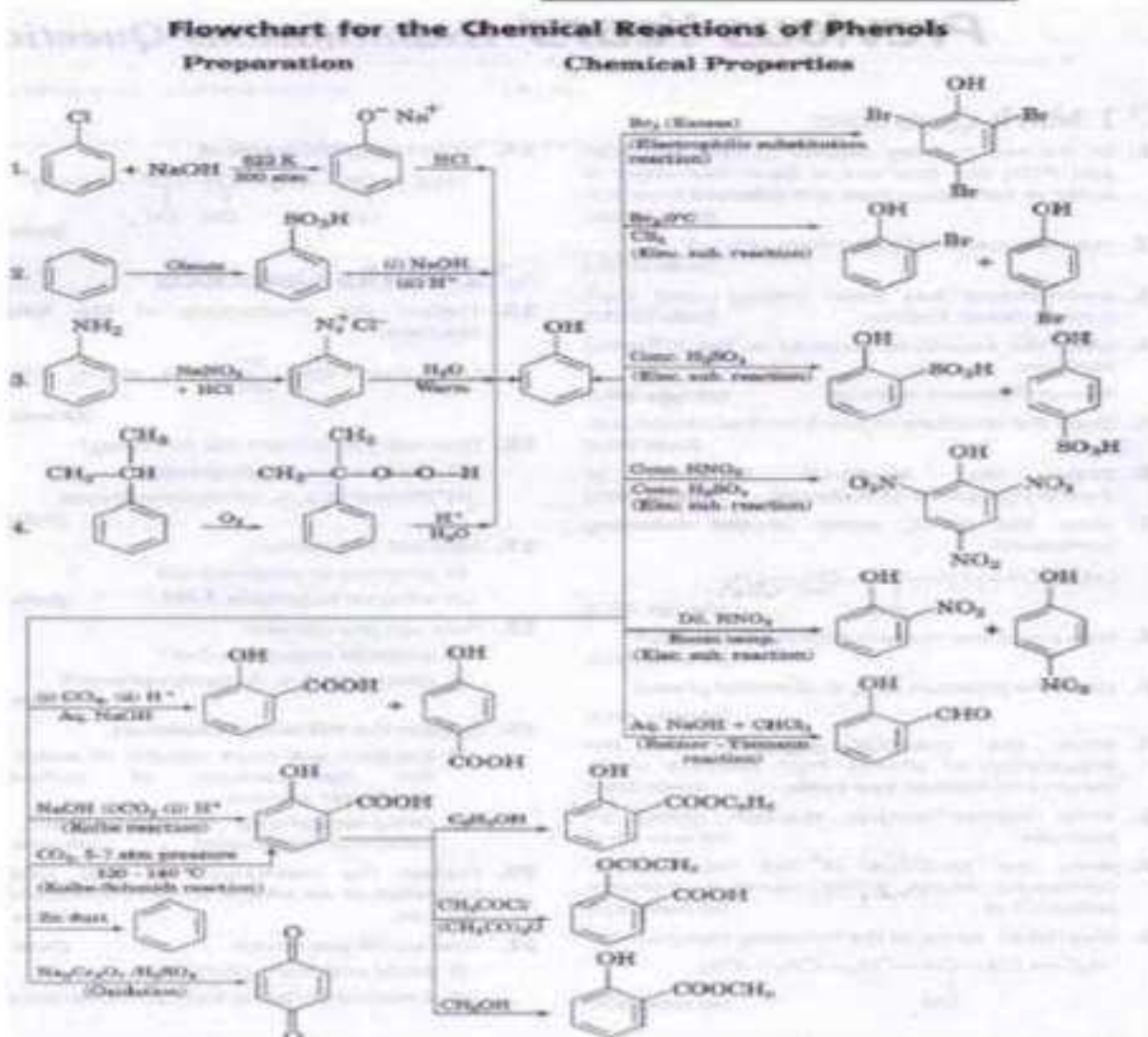


Physical Properties of Alcohols

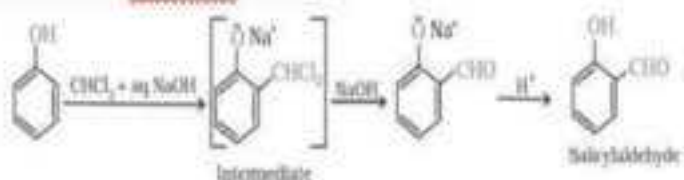
- The hydroxyl groups in alcohols can form **Hydrogen bonds with water**, so **alcohols are miscible with water**. The solubility decreases with increase in molecular mass.
- Boiling points of alcohols are **higher** than expected because of the presence of **intermolecular hydrogen bonding**.

The boiling point decreases in the order $1^\circ > 2^\circ > 3^\circ$. This is due to the fact that with branching, the **surface area decreases** and therefore, **Vander Waals forces decrease**, consequently, **boiling point also decreases**.

PHENOLS



(d) **Reimer-Tiemann reaction:** On treating phenol with chloroform in the presence of sodium hydroxide, a -CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemann reaction.



Distinction among 1°, 2° and 3° Alcohols:

1°, 2° and 3° alcohols are distinguished by Lucas test- In this test with an equimolar conc. HCl and anhydrous ZnCl_2 , the alcohols get converted into alkyl halides. Since the alkyl halides are insoluble in water, their formation is indicated by the appearance of turbidity in the reaction mixture.

If turbidity appears immediately, the alcohol is tertiary.

If turbidity appears within five minutes, the alcohol is secondary. If turbidity appears only upon heating, the alcohol may be primary.

Distinction among Alcohols and Phenols:

Alcohols give red or pink colour with Ammonium ceric nitrate while Phenol gives violet, blue or green colour with neutral FeCl_3 solution.

ETHERS

Functional Group-ROR

They are in general named as alkoxy alkanes while writing their IUPAC names.

Ethers can be classified into two categories; they are listed below.

Symmetrical Ethers:

If two identical groups are attached to either side of an oxygen atom, then it is referred to symmetrical ethers. These are also known as Simple Ethers.

Examples are diethyl ether, dipropyl ether, dimethyl ether, and more.

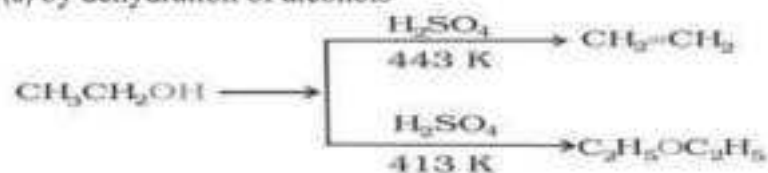
Asymmetrical Ethers:

If two different groups are attached to either side of an oxygen atom, it is said to be asymmetrical ethers. These are also known as Mixed Ethers.

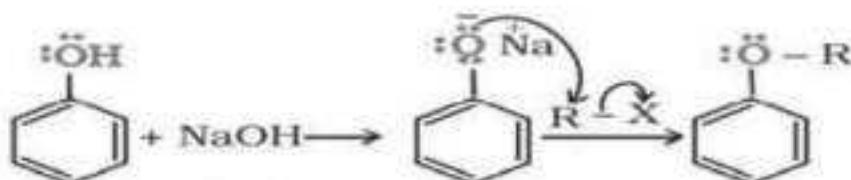
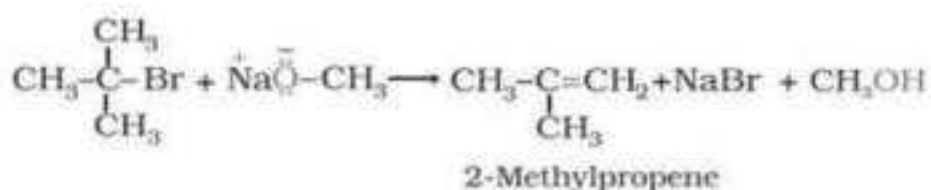
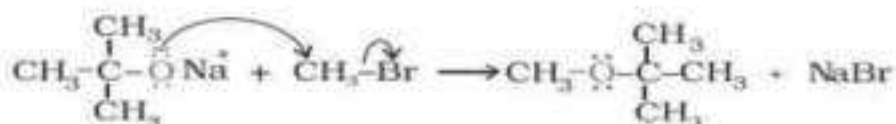
Examples are methyl phenyl ether, ethyl methyl ether, and more.

PREPARATION: Ethers can be prepared

(a) by dehydration of alcohols



(b) Williamson's synthesis: Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halides give alkene due to steric hindrance.



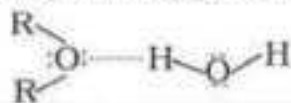
(c) For Aryl ethers, Phenol converted into ether.

PHYSICAL PROPERTIES:

1. The C – O bond in ethers are polar. The boiling point of alkanes, alcohols and ethers as follows:

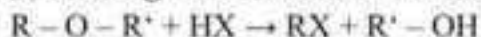
Formula	$CH_3(CH_2)_3CH_3$ n-Pentane	$C_2H_5-O-C_2H_5$ Ethoxyethane	$CH_3(CH_2)_3-OH$ Butan-1-ol
b.p./K	309.1	307.6	390

2. The miscibility of ethers with water due to hydrogen bond with water.



CHEMICAL PROPERTIES:

(a) Cleavage of C-O bond in ethers:



(b) Electrophilic substitution: In this, the alkoxy group activates the aromatic ring and directs the incoming group to ortho and para positions.

(i) Reaction with HX:

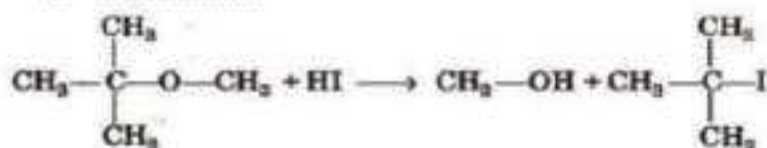




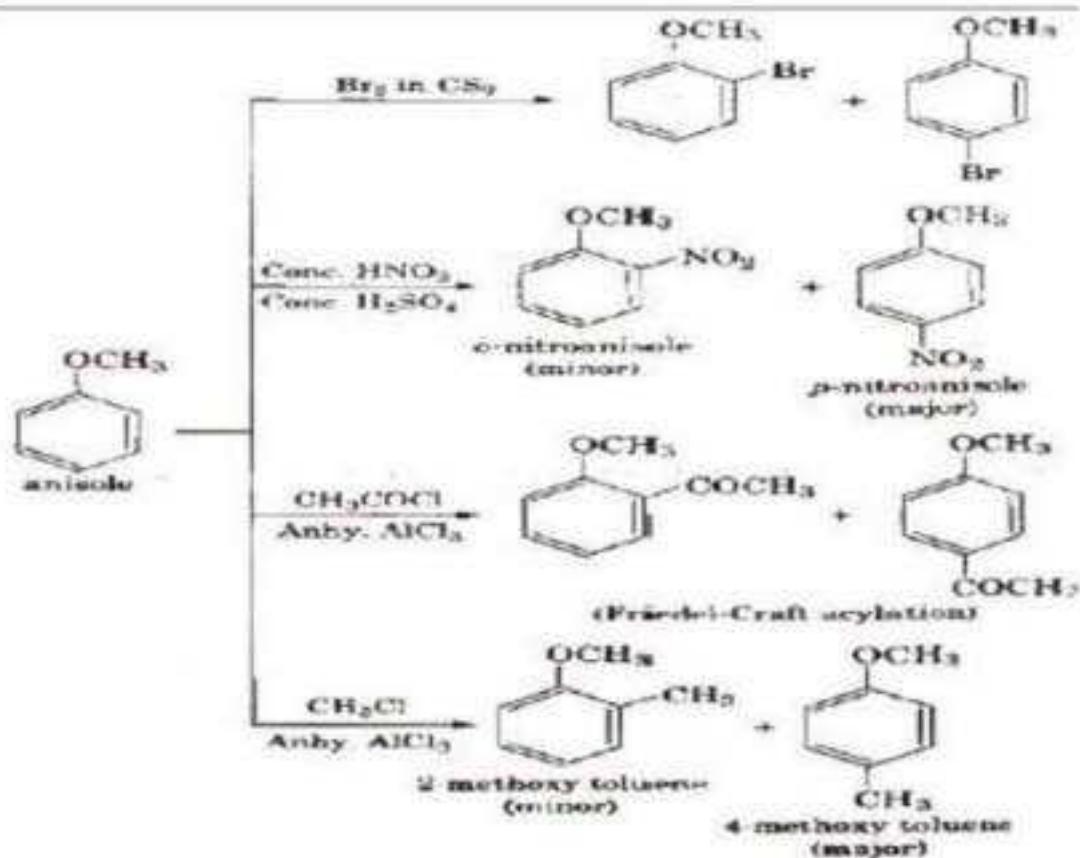
The order of reactivity of hydrogen halides is as follows: $\text{HI} > \text{HBr} > \text{HCl}$

In ethers if one of the alkyl groups is a tertiary group, the halide formed is a tertiary halide by

$\text{S}_\text{N}1$ mechanism.



Reactions of ether



ALCOHOLS, PHENOLS AND ETHERS

SECTION-A (MULTIPLE CHOICE QUESTIONS)

1. Phenol on reduction with H_2 in the Presence of Ni Catalyst gives ____

- . benzene
- a. toluene
- b. cyclohexane
- c. Cyclohexanol

Answer: (d)

2. Chloro-Ethane reacts with which of the Following to Give Diethyl Ether?

- . NaOH
- a. H_2SO_4
- b. C_2H_5ONa
- c. $Na_2S_2O_3$

Answer: (c)

3. Catalytic Dehydrogenation of Primary Alcohol gives a ____

- . Ketone
- a. Aldehyde
- b. Alcohol
- c. Ester

Answer: (b)

4. Due to _____ An ether is More Volatile than an Alcohol having the same Molecular Formula.

- . The dipolar character of ether
- a. Alcohols having resonance structures
- b. Intermolecular hydrogen bonding in ethers
- c. Intermolecular hydrogen bonding in alcohols

Answer: (d)

5. An Organic Compound with a Pleasant Odor and 78 Degrees Boiling Point is boiled with Concentrated H_2SO_4 . It gives a Colorless gas that Decolorizes Bromine Water and Alkaline Potassium Permanganate. What is this Organic Compound?

- . $C_2H_5COOCH_3$
- a. C_2H_5OH
- b. C_2H_5Cl
- c. C_2H_6

Answer: (b)

6. The Compound Obtained by the Reaction of Propene with Diborane Followed by Hydrolysis with Alkaline H_2O_2 is ____

- . Tripropylborane
- a. propan-2-ol
- b. Propan-1-ol
- c. Propane

Answer: (c)

7. Which of the Following is Formed when Phenol is Exposed to Air?

- . o-Benzoquinone
- a. p-Benzoquinone
- b. Phenoquinone
- c. o-and p-Benzoquinone

Answer: (d)

8. Which of the Following is Formed when Glycerol is heated with Oxalic Acid at 503K?

- . Glyceric acid
- a. Acrolein
- b. Allyl alcohol
- c. Methanoic acid

Answer:(c)

9. Which of the following is true?

- . Lower alcohols are liquid at room temperature and the higher ones are solid
- a. Lower alcohols and higher alcohols, both are liquid at room temperature
- b. Higher alcohols are liquid at room temperature and the lower ones are solid
- c. Both lower and higher alcohols are solid at room temperature

Answer: (a)

10. A compound X with the molecular formula $\text{C}_3\text{H}_8\text{O}$ can be oxidised to another compound Y whose molecular formulae is $\text{C}_3\text{H}_6\text{O}_2$. The compound X may be

- (a) $\text{CH}_3\text{CH}_2\text{OCH}_3$
- (b) $\text{CH}_3\text{CH}_2\text{CHO}$
- (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (d) $\text{CH}_3\text{CHOHCH}_3$

Answer: (c)

ASSERTION REASON QUESTIONS

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- a) Assertion and reason both are correct and reason is correct explanation of assertion.
- b) Both assertion and reason are correct statements but reason is not correct explanation

of assertion

- c) Assertion is correct statement but reason is wrong statement.
- d) Assertion is wrong statement but reason is correct statement.
- e) Assertion and reason both are wrong statements.

1. **Assertion :** Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol

Reason: Addition of water in acidic medium proceeds through the formation of primary carbocation.

2. **Assertion:** Bond angle in ethers is slightly greater than the tetrahedral angle.

Reason: There is a repulsion between the two bulky (—R) groups.

3. **Assertion:** In Lucas test, 3° alcohols react immediately.

Reason: An equimolar mixture of anhyd. ZnCl_2 and conc. HCl is called Lucas reagent.

4. **Assertion:** With HI , anisole gives phenol and methyl iodide.

Reason: Iodide ion combines with smaller group to avoid steric hindrance.

5. **Assertion:** With HI at 373 K , tert-butyl methyl ether gives tert-butyl iodide and methanol.

Reason: The reaction occurs by S_N^2 mechanism.

Answer: 1 (e), 2 (a), 3 (d), 4 (b), 5 (c)

SECTION-B (VERY SHORT ANSWER TYPE QUESTION) 2 M

1. Answer the following:

- i. What is the order of dehydration of primary, secondary and tertiary alcohols?

Ans: Tertiary alcohols > Secondary alcohols > Primary alcohols

- ii. Arrange Pentan-1-ol, n-butane, pentanal, ethoxy ethane in increasing order of boiling point?

Ans: n-butane < ethoxy ethane < pentanal < pentan-1-ol

2. Give reason for the following

- i. Phenol has smaller dipole moment than methanol.

Ans: Due to electron-withdrawing effect of the benzene ring, the C-O bond in phenol is less polar but in case of methanol due to electron-donating effect of —CH_3 group, C-O bond is more polar.

- ii. Phenol is more acidic than alcohol in nature.

Ans: Phenol is acidic in nature because the phenoxide ion formed by loss of H^+ from phenol is more resonance stabilized than phenol itself.

3. How will you distinguish between primary, secondary and tertiary alcohols?

Ans: When primary, secondary, tertiary alcohols are treated with Lucas reagent

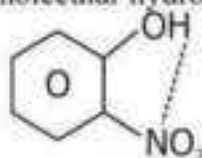
at room temperature, then

- (i) If turbidity appears immediately, alcohol is tertiary
- (ii) If turbidity appears in 5 minutes, alcohol is secondary
- (iii) If no reaction, alcohols are primary.

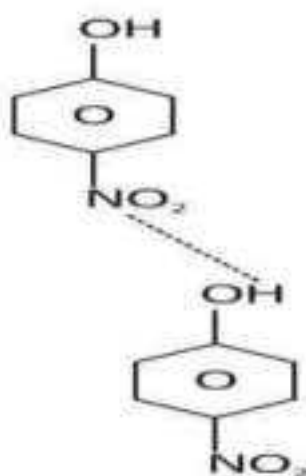
(Lucas reagent is conc. HCl + anhydrous zinc chloride)

4. While separating a mixture of ortho and para-nitro phenols by steam distillation, name the isomer which will be steam volatile. Give reasons.

Ans: In o-nitrophenol, there is intramolecular hydrogen bonding as follows:



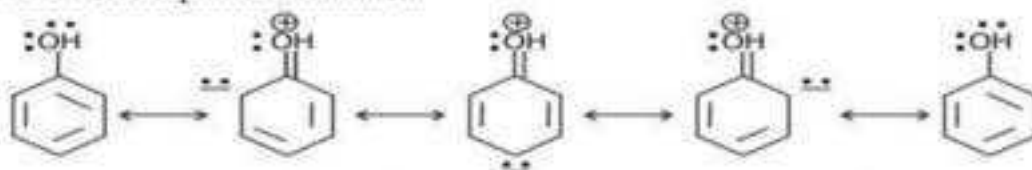
In p-nitrophenol, there is intermolecular hydrogen bonding as follows:



Due to intermolecular H-bonding in p-nitrophenol, its b. p. is much higher than that of o-nitrophenol. Hence o-nitrophenol due to its lower b. p. is steam volatile while p-nitrophenol is not.

5. How -OH group attached to carbon in the benzene ring activates benzene towards electrophilic substitution?

Ans: The lone pair of electrons present on oxygen atom enters into resonance with the benzene ring. As a result, the electron density becomes higher at ortho and para position and due to higher electron density, the ring gets activated towards electrophilic substitution.



6. An organic compound 'A' having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. When 'A' is treated with CO_2 and $NaOH$ at 400K under pressure 'B' is obtained. The compound 'B' on acidification gives compound 'C' which reacts with acetyl chloride to form 'D' which is a popular pain killer. Deduce the structure of A, B, C and D.

Ans. 'A' = phenol; 'B' = sodium salicylate; 'C' = Salicylic acid; 'D' = aspirin

7. Complete the following reactions: (any two for 2 marks)

- $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4$ (443K) $\rightarrow$
- $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_3 + \text{HBr}$ $\rightarrow$
- $\text{CH}_3\text{CH}_2\text{OH} + \text{Na}$ $\rightarrow$
- $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4$ (413K) $\rightarrow$

Ans:

- $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4$ (443K) $\rightarrow \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$
- $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_3 + \text{HBr} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH} + \text{CH}_3\text{-Br}$
- $\text{CH}_3\text{CH}_2\text{OH} + \text{Na} \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \frac{1}{2} \text{H}_2$
- $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{SO}_4$ (413K) $\rightarrow \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$

8. Give names of the reagents to bring about the following transformations:

- Ethanoic acid to ethanol
- Propane-1-ol to propanal

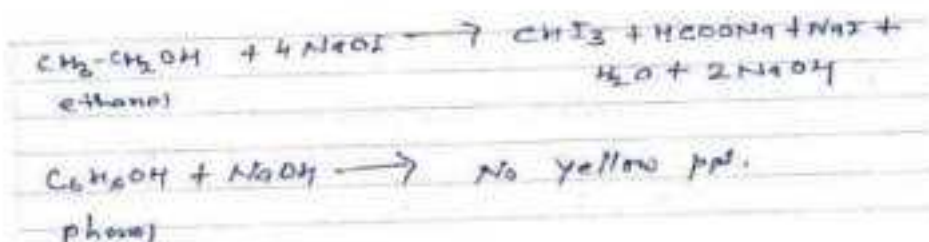
Ans: (a) (i) $\text{LiAlH}_4/\text{H}_3\text{O}^+$ (ii) PCC

9. How will you distinguish between the following pairs of compounds?

- Pentan-2-ol and pentan-3-ol
- Phenol and ethanol

Ans: (i) Pentan-2-ol respond to iodoform test and gives yellow ppt of iodoform but no reaction with pentan-3-ol (reaction reference given below)

(ii) Phenol respond to FeCl_3 test & gives violet colour but no reaction with ethanol. Also, Iodoform test can be used.



10. Name the reagent of the following reaction. (any 2 for 2 marks)

- Oxidation of primary alcohol to carboxylic acid
- Bromination of phenol to 2,4,6-tribromophenol.
- Benzyl alcohol to benzoic acid
- Butan-2-one to butan-2-ol

Ans:

- Acidified $\text{K}_2\text{Cr}_2\text{O}_7$ (followed by hydrolysis with dil H_2SO_4)
- Aqueous bromine
- Alkaline KMnO_4
- Reduction NaBH_4 or LiAlH_4

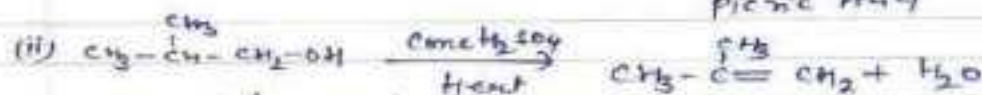
11. How would you obtain

- Picric acid from phenol
- 2 Methyl Propene from 2 methyl propanol ?

Ans:



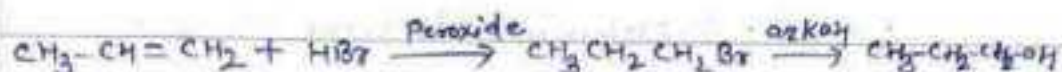
picnic buffet



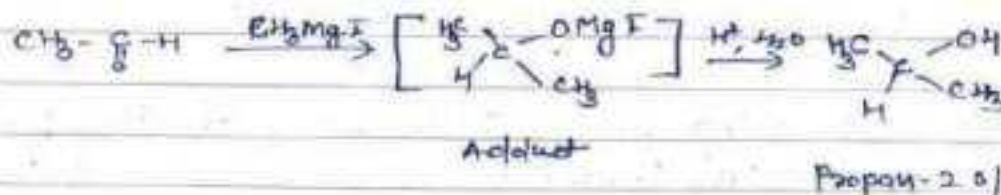
12. How will you convert

i) Propene to propan-1-ol ii) Ethanol to propan-2-ol

Ans: d)



ii)

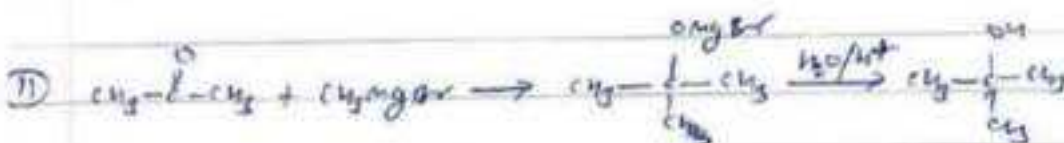
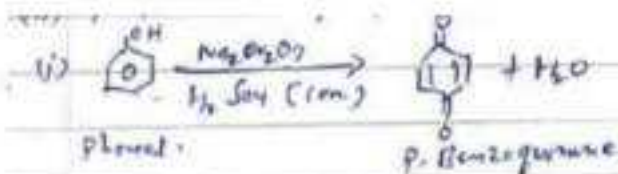


13. How would you convert the following :

i) Phenol to benzoquinone

ii) Propomone to 2-Methyl propam-2-ol

Ans:



14.Account for the following

i) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.

ii) Ortho-nitro phenol is more acidic than ortho-methyl phenol

Ans: i) It is because NO_2 group is electron withdrawing and $-\text{OCH}_3$ group is electron releasing. Therefore O-nitro phenoxide ion is more stable than O-methoxy phenoxide ion.

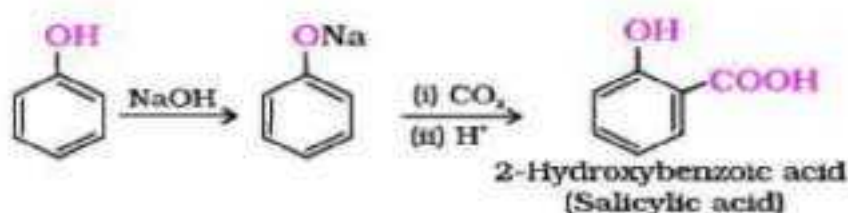
ii) It is because secondary and tertiary alcohols on dehydration lead to the formation of alkene and not ethers due to the stability of 2^o and 3^o carbocation.

SECTION-C(short answer type ques) 3 M

15. Write the reaction involved in i) Kolbes reaction ii) Williamson synthesis

iii) Reimer-Tiemann reaction

Ans: i) Kolbes reaction



ii) Williamson synthesis

It is an important laboratory method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.



iii) Reimer-Tiemann reaction

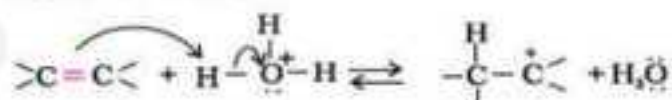
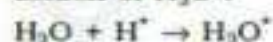


16. Write the mechanism of hydration of ethene to yield ethanol.

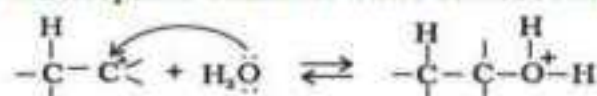
Mechanism

The mechanism of the reaction involves the following three steps:

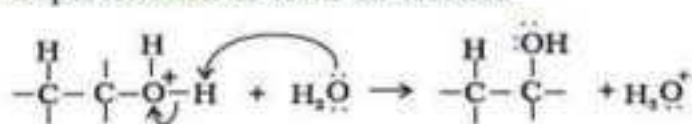
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



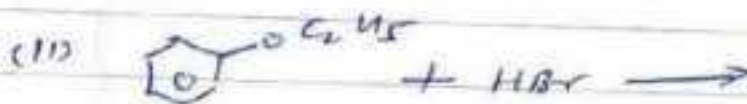
Step 2: Nucleophilic attack of water on carbocation.



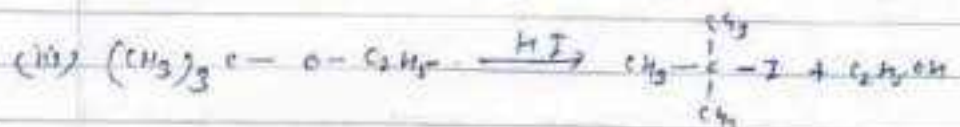
Step 3: Deprotonation to form an alcohol.



17. Complete the following reactions.



Ans:



18.

Match the items of column I with items of column II.

Column I

- (i) Antifreeze used in car engine
- (ii) Solvent used in perfumes
- (iii) Starting material for picric acid
- (iv) Wood spirit
- (v) Reagent used for detection of phenolic group
- (vi) By product of soap industry used in cosmetics

Column II

- (a) Neutral ferric chloride
- (b) Glycerol
- (c) Methanol
- (d) Phenol
- (e) Ethleneglycol
- (f) Ethanol

Ans: (i) — (e), (ii) — (f), (iii) — (d), (iv) — (c), (v) — (a), (vi) — (b)

19. Match the items of column I with column II

Column I

- (i) Methanol
- (ii) Kolbe's reaction
- (iii) Williamson's synthesis
- (iv) Conversion of 2° alcohol to ketone
- (v) Reimer-Tiemann reaction
- (vi) Fermentation

Column II

- (a) Conversion of phenol to o- hydroxysalicylic acid
- (b) Ethyl alcohol
- (c) Conversion of phenol to salicylaldehyde
- (d) Wood spirit
- (e) Heated copper at 573K
- (f) Reaction of alkyl halide with sodium alkoxide

Ans: (i) — (d), (ii) — (a), (iii) — (f), (iv) — (e), (v) — (c), (vi) — (b)

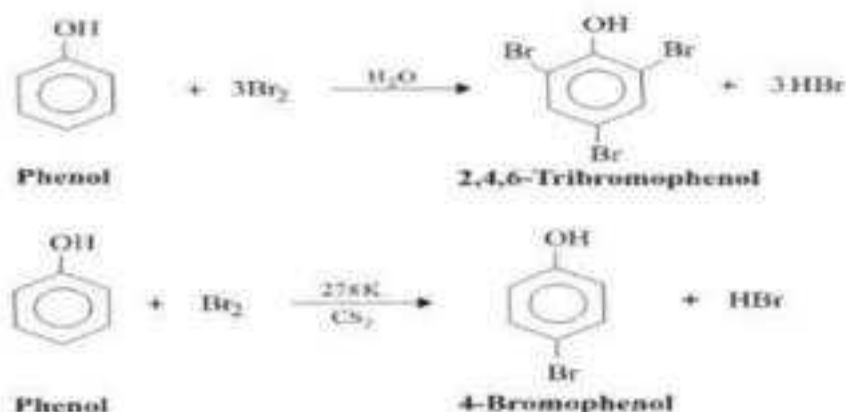
20.(a) Name the starting material used in the industrial preparation of phenol.

(b) Write complete reaction for the bromination of phenol in aqueous and non aqueous medium.

(c) Explain why Lewis acid is not required in bromination of phenol?

Ans: a) Cumene also known as Isopropyl benzene is the starting material.

b)



c) In case of highly polar phenol molecule, the oxygen atom present in the phenol molecule itself polarizes the incoming electrophile Br₂ to form ions. So in this case no additional lewis acid is required.

21. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C₄H₈O. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn (Hg)/conc. HCl, give the same product (D). Write the structures of (A), (B), (C) and (D).

Answer: A = CH₃CH₂CH₂CHO

B = CH₃COCH₂CH₃

C = (CH₃)₂CHCHO

D = CH₃CH₂CH₂CH₃

SECTION-D (Case study Based Questions) 4M

1. Read the passage given below and answer the following questions:

A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice questions. Choose the most appropriate answer:

(i) The compound (X) is an

- (a) acid (b) aldehyde (c) alcohol (d) ether

(ii) The IUPAC name of the acid formed is

- (a) methanoic acid (b) ethanoic acid (c) propanoic acid (d) butanoic acid.

(iii) Compound (Y) is

- (a) ethyl iodide (b) methyl iodide (c) propyl iodide (d) mixture of (a) and (b).

(iv) Compound (X) on treatment with excess of Cl_2 in presence of light gives

- (a) α -chlorodiethyl ether (b) α, α' -dichlorodiethyl ether
(c) perchlorodiethyl ether (d) none of these.

Answer: i) d, ii) b iii) a iv) c

2. Read the given passage and answer the questions that follow:

Alcohols and phenols are the most important compounds used in our daily life.

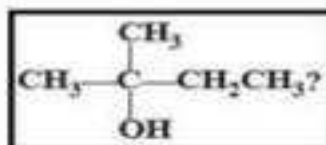
Alcohols are prepared by hydration of alkenes, fermentation of glucose, reduction of aldehydes, ketones, carboxylic acids, and esters.

Alcohols are soluble in water. Boiling points increase with an increase in molar mass and decrease with branching. Alcohols on dehydration give alkene at 443K, follow the carbocation mechanism. Excess of alcohol at 413K on dehydration with conc.

H_2SO_4 also follows a carbocation mechanism but gives diethyl ether. Alcohols undergo nucleophilic substitution reactions, esterification with carboxylic acids and derivatives like amides, acid halides, acid anhydride. Phenol is prepared from cumene, diazonium salts, anisole, chlorobenzene. Phenol is used to prepare salicylaldehyde, salicylic acid, aspirin, methyl salicylate, *p*-benzoquinone. Phenol undergoes electrophilic substitution reaction at *o* & *p*-position. Ethers are functional isomers of alcohols, have low boiling points. Ethers are used as solvents. Unsymmetrical ethers are prepared by Williamson synthesis. Ethers react with HI and undergo $\text{S}_{\text{N}}1$ or $\text{S}_{\text{N}}2$ mechanisms depending upon the stability of carbocation formed. Aromatic ethers like anisole undergo electrophilic substitution at *o* & *p*-position.

Answer the following questions:

Q1. The IUPAC name of



- (a) 2-methylbutanol
(b) 2-methylbutan-2-ol
(c) Methylbutan-2-ol
(d) 2-methylpropan-2-ol

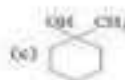
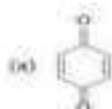
Ans 1. (b) 2-methyl butan-2-ol

Q 2. Out of tert, butyl alcohol, and *n*-butanol, which will undergo dehydration faster?

- (a) tert, butyl alcohol
- (b) *n*-butanol
- (c) Both have the same tendency
- (d) None undergo dehydration

Ans 2. Tertiary butyl alcohol will undergo dehydration faster because 3° carbocation is more stable.

Q 3. Complete the reaction



Ans 3. (a)

Q 4. Why is C—OH bond length in CH₃OH longer than C—OH bond length in phenol?

Ans 4. It is due to resonance in phenol, there is a double bond character in C=O bond, therefore shorter than the single bond in methanol.

CHAPTER 8

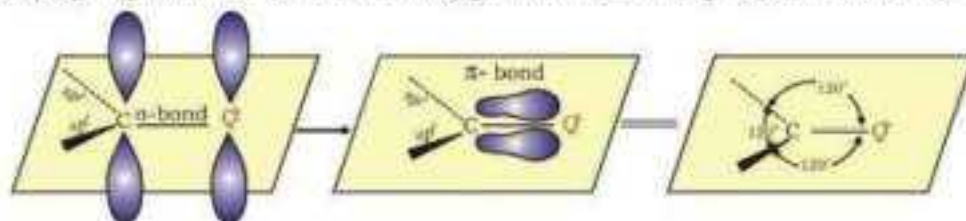
ALDEHYDES KETONES AND CARBOXYLIC ACIDS

ALDEHYDES & KETONES

Aldehydes and ketones are carbonyl compounds with general formula $R-CHO$ where R = alkyl/aryl group or hydrogen atom and $R-CO-R$, where R - is alkyl /aryl group.

Structure of carbonyl group

In carbonyl group both the carbon and oxygen atoms are in sp^2 hybridised state.



Comparison of $C=O$ Bond with $C=C$ Bond

Both atoms in both the cases are in the sp^2 hybridised state.

Both the cases contain one σ -bond and one π -bond.

The difference between $C=O$ and $C=C$

Carbonyl group is a polar group and due to this polarity of $>C=O$ bond, carbonyl compounds undergo nucleophilic addition reaction in the carbonyl compound on other hand in alkene ($C=C$) there is electrophilic addition reaction



General Methods of Preparation for both $R-CHO$ and $R-CO-R$

1. From hydrocarbons

By ozonolysis of alkenes followed by hydrolysis give aldehydes and ketones

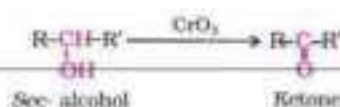
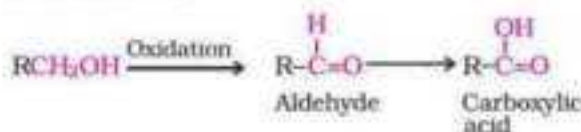
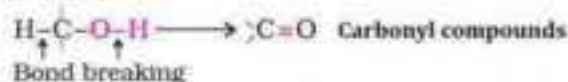
By hydration of alkynes



Acetylene/ethyne gives Acetaldehyde Propyne gives Acetone.

2. From alcohols

Oxidation



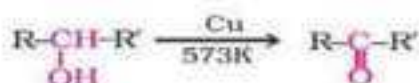
Primary alcohols give aldehydes and secondary alcohols give ketones. Stronger oxidizing agents further oxidize aldehydes into acids.

PCC (Pyridinium chlorochromate) or Corey's reagent is a better selective oxidizing agent for conversion of 1° alcohols to aldehyde. It will not attack $>C=C<$

Allylic and benzylic alcohols are oxidized with CrO_3/H_2SO_4

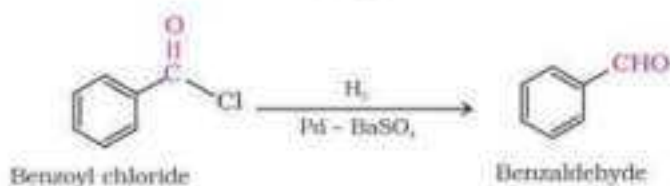
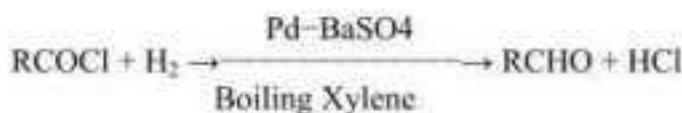
Catalytic dehydrogenation (Cu/573K)

Primary and secondary alcohols give aldehydes and ketones, respectively



Preparation of aldehydes only

1. From acid chlorides: Rosenmund reduction.



Note: Formaldehyde cannot be prepared by this method as formyl chloride is unstable at room temperature

2. From nitriles and esters by reduction Stephen reaction.



Using reducing agent DiBAL-H

Nitriles are reduced by diisobutyl aluminium hydride, (DIBAL-H) to imines followed by hydrolysis to aldehydes:

Esters are also reduced to aldehydes with DIBAL-H.



From aromatic hydrocarbons: Oxidation of methyl benzene
Etard's reaction (Using Chromyl chloride)



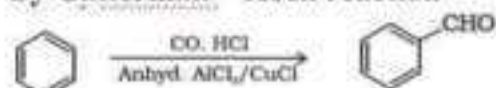
(b) Use of chromic oxide (CrO_3):



Use of chromic oxide (CrO_3):

Toluene or substituted toluene is converted to benzylidene diacetate on treating with chromic oxide in acetic anhydride. The benzylidene diacetate can be hydrolysed to corresponding benzaldehyde with aqueous acid.

By Gatterman – Koch reaction



Preparation of ketones only:

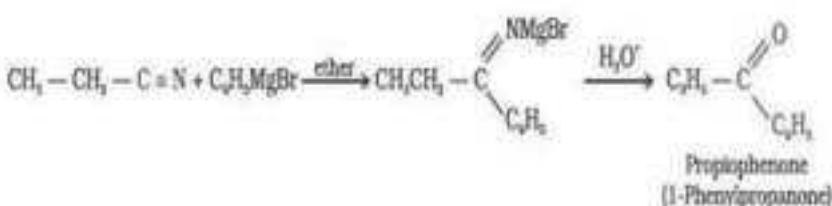
From acyl chlorides using dialkyl cadmium



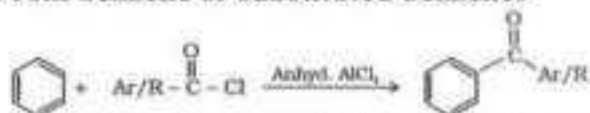
Acetyl chloride & benzoyl chloride give butanone and acetophenone respectively.

From nitriles

Treating a nitrile with Grignard reagent followed by hydrolysis yields a ketone.



From benzene or substituted benzenes



This reaction is known as Friedel-Crafts acylation reaction.

Physical Properties of Aldehydes and Ketones

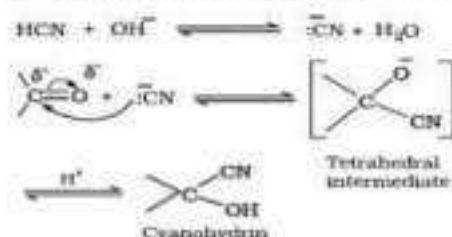
The boiling points of aldehydes and ketones are **higher than hydrocarbons** and **ethers** of comparable molecular masses. It is **due to dipole-dipole interactions**. Their boiling points are **lower than those of alcohols** of similar molecular masses due to **absence of intermolecular hydrogen bonding**.

Solubility : Lower aldehydes and ketones are soluble in water as they form H-bonds. Solubility decreases on increase in the length of alkyl chain.

Chemical Reactions of Aldehydes and Ketones

Nucleophilic Addition Reactions:

Mechanism: Addition of hydrogen cyanide (HCN)



Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons.

Sterically, the presence of two alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes which have only one alkyl group.

Electronically, in ketones two alkyl groups (+I effect, electron releasing effect) reduce the electrophilicity (positive charge) of the carbonyl carbon more effectively than in aldehyde.

The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance hence it is less reactive than propanal.

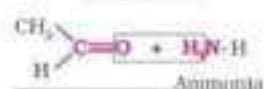


Summary of important reactions

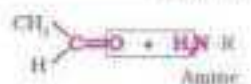
Nucleophilic addition-elimination reactions

(Addition of Addition of ammonia and its derivatives)

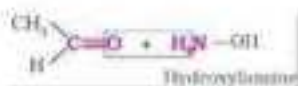
Ammonia derivative used (NH₂-Z)



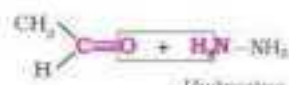
Ammonia



Amine



Hydroxylamine



Hydrazine



Phenylhydrazine



2,4-Dinitrophenylhydrazine



Semicarbazide

Product Obtained



Imines



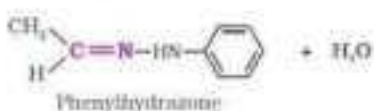
Substituted imine
(Schiff's base)



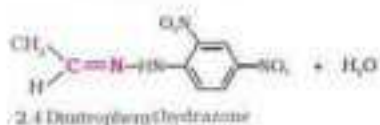
Oxime



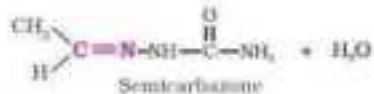
Hydrazine



Phenylhydrazine



2,4-Dinitrophenylhydrazine



Semicarbazone

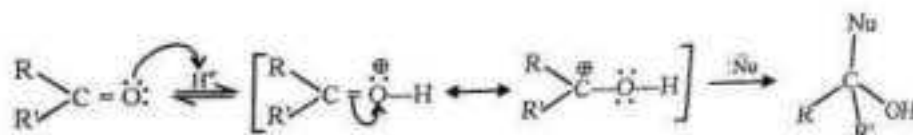
Note:

While preparing ammonia derivatives of carbonyl compounds, pH must be carefully controlled. The reaction is usually carried out in weakly acidic medium.

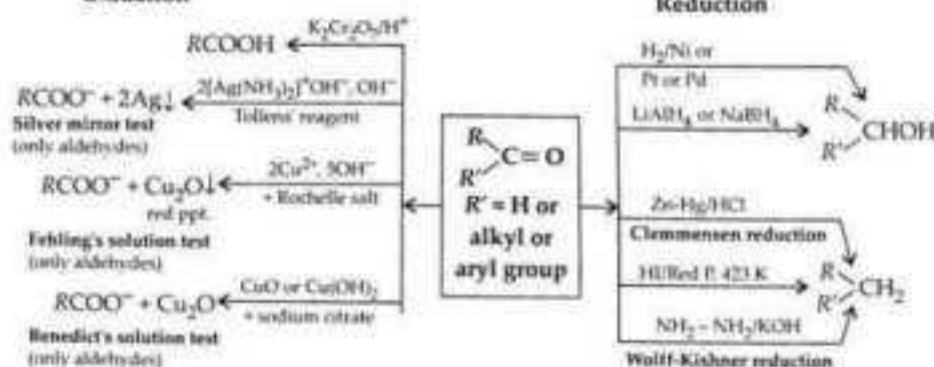
In strongly acidic medium, ammonia derivatives being basic will react with acids and will not react with carbonyl compounds.

In basic medium, OH⁻ will attack carbonyl group.

If the attacking Nu is weak like R-OH or NH₂OH etc. then, the nucleophilic attack gets accelerated if the medium is weakly acidic. The carbonyl group gets protonated and the resulting ion is resonance stabilized.



Oxidation-Reduction reactions

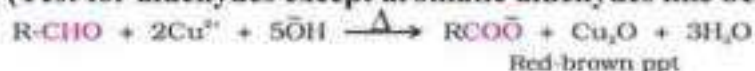


Tollens' test: (Silver mirror test)

Aldehydes + Tollen's reagent (Ammoniacal silver nitrate) $\xrightarrow{\Delta}$ Silver mirror

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} RCOO^- + 2Ag + 2H_2O + 4NH_3$$

Fehling's test (Test for aldehydes except aromatic aldehydes like benzaldehyde)



Fehling solution A : aqueous copper sulphate and

Fehling solution B : alkaline sodium potassium tartarate (Rochelle salt).

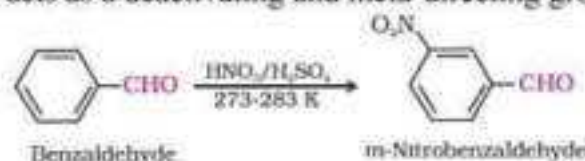
Haloform reaction: It is given by aldehydes & ketones having CH₃CO group or alcohols with CH₃CH(OH) group



Iodoform test is a distinction test for aldehydes and ketones (Methyl Ketones)

Electrophilic substitution reaction:

Carbonyl group acts as a deactivating and meta-directing group.



Distinction between aldehydes and ketones

Test with	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red ppt	No ppt
Tollen's reagent	Silver mirror	No silver mirror
2,4-DNP	Orange yellow or red ppt/colour	Orange yellow or red ppt/colour

Note: Formic acid also gives Tollen's test whereas acetic acid does not.

CARBOXYLIC ACIDS (R-COOH)

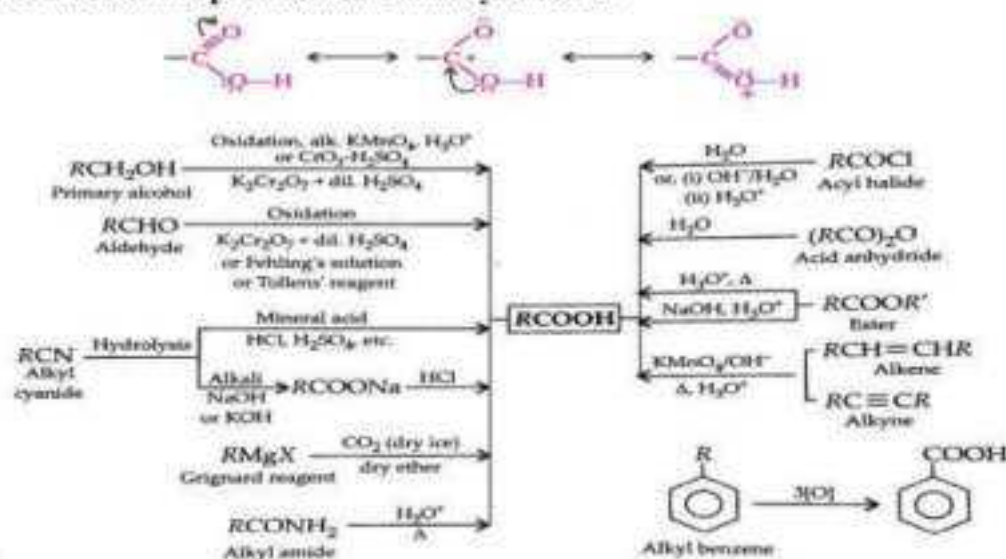
Higher members of aliphatic carboxylic acids (C12 – C18) known as fatty acids as they occur in natural fats as esters of glycerol.

Structure of Carboxyl Group

In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120° .

The carboxylic carbon is less electrophilic than carbonyl carbon because of resonance structure. Therefore, carboxylic acids do not show the characteristic reactions of carbonyl compounds (Nucleophilic addition reactions)

Methods of Preparation of Carboxylic Acids

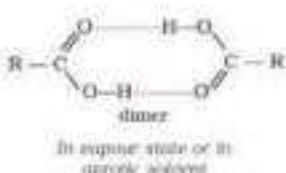


Physical Properties of Carboxylic Acids

Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours.

The higher acids are wax like solids and are practically odourless due to their low volatility.

Boiling points of carboxylic acids are higher than aldehydes, ketones and even alcohols of comparable molecular masses. It is due to strong intermolecular hydrogen bonding.



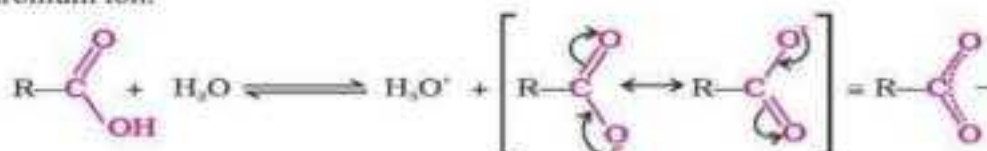
Lower members are soluble in water due to inter molecular hydrogen bonding. The solubility decreases with increasing number of carbon atoms.

Chemical Reactions

Reactions Involving Cleavage of O-H Bond

Acidic Strength of Carboxylic Acids

Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.



The strength of an acid is generally indicated by its pK_a . Smaller the pK_a , the stronger the acid.

The carboxylate ion is more stabilised than phenoxide ion, so carboxylic acids are more acidic than phenols even though phenol has more number of resonance structures.

Reasons:

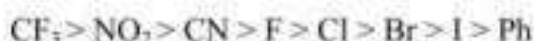
The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion.

Carboxylate ion, is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. The phenoxide ion, has resonance structures in which the negative charge is at the less electronegative carbon atom.

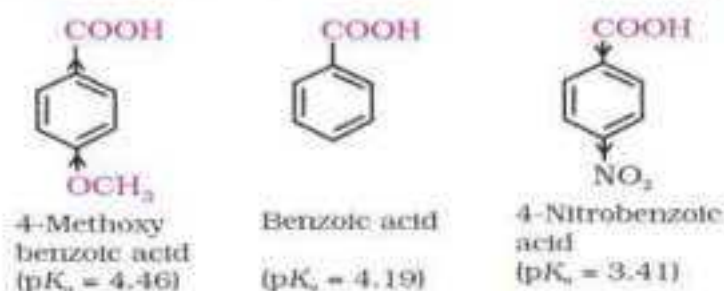
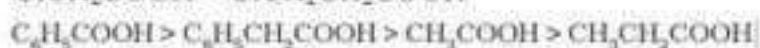
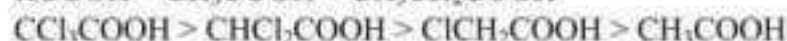
Effect of substituents on the acidity of carboxylic acids:



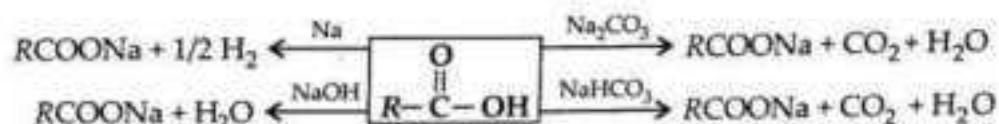
Order of various groups based on their power as electron withdrawing tendency is given below:



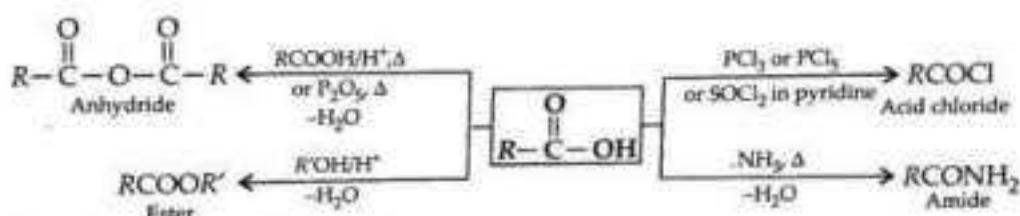
Order of acidity of a few acids



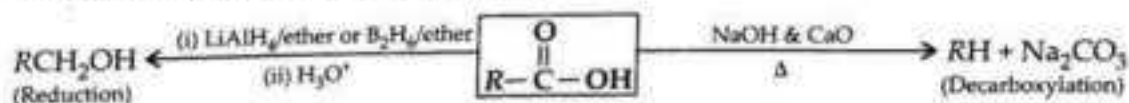
Reaction with active metals and bases.



Reactions Involving Cleavage of C–OH Bond



Reactions Involving –COOH Group and

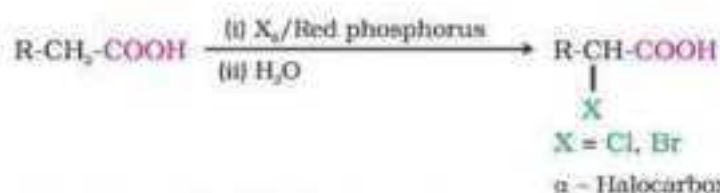


Reactions Involving hydrocarbon Part

Halogenation

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids.

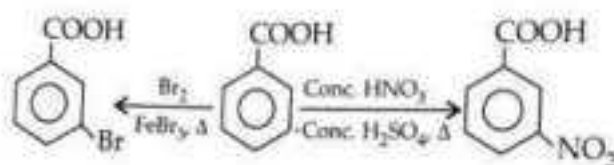
The reaction is known as **Hell-Volhard-Zelinsky (HVZ) reaction**.



TEST FOR -COOH GROUP: The organic compound containing -COOH group when reacts with NaHCO_3 gives brisk effervescence due to evolution of CO_2 .

Ring substitution

Aromatic carboxylic acids undergo electrophilic substitution reactions. carboxyl group -deactivating and meta-directing group. They do not undergo Friedel-Crafts reaction (because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group).



Nomenclature of aldehydes ketones and carboxylic acids

Structure	Common name	IUPAC name
Aldehydes		
HCHO	Formaldehyde	Methanal
CH ₃ CHO	Acetaldehyde	Ethanal
(CH ₃) ₂ CHCHO	Isobutyraldehyde	2-Methylpropanal
	γ -Methylcyclohexanecarbaldehyde	3-Methylcyclohexanecarbaldehyde
CH ₃ CH(OCH ₃)CHO	α -Methoxypropanaldehyde	2-Methoxypropanal
CH ₃ CH ₂ CH ₂ CH ₂ CHO	Valeraldehyde	Pentanal
CH ₂ =CHCHO	Acrolein	Prop-2-enal
	Phthalaldehyde	Benzene-1,2-dicarbaldehyde
	m-Bromobenzaldehyde	3-Bromobenzenealdehyde or 3-Bromobenzaldehyde

Structure	Common name	IUPAC name
Ketones		
CH ₃ COCH ₂ CH ₂ CH ₃	Methyl n-propyl ketone	Pentan-2-one
(CH ₃) ₂ CHCOCH(CH ₃) ₂	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	α -Methylcyclohexanone	2-Methylcyclohexanone
(CH ₃) ₂ C=CHCOCH ₃	Mesityl oxide	4-Methylpent-3-en-2-one

Structure	Common name	IUPAC name
HOOC-CH ₂ -COOH	Malonic acid	Propanedioic acid
HOOC-(CH ₂) ₂ -COOH	Succinic acid	Butanedioic acid
HOOC-(CH ₂) ₃ -COOH	Glutaric acid	Pentanedioic acid
HOOC-(CH ₂) ₄ -COOH	Adipic acid	Hexanedioic acid
HOOC-CH ₂ -CH(COOH)-CH ₂ -COOH	Tricarballic acid or carballic acid	Propane-1, 2, 3-tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
	Phenylacetic acid	2-Phenylethanoic acid
	Phthalic acid	Benzene-1, 2-dicarboxylic acid

QUESTION BANK-CHAPTER- Aldehydes, Ketones and Carboxylic Acid

SECTION A Multiple Choice Questions

1. The correct order of increasing acidic strength is _____.

- (a) Phenol < Ethanol < Chloroacetic acid < Acetic acid
- (b) Ethanol < Phenol < Chloroacetic acid < Acetic acid
- (c) Ethanol < Phenol < Acetic acid < Chloroacetic acid
- (d) Chloroacetic acid < Acetic acid < Phenol < Ethanol

Answer- c

2. The reagent which does not react with both, acetone and benzaldehyde.

- (a) Sodium hydrogensulphite
- (b) Phenyl hydrazine
- (c) Fehling's solution
- (d) Grignard reagent

Answer- c

3. Which of the following compounds will give butanone on oxidation with alkaline KMnO_4 solution?

- (a) Butan-1-ol
- (b) Butan-2-ol
- (c) Both of these
- (d) None of these

Answer- b

4. In Clemmensen Reduction carbonyl compound is treated with _____.

- (a) Zinc amalgam + HCl
- (b) Sodium amalgam + HCl
- (c) Zinc amalgam + nitric acid
- (d) Sodium amalgam + HNO_3

Answer- a

5. Which of the following conversions can be carried out by Clemmensen Reduction?

- (a) Benzaldehyde into benzyl alcohol
- (b) Cyclohexanone into cyclohexane
- (c) Benzoyl chloride into benzaldehyde
- (d) Benzophenone into phenyl methane

Answer- b

6. Through which of the following reactions number of carbon atoms can be increased in the chain?

- (a) Sandmeyer reaction
- (b) Cannizaro's reaction
- (c) Aldol condensation
- (d) HVZ reaction

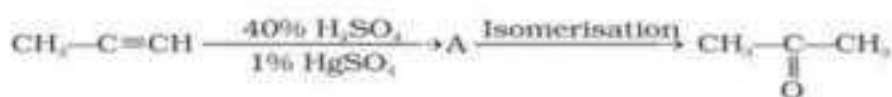
Answer: c

7. Benzophenone can be obtained by _____.

- (a) Benzoyl chloride + Benzene + AlCl_3
- (b) Benzoyl chloride + cadmium
- (c) Benzoyl chloride + Phenyl magnesium chloride
- (d) Benzene + Carbon monoxide + ZnCl_2

Answer: a

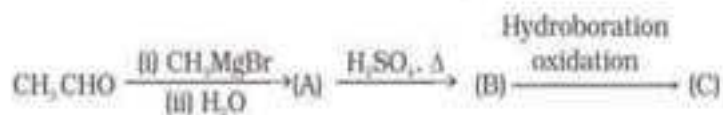
8. Structure of 'A' and type of isomerism in the above reaction are respectively.



- (a) Prop-1-en-2-ol, metamerism
- (b) Prop-1-en-1-ol, tautomerism
- (c) Prop-2-en-2-ol, geometrical isomerism
- (d) Prop-1-en-2-ol, tautomerism

Answer: d

9. Compounds A and C in the following reaction are _____.



- (a) Identical isomers
- (b) positional isomers
- (c) functional isomers
- (d) optical isomers

Answer: b

10. Compound PhCOOPh can be prepared by the reaction of _____.

- (a) Phenol and benzoic acid in the presence of NaOH
- (b) Phenol and benzoyl chloride in the presence of pyridine
- (c) Phenol and benzoyl chloride in the presence of ZnCl₂
- (d) Phenol and benzaldehyde in the presence of palladium

Answer: b

Assertion and Reason Type

Note : In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct and reason is correct explanation of assertion.
- (b) Assertion and reason both are wrong statements.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.
- (e) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

1. Assertion : Formaldehyde is a planar molecule.

Reason : It contains sp^2 hybridised carbon atom.

2. Assertion : Compounds containing —CHO group are easily oxidised to corresponding carboxylic acids.

Reason : Carboxylic acids can be reduced to alcohols by treatment with LiAlH_4 .

3. Assertion : The α -hydrogen atom in carbonyl compounds is less acidic.

Reason : The anion formed after the loss of α -hydrogen atom is resonance stabilised.

4. Assertion : Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.

Reason : Aromatic aldehydes are almost as reactive as formaldehyde.

5. Assertion : Aldehydes and ketones, both react with Tollen's reagent to form silver mirror.

Reason : Both, aldehydes and ketones contain a carbonyl group.

SECTION-B Very Short Answer Type Questions

Q.1 How will you distinguish between ethanol and acetone by suitable chemical test?

Ans. Add 2, 4 – DNP. Acetone will give orange ppt. whereas ethanol does not.

Or

Add Ceric ammonium nitrate. Ethanol gives wine red colouration, Acetone does not.

Or

Add conc. HCl and ZnCl_2 (anhy.) and heat. Ethanol will give turbidity but acetone will not.

Q.2 What is the function of BaSO_4 in rosenmund reaction?

Ans. BaSO_4 acts as a catalytic poison which prevents further reduction of aldehyde to alcohol.

Q.3 Write a chemical test to distinguish between aldehyde and ketone.

Ans. Aldehydes and ketones can be distinguished by Tollen's test. Aldehydes give a silver mirror on reacting with Tollen's reagent whereas ketones will not react.

Q.4 What is the chemical name of Tollen's reagent and Fehling's solution.

Ans. Tollen's reagent = Ammoniacal Silver Nitrate

Fehlings solution = Sodium Potassium Tartarate.

Q.5 Name the isomers with molecular formula C_3H_6O . Which one will have high boiling point?

Ans. The two isomers are CH_3COCH_3 and CH_3CH_2CHO . Acetone boils at higher temperature due to presence of two electron donating alkyl groups.

SECTION-C Short Answer Type Questions

1. A compound 'A' with formula $C_5H_{10}O$ gives a positive 2, 4 -DNP test but a negative Tollen's test. It can be oxidized to carboxylic acid 'B' of molecular formula $C_5H_8O_2$, when treated with alk. $KMnO_4$ under vigorous conditions. The salt of 'B' gives a hydrocarbon 'C' on Kolbe's electrolytic decarboxylation. Identify A, B and C.

Ans: A = Pentan-3-one, B = Propanoic acid And C = Butane

2. A compound A with molecular formula $C_5H_{12}O$ on oxidation forms compound B with molecular formula $C_5H_{10}O$. The compound B gives iodoform test but does not reduce ammoniacal silver nitrate. The compound B on reduction with $Zn - Hg / HCl$ gives compound C with molecular formula C_5H_{12} . Identify A, B and C.

Ans: A = $CH_3CHOHCH_2CH_2CH_3$

B = $CH_3COCH_2CH_2CH_3$

C = $CH_3CH_2CH_2CH_2CH_3$

3. An organic compound A, which has a characteristic odour, on treatment with $NaOH$ forms two compounds B and C. Compound B has molecular formula C_7H_8O which on oxidation gives back A. Compound C is the sodium salt of an acid. C, when heated with soda lime yields an aromatic hydrocarbon D. Deduce the structures of A to D.

Ans: The molecular formula of (B) and characteristic odour of (A) suggests that (A) is an aromatic aldehyde, C_6H_5CHO and (B) is alcohol, $C_6H_5CH_2OH$. As (C) is a sodium salt of an acid & gives hydrocarbon (D) on heating with soda lime, (C) is sodium

benzoate and (D) is benzene.

SECTION-D CASE STUDY BASED QUESTIONS

1. The following table has boiling points of different classes of compounds. Study the table and answer the Questions based on table and related studied concepts.

Compound	Boiling point
1. Ethanal	20.2 °C
2. Ethanol	78 °C
3. Acetone	56.2 °C
4. Acetic acid	118 °C
5. Acetic anhydride	139.8 °C
6. Diethyl ether	34.6 °C
7. Acetamide	222 °C
8. Ethyl acetate	77.1 °C

(a) Why diethyl ether has lower boiling point than C_2H_5OH ?

Ans. It is because diethyl ether have weaker dipole-dipole attraction than C_2H_5OH which has intermolecular H-bonding.

(b) Why acetic anhydride has high boiling point than acetic acid?

Ans. It is because acetic anhydride has higher molar mass, more surface area, more van der Waals' forces of attraction than acetic acid.

(c) Why amides have higher boiling point among-acid derivatives?

Ans. Most of amides are solids and have strong forces of attraction, hence higher boiling point.

(d) Why does aqueous solution of CH_3COOH conducts electricity but ethanol does not?

Ans. It is because acetic acid ionise in aqueous solution early whereas ethanol does not.

2. Study the table in which pka of various is given. Answer the questions based on table and related studied

concepts.

Compounds	pka
1. Acetic acid	4.76
2. HCOOH	3.75
3. CH ₃ CH ₂ COOH	4.38
4. ClCH ₂ COOH	2.87
5. FCH ₂ COOH	2.59
6. CH ₂ =CH-COOH	4.30
7. Benzoic acid	4.19
8. p-Toluic acid	4.38
9. Salicylic acid	2.98
10. p-nitro benzoic acid	3.44
11. p-methoxy benzoic acid	4.88
12. p-chloro benzoic acid	3.99
13. p-hydroxy benzoic acid	4.58

(a) Why is HCOOH stronger than CH₃COOH?

Ans. It is because HCOO⁻ is more stable than CH₃COO⁻.

(b) Why is p-hydroxy benzoic acid more acidic than p-methoxy benzoic acid?

Ans. It is because —OH has more —I effect than —OCH₃ group.

(c) Why is salicylic acid stronger than benzoic acid?

Ans. It is because salicylate is more stable than benzoate ion due to intra molecular H-bonding.

(d) Give one use of salicylic acid.

Ans. It is used for preparation of Aspirin which is an important Analgesics, Antipyretic and prevents heart attack.

SECTION- E –(Long Answer Type Questions)

Q.1 Give Reasons :-

1. Carboxylic acid is stronger acid than phenol.
2. Ethanol is more soluble in water than ethyl chloride
3. Aldehydes are more reactive than Ketones towards nucleophilic additions.
4. Carboxylic acids have higher boiling points than alcohols of same no. of carbon atoms.
5. Ethanoic acid has molar mass of 120 in vapour state.

Answer-

1. Carboxylic acid on dissociation form carboxylate ion which is stabilized by two equivalent resonance structure in which negative charge is at the more electronegative oxygen atom, whereas the conjugate base of phenol, phenoxide ion, has non – equivalent resonance structures in which negative charge is at the less electronegative carbon atom. Therefore resonance is not as important as it is in carboxylate ion. Moreover the negative charge is delocalized over two more electronegative oxygen atoms in carboxylate ion whereas it is less effectively delocalized over one oxygen atom and one carbon atom in phenoxide ion. Therefore the carboxylate ion is more stabilized than phenoxide ion and carboxylic acids are stronger acids than phenol.
2. Ethanol can form intermolecular Hydrogen bonding with water molecules, ethyl chloride can not. Therefore ethanol is soluble in water and ethyl chloride is not.
3. Aldehydes are more reactive than Ketones due to steric and electronic reasons. In Ketones due to presence of two relatively large alkyl groups, the approach of nucleophile is more hindered than in aldehydes having only one such substitute. Moreover the +I effect of alkyl groups reduces the electrophilicity of carbonyl group more in Ketone than in aldehydes.
4. Carboxylic acids have more extensive association of molecules through intermolecular hydrogen bonding than alcohols. Moreover their boiling points are

higher than alcohols of same carbon atoms.

5. Ethanoic acid exists as dimer in vapour state in which two molecules remain together by hydrogen bonding. This increases the effective molecular mass to 120.

Q.2. Write down functional isomers of a carbonyl compound with molecular formula C_3H_6O . Which isomer will react faster with HCN and why? Explain the mechanism of the reaction also. Will the reaction lead to the completion with the conversion of whole reactant into product at reaction conditions? If a strong acid is added to the reaction mixture what will be the effect on concentration of the product and why?

Ans: CH_3CH_2CHO

(I)

CH_3COCH_3

(II)

* Compound I will react faster with HCN due to less steric hindrance and electronic reasons than II.

* No, It is a reversible reaction. Hence equilibrium is established.

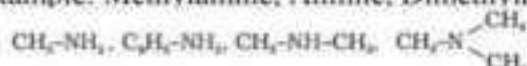
* Addition of acid inhibits the reaction because the formation of $-CN$ ions is prevented.

CHAPTER-9-AMINES

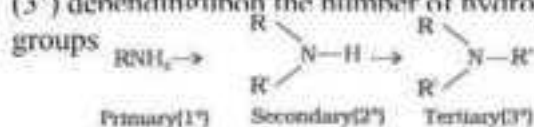
Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.

Amines can be considered as derivatives of ammonia, obtained by replacement of one, two or all the three hydrogen atoms by alkyl and/or aryl groups.

For example: Methylamine, Aniline, Dimethylamine, and Trimethylamine



Classification: Amines are classified as primary (1°), secondary (2°) and tertiary (3°) depending upon the number of hydrogen atoms replaced by alkyl or aryl groups

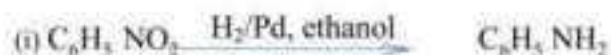


Structure of Amines:

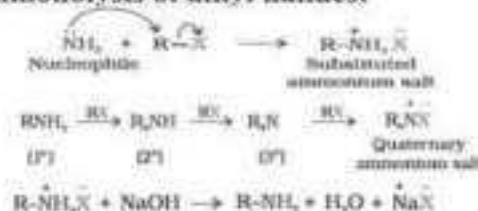


Preparation of Amines:

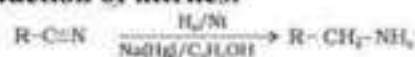
1. Reduction of nitro compounds:



2. Ammonolysis of alkyl halides:



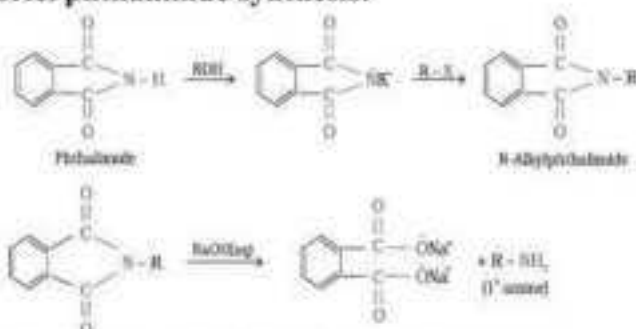
3. Reduction of nitriles:



4. Reduction of amides



5. Gabriel phthalimide synthesis:



6. Hoffmann bromamide degradation reaction:

7.



Physical Properties:**Solubility in water:**

Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.

Higher amines are essentially insoluble in water.

Boiling Point:

Primary and secondary amines are engaged in intermolecular association due to hydrogen bonding between nitrogen of one and hydrogen of another molecule.

This intermolecular association is more in primary amines than in secondary amines as there are two hydrogen atoms available for hydrogen bond formation in it. Tertiary amines do not have intermolecular association due to the absence of hydrogen atom available for hydrogen bond formation.

Therefore, the order of boiling points of isomeric amines is as follows: Primary > Secondary > Tertiary

Boiling Points of Amines of Similar Molecular Masses:

S.No.	COMPOUND	MOLAR MASS	BOILING POINT
1	n-C ₄ H ₉ NH ₂ (Primary)	73	350.8
2	(C ₂ H ₅) ₂ NH (Secondary)	73	329.3
3	C ₂ H ₅ N(CH ₃) ₂ (Tertiary)	73	310.5

Chemical Reactions:

1. Basic character of amines: Amines, being basic in nature, react with acids to form salts.



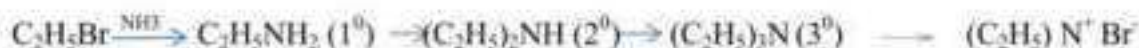
$$K = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2][H_2O]}$$

$$K_b = \frac{[R-\overset{+}{N}H_3][\overset{-}{O}H]}{[R-NH_2]}$$

$$pK_b = -\log K_b$$

Larger the value of K_b or smaller the value of pK_b , stronger is the base.

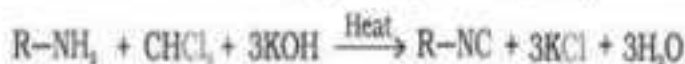
2. Alkylation: Amines undergo alkylation on reaction with alkyl halides.



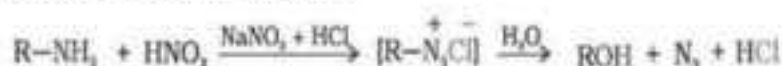
3. Acylation: Ethanamine to N-ethyl ethanamide



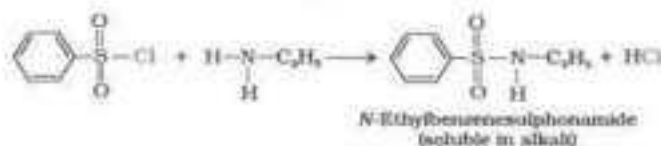
4. Carbylamine reaction: Test for primary amines (Aliphatic and aromatic)



5. Reaction with nitrous acid:

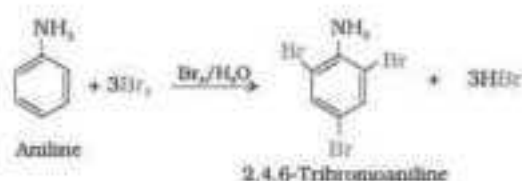


6. Reaction with arylsulphonyl chloride: Benzenesulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$), which is also known as Hinsberg's reagent, reacts with Ethyl amine to form N- Ethylbenzenesulphonamide.

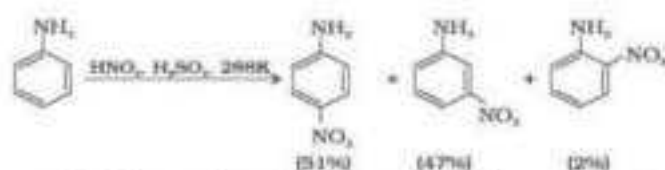


7. Electrophilic substitution:

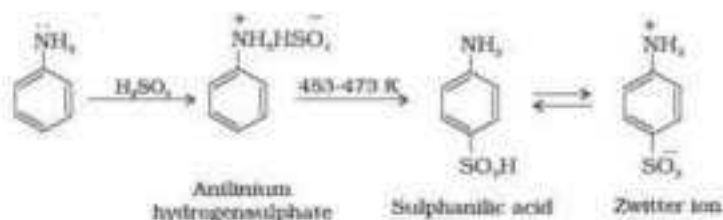
(a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of 2, 4, 6-tribromoaniline.



(b) **Nitration:** Aniline reacts with nitric acid to give o-, m- & p-nitro aniline.



(c) **Sulphonation:** Aniline reacts with concentrated Sulphuric acid to form anilinium hydrogensulphate which on heating with Sulphuric acid at 453-473K produces p-amino benzenesulphonic acid, known as sulphanilic acid followed by Zwitter ion structure.



USES OF AMINES: The important uses of aliphatic and aromatic amines are given below:

1. Aliphatic amines of low molecular mass are used as solvents.
2. Amines are also used as intermediates in drug manufacture and as reagents in organic synthesis.
3. Aromatic amines are used for the manufacture of polymers, dyes and as intermediates for additives in the rubber industry.
4. The quaternary ammonium salts derived from long chain aliphatic tertiary amines are widely used as detergents.
5. Aromatic amines are converted into arene Diazonium salts which are used for the preparation of variety of aromatic compounds via substitution and coupling reactions.

Identification of primary, secondary and tertiary amines.

S.No	Characteristic reaction	Primary	Secondary	Tertiary
1	Action with nitrous acid ($\text{NaNO}_2 + \text{HCl}$)	N_2 is given out with the formation of alcohols.	Nitrosoamines are formed which give Liebermann's Nitroso test.	They remain dissolved forming amine nitrite salt which decomposes on warming to Nitrosoamines and alcohol.
2	Carbylamine reaction (CHCl_3 & alc. KOH)	Give foul smelling Carbylamine.	No reaction	No reaction
3	Acylation	Form amides	Form amides	No reaction
4	Hinsberg's test	Give clear solution which on acidification gives insoluble material	Give insoluble substance which is not affected by acid	Does not react
5	Azo dye test	Give coloured dyes	No reaction	No reaction

II. DIAZONIUM SALTS: The general formula of Diazonium salts is $RN_2^+ X^-$ where R stands for an aryl group and X^- ion may be Cl^- , Br^- , HSO_4^- , BF_4^- , etc. and the group N_2^+ is called Diazonium group. These are obtained when aromatic primary amine react with nitrous acid.

NOMENCLATURE:

For example, $C_6H_5N_2^+Cl^-$ are named as Benzenediazonium chloride and $C_6H_5N_2^+HSO_4^-$ is known as Benzenediazonium hydrogensulphate.

Method of Preparation of Diazonium Salts

Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278K. Nitrous acid is produced in the reaction mixture by the reaction of sodium nitrite with hydrochloric acid. The conversion of primary aromatic amines into Diazonium salts is known as diazotization.



Physical Properties:

Benzenediazonium chloride is a colourless crystalline solid. It is readily soluble in water and is stable in cold but reacts with water when warmed. It decomposes easily in the dry state.

Chemical Reactions:

The reactions of Diazonium salts can be divided into two categories:

(A) Reactions involving displacement of nitrogen

Diazonium group being a very good leaving group is substituted by other groups such as Cl^- , Br^-

, I^- , CN^- and OH^- which displace nitrogen from the aromatic ring. The nitrogen formed escapes from the reaction mixture as a gas.

1. Replacement by halide or cyanide ion (Sandmeyer Reaction)

The Cl^- , Br^- and CN^- nucleophiles can easily be introduced in the benzene ring in the presence of Cu (I) ion. This reaction is called Sandmeyer reaction.



Alternatively, chlorine or bromine can also be introduced in the benzene ring by treating the Diazonium salt solution with corresponding halogen acid in the presence of copper powder. This is referred to as **Gatterman reaction**.



Replacement by iodide ion: When the Diazonium salt solution is treated with potassiumiodide, Iodobenzene is formed.



2. Replacement by fluoride ion: When Benzenediazonium chloride is treated with fluoroboric acid, Benzenediazonium fluoroborate is precipitated which on heating decomposes to yield fluorobenzene.



3. Replacement by H: Certain mild reducing agents like hypo phosphorous acid (phosphinic acid) or ethanol reduce Diazonium salts to benzene and they get oxidized to phosphorous acid and ethanal, respectively.



4. Replacement by hydroxyl group: When aqueous solution of Diazonium salt is boiled upto 283K, it gives phenol. Therefore, Diazonium group replaced by hydroxyl group.



5. Replacement by -NO₂ group: Nitrobenzene is prepared by heating Benzenediazonium fluoroborate with aqueous sodium nitrite solution in the presence of copper, the Diazonium group is replaced by -NO₂ group.



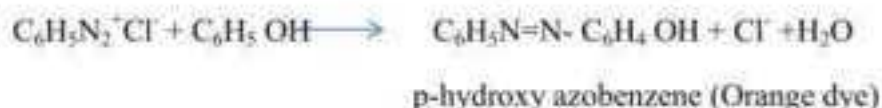
(A) Reactions involving retention of diazo

groupCoupling reactions:

Benzenediazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the Diazonium salt to form p-hydroxy azobenzene. This type of reaction is known as coupling reaction.

Similarly, the reaction of Benzenediazonium chloride with aniline yields p-

amino azobenzene. This is an example of electrophilic substitution reaction.



QUESTION BANK-CHAPTER-AMINE
SECTION- A (MCQ/ASSERTION REASON)

1. What is the correct IUPAC name of $\text{H}_2\text{N}-(\text{CH}_2)_5-\text{NH}_2$?

- a. Pentan-1,5-diamine
- b. 1,5-Diaminopentane
- c. Pentamethylenediamine
- d. Pentane-1,5-diamine

ANS-D

2. Which of the following does not react with Hinsberg reagent?

- a. $\text{C}_2\text{H}_5\text{NH}_2$
- b. $(\text{CH}_3)_2\text{NH}$
- c. $(\text{CH}_3)_3\text{N}$
- d. $\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_3$

ANS-C

3. Which of the following amines are insoluble in water?

- a. Methanamine
- b. Ethanamine
- c. Propanamine
- d. Benzenamine

ANS-D

4. Which of the following is formed when an alkyl primary amine reacts with nitrous acid?

- a. Alkyl nitrite
- b. Secondary amine
- c. Nitro alkane
- d. Alcohol

ANS-D

5. Arrange the following compounds in increasing order of basicity: CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, NH_3 , $\text{C}_6\text{H}_5\text{NH}_2$ in aqueous medium

- a. $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < (\text{CH}_3)_2\text{NH} < \text{CH}_3\text{NH}_2$
- b. $\text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2$
- c. $\text{C}_6\text{H}_5\text{NH}_2 < \text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}_2$

d. $(\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{C}_6\text{H}_5\text{NH}_2 < \text{CH}_3\text{NH}_2$

ANS-C

6. The correct IUPAC name for $\text{CH}_2=\text{CHCH}_2\text{NHCH}_3$ is

- a. Allylmethylamine
- b. 2-amino-4-pentene
- c. 4-aminopent-1-ene
- d. N-methylprop-2-en-1-amine

ANS-D

7. $\text{C}_3\text{H}_8\text{N}$ cannot represent

- a. 1° ammine
- b. 2° ammine
- c. 3° ammine
- d. Quarternary ammonium salt

ANS-D

8. In this reaction acetamide is converted to methanamine

- a. Gabriel phthalimide synthesis
- b. Carbylamine reaction
- c. Stephen's reaction
- d. Hoffmann bromamide reaction

ANS-A

9. Which of the following is not a final product of the reaction between propylamine and nitrous acid?

- a. $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}_2\text{Cl}$
- b. $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- c. N_2 gas
- d. HCl

ANS-A

10. Hinsberg's reagent is

- a. Benzenesulphonic acid
- b. Benzenesulphonyl chloride
- c. p-toluenesulphonyl chloride
- d. Chlorosulphuric acid

ANS-B

ASSERTION -REASON TYPE QUESTIONS

Choose the correct answer from the following choices

- a Both assertion and reason are correct statements and reason is correct explanation of assertion
- b Both assertion and reason are correct statements but reason is not correct explanation of assertion
- c Assertion is correct statement but reason is wrong statement
- d Assertion is wrong statement but reason is correct statement

1.	Assertion: Alkylation of amines gives polysubstituted product where as acylation of amines gives a monosubstituted product Reason: Steric hindrance of an acyl group prevents the approach of further acyl groups.
2.	Assertion: Anilinium chloride is more acidic than ammonium chloride Reason: Anilinium ion is resonance stabilized.
3.	Assertion: Gabriel phthalimide reaction can be used to prepare aryl and alkyl amines. Reason: Aryl halides have same reactivity as alkyl halides towards nucleophilic substitution reactions.
4.	Assertion: Aniline does not undergo Friedel -Crafts reaction Reason: Friedel-Crafts reaction is electrophilic substitution reaction
5.	Assertion: CuCl_2 gives a deep blue colored solution with ethyl amine Reason: Ethylamine molecules coordinate with cupric ions forming a blue coloured complex.

ANSWERS

1.	C Due to delocalization of the lone pair of electrons of the nitrogen atom over the carbonyl group in the acyl derivative, the electron density on the N atom decreases to such an extent that it does not act as a nucleophile at all.
2.	C Ammonia is a stronger base than aniline and the conjugate acid of aniline is more acidic than conjugate acid of ammonia
3.	D Gabriel phthalimide reaction is used to prepare only primary alkyl amines. Aryl halides do not undergo nucleophilic substitution reactions.
4.	B AlCl_3 forms a salt with aniline which deactivates the benzene ring
5.	A

SECTION-B SHORT ANSWER QUESTION 2 MARKS

1. Give reasons for the following:

Primary amines have higher boiling point than tertiary amines.

ANS- Primary amines ($\text{R}-\text{NH}_2$) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

2. Arrange the following in the increasing order of their boiling point:

$\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{OH}$, $(\text{CH}_3)_3\text{N}$

ANS- increasing order of boiling points : $(\text{CH}_3)_3\text{N} < \text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH}$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of amines because oxygen is more electronegative than nitrogen.

3. Give a simple chemical test to distinguish between the following pair of compounds:

$(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$

ANS- When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(\text{CH}_3)_2\text{NH}$ forms

insoluble *N,N*-dialkylbenzenesulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

4. Arrange the following in increasing order of basic strength:
Aniline, *p*-nitro aniline, and *p*-toluidine

ANS-



5. Why do amines act as nucleophiles?

ANS- Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles

6. Complete the following reaction equation: $\text{C}_6\text{H}_5\text{N}_2\text{Cl} + \text{H}_3\text{PO}_2 + \text{H}_2\text{O} \longrightarrow$



7. Give reasons for the following:

i) Aniline does not undergo Friedel-Crafts reaction.

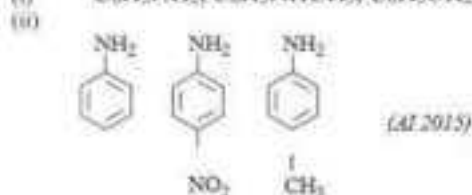
ANS- (i) In Friedel-Crafts reaction, AlCl_3 is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel-Crafts reaction.

ii) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

(ii) In aqueous solution 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.

8. Arrange the following in increasing order of their basic strength:

(i) $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$



ANS- (i) $\text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_5\text{NHCH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$. $\text{C}_6\text{H}_5\text{NH}_2$ and $\text{C}_6\text{H}_5\text{NHCH}_3$ are less basic than aliphatic amine $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to +I effect of $-\text{CH}_3$ group in $\text{C}_6\text{H}_5\text{NHCH}_3$, it is more basic than $\text{C}_6\text{H}_5\text{NH}_2$.

(ii)



SECTION -C-LONG ANSWER QUESTION (3 MARK EACH)

1. Illustrate the following reactions giving suitable example in each case:
 - a. Ammonolysis
 - b. Acetylation of amine

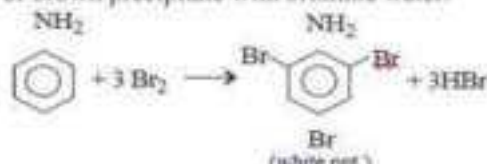
(i) Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



(ii) Acylation of amines. The process of introducing an acetyl group in a molecule is called acetylation

2. Give one chemical test each to distinguish between the following pairs of compounds:
 - a. Ethylamine and aniline
 - b. Aniline and *N*-methylaniline

ANS-a) Aniline gives white or brown precipitate with bromine water.

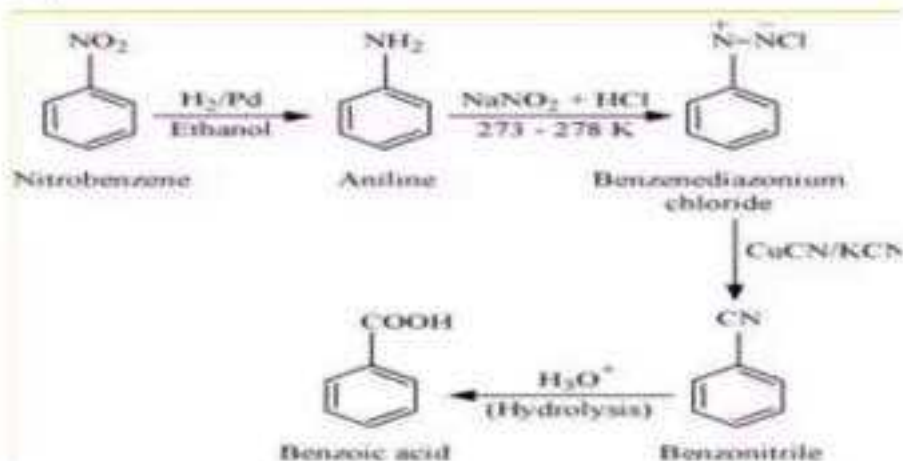


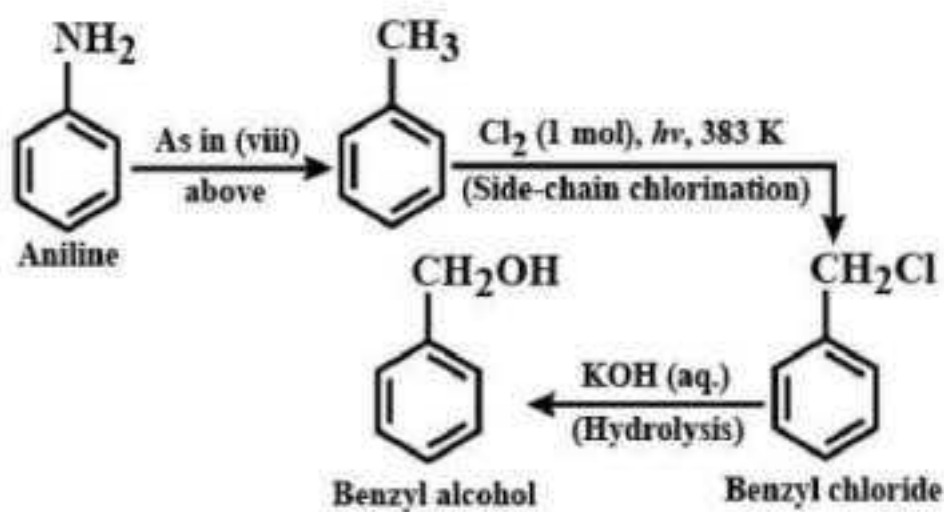
ANS- b) Aniline gives carbylamines test, i.e., on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methyl aniline being secondary amine, does not show this test

3. Write chemical equations for the following conversions:

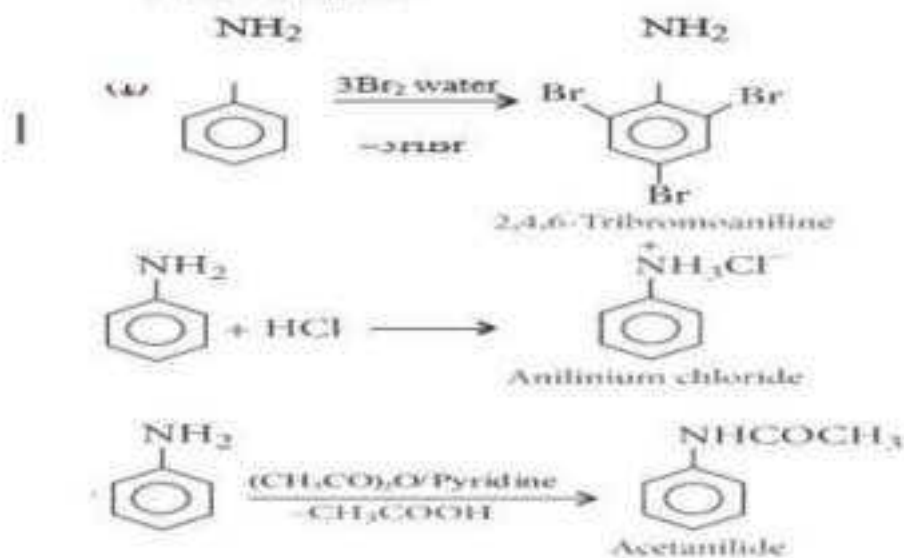
- (i) Nitrobenzene to benzoic acid
- (ii) Aniline to benzyl alcohol

ANS-i)



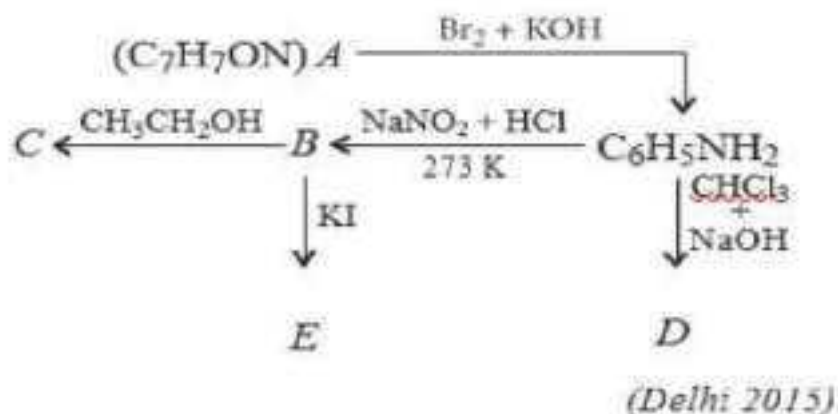


4. Write the structures of main products when aniline reacts with the following reagents:
- Br_2 water
 - HCl
 - $(\text{CH}_3\text{CO})_2\text{O}$ /pyridine

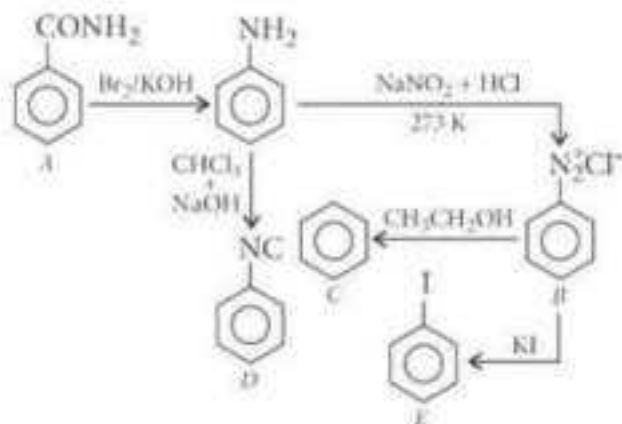


SECTION- D VERY LONG ANSWER QUESTION 5 MARK

1. An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:



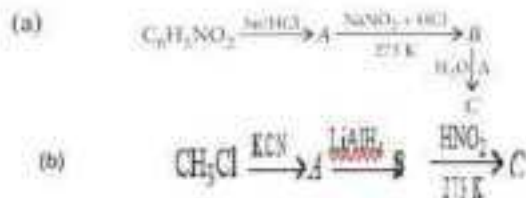
ANS:

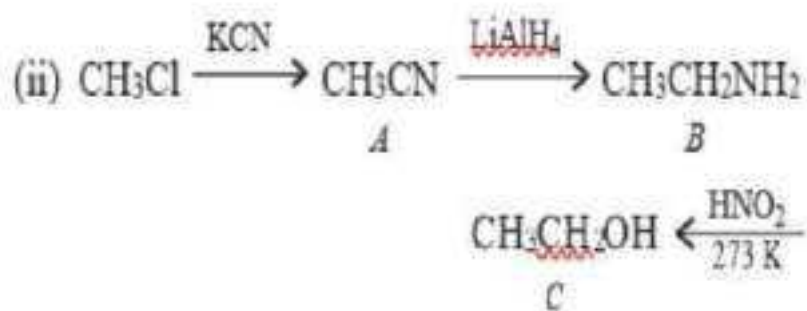
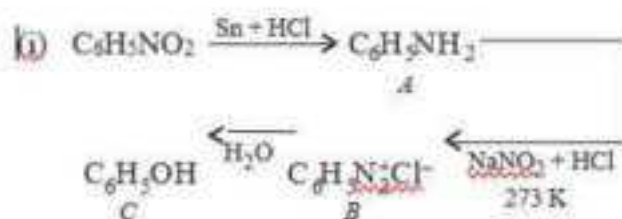
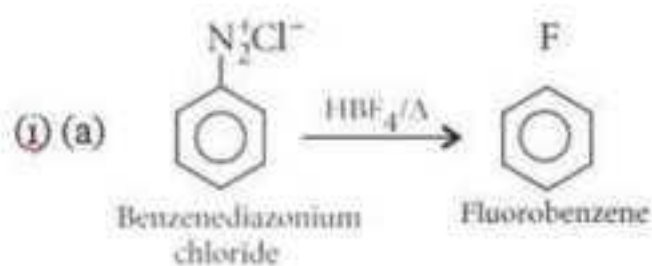


- (i) Write the structures of main products when benzenediazonium chloride ($\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$) reacts with the following reagents:

(a) HBF_4 (b) Cu/HBr

- (ii) Write the structures of A, B and C in the following reactions:





SECTION- E CASE BASED QUESTIONS

- 1 The basicity of amines of different classes do not follow a simple pattern because the number of groups bonded to nitrogen affects the electron density at the nitrogen atom. And, the stability of the conjugate acid in the solvent has a major effect on basicity. Thus, the basicity of amines can be explained only for amines with similar structures at the nitrogen atoms.
- The basicity of an amine is increased by electron-donating groups and decreased by electron-withdrawing groups. Aryl amines are less basic than alkyl-substituted amines because some electron density provided by the nitrogen atom is distributed throughout the aromatic ring. Basicity is expressed using K_b values measured from the reaction of the amine with water. An alternate indicator of basicity is pK_b , which is $-\log K_b$. A strong base has a large K_b and a small pK_b . The basicity of amines is also expressed by the acidity of their conjugate acids. A strong base has a weak conjugate acid, as given by a small value of K_a and a large pK_a . [Robert J. Ouellette, J. David Rawn, in Organic Chemistry Study Guide, 2015]
- pK_b values for NH_3 , CH_3NH_2 , $(CH_3)_2NH$ and $(CH_3)_3N$ has 4.75, 3.38, 3.27 and 4.22 respectively.
Write them in the decreasing order of basic strength. Usually the order of basicity of amines will be different from the expected order.
 - Which are the three main factors affecting basicity of amines?
 - Write the decreasing order of basicity for $CH_3CH_2NH_2$, $(CH_3CH_2)_2NH$ and $(CH_3CH_2)_3N$
 - Compare the basicity of m-toluidine and Aniline.

Answer

- $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- +I effect, extent of hydrogen bonding with water molecules and steric effects of the alkyl group
- $(CH_3CH_2)_2NH > (CH_3CH_2)_3N > CH_3CH_2NH_2 > NH_3$
- m-Toluidine is more basic than aniline due to +I effect from meta position

CHAPTER-10-BIOMOLECULES

TOPIC: CARBOHYDRATES

1. **CARBOHYDRATES:** It is defined as optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. Most of them have a general formula, $C_x(H_2O)_y$, and were considered as hydrates of carbon from where the name carbohydrate was derived.

For example, the molecular formula of glucose ($C_6H_{12}O_6$) fits into this general formula, $C_6(H_2O)_6$. But all the compounds which fit into this formula may not be classified as carbohydrates. Acetic acid (CH_3COOH) fits into this general formula, $C_2(H_2O)_2$ but is not a carbohydrate.
2. **CLASSIFICATION OF CARBOHYDRATES:** Carbohydrates are classified on the basis of their behavior on hydrolysis. They have been broadly divided into following three groups.
 - (a) **MONOSACCHARIDES:** A carbohydrate that cannot be hydrolyzed further to give simpler unit of polyhydroxy aldehyde or ketone is called a monosaccharide. Some common examples are *glucose, fructose, ribose*, etc.
 - (b) **OLIGOSACCHARIDES:** Carbohydrates that yield **two to ten** monosaccharide units, on hydrolysis, are called oligosaccharides. They are further classified as disaccharides, trisaccharides, tetrasaccharides, etc. depending upon the number of monosaccharides, they provide on hydrolysis. For example,
 - **Sucrose** on hydrolysis gives one molecule each of **glucose and fructose**.
 - **Maltose** on hydrolysis gives **two molecules of glucose** only.
 - **Lactose** on hydrolysis gives **galactose and glucose**.
 - (c) **POLYSACCHARIDES:** Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides. Some common examples are **starch, cellulose, glycogen, gums, etc.** Polysaccharides are not sweet in taste, hence they are also called non-sugars.
3. **REDUCING SUGARS & NON-REDUCING SUGARS**
 - All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars.
 - All monosaccharides whether aldose or ketose are **reducing sugars**.
 - In disaccharides, if the reducing groups of monosaccharides i.e., aldehydic or ketonic groups are bonded, these are **non-reducing sugars e.g. sucrose**.
 - On the other hand, sugars in which these functional groups are

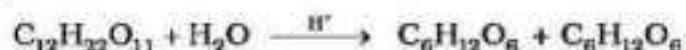
free, are called **reducing sugars**, for example, **maltose** and **lactose**.

4. **MONOSACCHARIDES:** Monosaccharides can be classified on the basis of number of carbon atoms and the functional group present in them. If a monosaccharide contains an aldehyde group, it is known as an **aldose** and if it contains a keto group, it is known as a **ketose**.

5. GLUCOSE

(a) Preparation of Glucose

(i) From sucrose (Cane sugar):

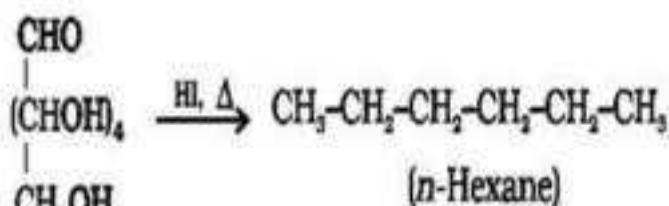


(ii) From starch:

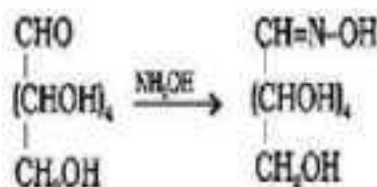


- (i) **STRUCTURE & REACTIONS OF GLUCOSE:** Glucose is an aldohexose and is also known as dextrose. It is the monomer of many of the larger carbohydrates, namely starch, cellulose. Its **molecular formula** was found to be $\text{C}_6\text{H}_{12}\text{O}_6$.

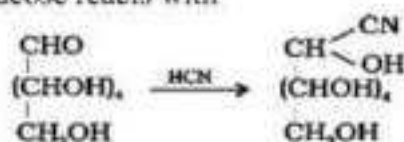
- (ii) **Reaction with HI:** On prolonged heating with HI, it forms **n-hexane**, suggesting that **all the six carbon atoms are linked in a straight chain**



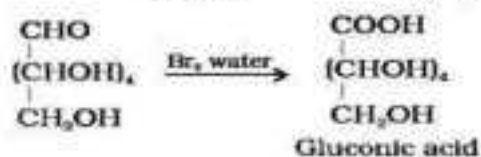
- (iii) **Reaction with Hydroxylamine:** Glucose reacts with hydroxylamine to form an oxime.



Reaction with HCN (Hydrogen Cyanide): Glucose reacts with hydrogen cyanide to give cyanohydrin. These reactions confirm the presence of a **carbonyl group** ($>\text{C}=\text{O}$) in glucose.



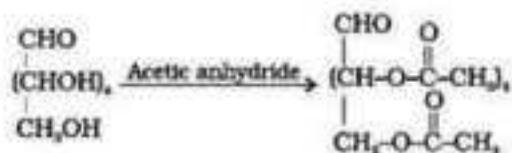
- (iv) **Reaction with Bromine water (Br_2):** Glucose gets oxidized to six



carbon carboxylic acid (**Gluconic acid**) on reaction with a mild oxidising agent like bromine water. *This indicates that the carbonyl group is present as an aldehydic group.*

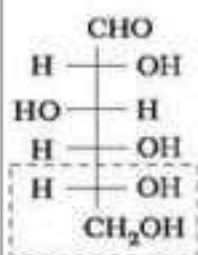
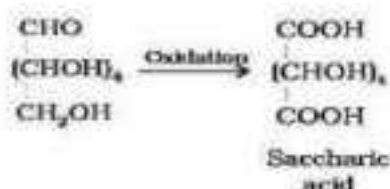
(v) **Reaction with Acetic anhydride:**

Acetylation of glucose with acetic anhydride gives **glucose pentaacetate** which confirms the presence of five $-OH$ groups. Since it exists as a stable compound, *five $-OH$ groups should be attached to different carbon atoms.*



(vi) **Reaction with nitric acid HNO_3 :** On

oxidation with nitric acid, glucose yield a dicarboxylic acid, saccharic acid. *This indicates the presence of a primary alcoholic ($-OH$) group in glucose.*

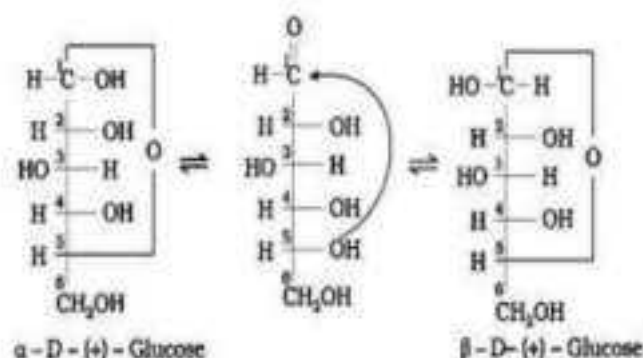


D-(+)-Glucose

- Glucose is correctly named as D(+)-glucose. 'D' before the name of glucose represents the configuration whereas '(+)' represents dextrorotatory nature of the molecule.
- The structure (I) of glucose explained most of its properties but the following ~~facts~~ facts could not be explained by this structure.
 - (i) Despite having the aldehyde group, glucose does not give 2,4-DNP test, Schiff's test and it does not form the hydrogensulphite addition product with NaHSO_3 .
 - (ii) The pentaacetate of glucose does not react with hydroxylamine indicating the absence of free $-\text{CHO}$ group.
- (iii) Glucose is found to exist in two different crystalline forms which are named as α and β . The α -form (m.p. 419 K) is obtained by crystallization from conc. solution of glucose at 303 K while the β -form (m.p. 423 K) is obtained by crystallization from hot and saturated aqueous solution at 371

K. This behaviour could not be explained by the open chain structure (I) for glucose.

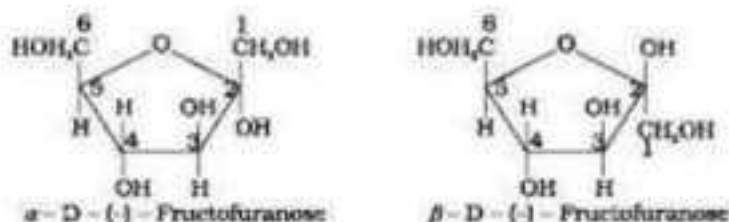
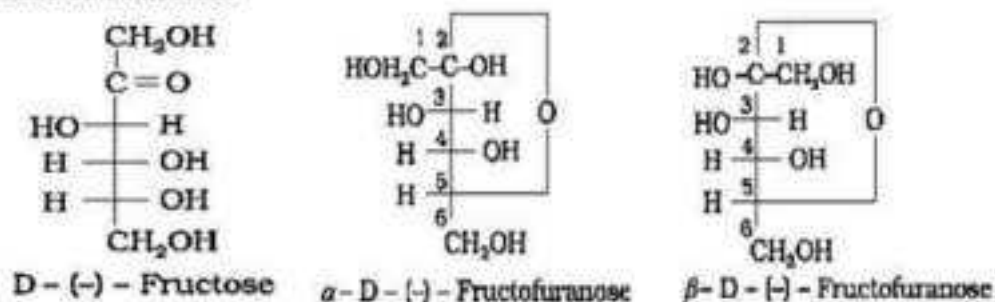
ANOMERS OF GLUCOSE: The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* (the aldehyde carbon before cyclisation). Such isomers, i.e., α -form and β -form, are called **anomers**.



PYRANOSE STRUCTURE OF GLUCOSE: The six membered cyclic structure of glucose is called **pyranose structure** (α - or β -), in analogy with pyran. The cyclic structure of glucose is more correctly represented by Haworth structure.

6. **Fructose** is an important ketohexose. It is obtained along with glucose by the hydrolysis of disaccharide, sucrose. It also has the molecular formula $C_6H_{12}O_6$. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(-)-fructose.

Structure of Fructose:



7. DISACCHARIDES & GLYCOSIDIC LINKAGE The two monosaccharides are joined together by an oxide linkage formed by the loss of a water molecule. Such a linkage between two monosaccharide units through oxygen atom is called **Glycosidic Linkage**

8. SUCROSE: sucrose on hydrolysis gives equimolar mixture of D-(+)-glucose and D-(-) fructose. Sucrose is a non-reducing sugar.

□ Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and levorotatory fructose. Since the levorotation of fructose (-92.4°) is more than dextrorotation of glucose ($+52.5^\circ$), the mixture is levorotatory. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (-) and the product is named as **INVERT SUGAR**.

9. MALTOSE: on hydrolysis gives two α -D-glucose units in which C1 of one glucose (I) is linked to C4 of another glucose unit (II). The free aldehyde group can be produced at C1 of second glucose in solution and it shows reducing properties so it is a reducing sugar.

10. LACTOSE (milk sugar): on hydrolysis gives β -D-galactose and β -D-glucose. The linkage is between C1 of galactose and C4 of glucose. Hence it is also a reducing sugar. -

11. POLYSACCHARIDES contain a large number of monosaccharide units joined together by glycosidic linkages.

12. STARCH: Starch is the main storage polysaccharide of plants. It is a polymer of α -glucose and consists of two components — **Amylose** and **Amylopectin**.

- **Amylose** is water soluble component which constitutes about 15-20% of starch. Chemically amylose is a long unbranched chain with 200-1000 α -D-(+)-glucose units held by C1–C4 glycosidic linkage.
- **Amylopectin** is insoluble in water and constitutes about 80-85% of starch. It is a branched chain polymer of α -D-glucose units in which chain is formed by C1–C4 glycosidic linkage whereas branching occurs by C1–C6 glycosidic linkage.

13. CELLULOSE: Cellulose occurs exclusively in plants and it is the most abundant organic substance in plant kingdom. It is a predominant constituent of cell wall of plant cells. Cellulose is a straight chain polysaccharide composed only of β -D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

14. GLYCOGEN: The carbohydrates are stored in animal body as glycogen. It is also known as animal starch because its structure is similar to

amylopectin and is rather more highly branched. It is present in liver, muscles and brain. When the body needs glucose, enzymes break the glycogen down to glucose. Glycogen is also found in yeast and fungi.

15.IMPORTANCE OF CARBOHYDRATES:

- Carbohydrates are essential for life in both plants and animals. They form a major portion of our food.
- Honey has been used for a long time as an instant source of energy by 'Vaid's' in ayurvedic system of medicine.
- Carbohydrates are used as storage molecules as starch in plants and **glycogen** in animals.
- Cell wall of bacteria and plants is made up of cellulose.
- We build furniture, etc. from cellulose in the form of wood and clothe ourselves with cellulose in the form of cotton fibre.
- They provide raw materials for many important industries like textiles, paper, lacquers and breweries. Carbohydrates are found in bio system in combination with many proteins and lipids.

(QUESTIONS RELATED TO CARBOHYDRATES)

1. Define carbohydrates.
2. How are carbohydrates classified on the basis of their behaviour on hydrolysis?
3. What are reducing and non-reducing sugars? Give example of each.
4. How is Glucose prepared? Write the reactions when D-Glucose reacts with following: (a) Hydrocyanic acid, HCN (b) acetic anhydride (c) Tollens reagent (d) HI (e) Conc. HNO₃ (f) Phenyl Hydrazine (g) Hydroxylamine (h) Bromine
5. Write the reaction which show that all the carbon atoms in glucose are linked in a straight chain.
6. How do you explain the presence of an aldehydic group in a glucose molecule?
7. How do you explain the presence of five —OH groups in glucose molecule?
8. Under what conditions glucose is converted to gluconic and saccharic acid?
9. Explain Pyranose structure of glucose.
10. Write such reactions & facts of Glucose which cannot be explained by its open chain structure.
11. What is the basic structural difference Glucose and Fructose?
12. Despite having an aldehyde group glucose does not give 2, 4 - DNP test. What does this indicate?
13. What is the significance of D and (+) in D-(+)-glucose?
14. Explain the structure of Sucrose.
15. Classify the following into monosaccharides and

disaccharides. Ribose, 2 deoxyribose, maltose, galactose, fructose and lactose.

16. Monosaccharides contain carbonyl group hence are classified, as aldose or ketose. The number of carbon atoms present in the monosaccharide molecule are also considered for classification. In which class of monosaccharide will you place fructose?
17. What are the hydrolysis products of (a) Sucrose (b) Lactose (c) Maltose.
18. Glucose or sucrose are soluble in water but cyclohexane or benzene are insoluble in water. Explain
19. How do you explain the absence of aldehyde group in the pentaacetate of D-glucose?
20. Write two main functions of carbohydrates in plants.
21. What do you understand by the term glycosidic linkage?
22. Name the linkage connecting monosaccharide units in polysaccharides.
23. Which sugar is called invert sugar?
24. What is meant by Invert Sugar?
25. An optically active compound having molecular formula $C_6H_{12}O_6$ is found in two isomeric forms (A) and (B) in nature. When (A) and (B) are dissolved in water they show the following equilibrium.

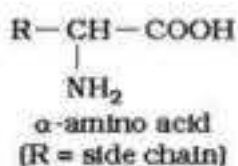
(A)	$\leftrightarrow$	Equilibrium	$\leftrightarrow$	(B)
		mixture		
111°		52.2°		19.2°

 - (i) What are such isomers called? (ii) Can they be called enantiomers? Justify your answer.
 - (iii) Draw the cyclic structure of isomer (A)
26. Name the two components of starch. How do they differ from each other structurally?
27. Which of the two components of starch is water soluble?

TOPIC: PROTEINS

1. **PROTEINS:** are the most abundant biomolecules of the living system. Chief sources of proteins are milk, cheese, pulses, peanuts, fish, meat, etc. They are also required for growth and maintenance of body. The word protein is derived from Greek word, "**proteios**" which means primary or of prime importance. **All proteins are polymers of α -amino acids.**
2. **α -AMINO ACIDS :**
 - All proteins are polymers of **α -amino acids**. Amino acids contain amino ($-NH_2$) and carboxyl ($-COOH$) functional groups. Amino acids are generally represented by a three letter symbol, sometimes

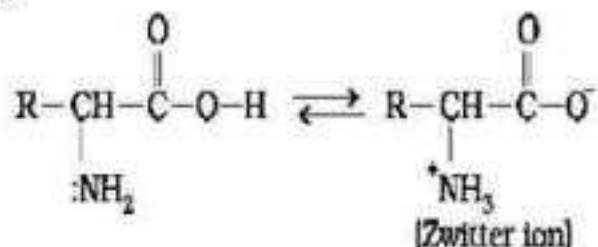
one letter symbol is also used. For example :



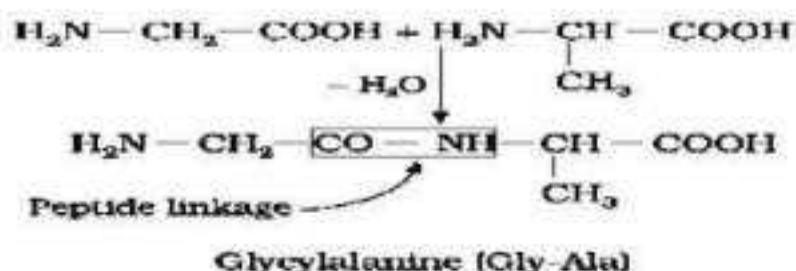
- Glycine (where R is H) Gly (G)
- Alanine (where R is CH₃) Ala (A)
- Valine* (H₃C)₂CH- Val (V)
- Leucine* (where R is (H₃C)₂CH-CH₂-) Leu (L)
- Phenylalanine* (where R is C₆H₅-CH₂-) Phe (F)

- **NONESSENTIAL AMINO ACIDS:** The amino acids, which can be synthesized in the body, are known as **nonessential amino acids**. e.g Glycine , Alanine etc.
- **ESSENTIAL AMINO ACIDS:** Those which cannot be synthesized in the body and must be obtained through diet, are known as **essential amino acids** .e.g. Valine*, Leucine*, Phenylalanine* etc.

3. **PROPERTIES OF AMINO ACIDS:** Amino acids are usually colourless, crystalline solids. These are water-soluble, high melting solids and behave like salts rather than simple amines or carboxylic acids. This behaviour is due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.
4. **ZWITTER ION:** In aqueous solution, the carboxyl group can lose a proton and amino group can accept a proton, giving rise to a dipolar ion known as *zwitter ion*. This is neutral but contains both positive and negative charges. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.



5. **ISOELECTRIC POINT:** The *pH* at which the amino acid molecule has no net charge & do not migrate towards any electrode is called its Isoelectric point.
6. **PEPTIDE BOND :** peptide linkage is an amide formed between -COOH group and -NH₂ group. The bond formed between two amino acids by the elimination of a water molecule is called a **peptide linkage or bond**(-CO-NH-)



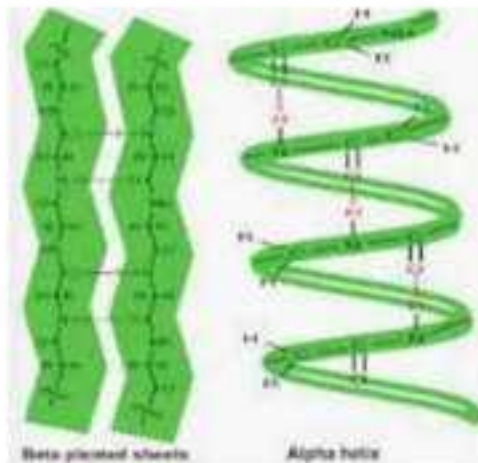
A dipeptide contains two amino acids linked by one peptide Linkages, A tripeptide contains three amino acids linked by two peptide linkages. **When the number of such amino acids is more than ten, then the products are called polypeptides.** A polypeptide with more than hundred amino acid residues, having molecular mass higher than 10,000u is called a protein.

7. **GLOBULAR PROTEINS & FIBROUS PROTEINS:** Proteins can be classified into two types (**Globular Proteins & fibrous proteins**) on the basis of their molecular shape.

Globular proteins	Fibrous proteins
This structure results when the chains of polypeptides coil around to give a spherical shape .	When the polypeptide chains run parallel and are held together by hydrogen and disulphide bonds, then fibre- like structure is formed They can be stretched and contracted like a thread
usually soluble in water	Insoluble in water
Example : Insulin and albumins	Examples are keratin (present in hair, wool, silk) and myosin (present in muscles)

8. **Primary structure of proteins:** The primary structure of a protein refers to the number and sequence of the amino acids in its polypeptide chains. Any change in this primary structure i.e., the sequence of amino acids creates a different protein.
9. **Secondary structure of proteins:** (α -helix and β -pleated sheet structure): The secondary structure of protein refers to the shape in which a long polypeptide chain can exist. It gives information: (a) about the manner in which the protein chain is folded and bent; (b) about the nature of the bonds which stabilize this structure. They are found to exist in two different types of structures viz. α -helix and β -pleated sheet structure.

- **α -Helix** : This structure is formed when the chain of α -amino acids coils as a right handed screw (called α -helix) because of the formation of hydrogen bonds between amide groups of the same peptide chain. It is stabilized by **intramolecular hydrogen bonding**. **Wool and hair have α -helix structure.**
- **In β -structure** all peptide chains held together by intermolecular hydrogen bonds. The structure resembles the pleated folds of drapery and therefore is known as β -pleated sheet. **Silk has a beta pleated structure.**



10. TERTIARY STRUCTURE OF PROTEINS: It involves further folding of the secondary structure. It gives rise to two major molecular shapes viz. **fibrous and globular**. The main forces which stabilise the 2^o and 3^o structures of proteins are hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.

11. QUATERNARY STRUCTURE OF PROTEINS: Some of the proteins are composed of two or more polypeptide chains referred to as sub-units. The spatial arrangement of these subunits with respect to each other is known as quaternary structure

12. DENATURATION OF PROTEINS: When a protein is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. Due to this protein loses its biological activity. This is called denaturation of protein. **During denaturation 2^o and 3^o structures are destroyed but 1^o structure remains intact.** For example : the heating of white of an egg (water soluble) gives a hard and rubbery insoluble mass (coagulation of egg white on boiling) ,curdling of milk which is caused due to the formation of lactic acid by the bacteria present in milk.

QUESTIONS RELATED TO PROTEINS

1. Draw the structure of Glycine, Alanine, and Phenylalanine.
2. Amino acids may be acidic, alkaline or neutral. How does this happen?
3. What are essential and non-essential amino acids? Give two examples of each type.
4. Write a note on zwitter ion and isoelectric point.
5. Amino acids behave like salts rather than simple amines or carboxylic acids. Explain
6. What do you understand by the term Peptide linkage & Polypeptide linkage?
7. Write the name of linkage joining two amino acids.
8. Distinguish between the following: (a) Essential & Nonessential amino acids (b) Fibrous & Globular proteins (c) α -helix and β -pleated sheet proteins
9. Write a note on: (a) Primary structure of proteins (b) secondary structure of proteins
10. What are the common types of secondary structure of proteins?
11. What type of bonding helps in stabilizing the α -helix structure of proteins?
12. How do you explain the amphoteric behaviour of amino acids?
13. What is Denaturation of proteins?
14. What is the biological effect of Denaturation on the structure of proteins?
15. Where does the water present in the egg go after boiling the egg?
16. Coagulation of egg white on boiling is an example of denaturation of protein. Explain it in terms of structural changes.
17. The melting point and solubility in water of amino acids are generally higher than that of the corresponding haloacids. Explain.
18. Where does the water present in the egg go after boiling the egg?
19. What changes occur in the nature of egg proteins on boiling?
20. Name the type of bonding which stabilizes α -helix structure of proteins.
21. Name the type of bonding which stabilizes β -pleated sheet proteins.
22. Name the type of bonding which stabilizes tertiary structure of proteins.
23. An optically active amino acid (A) can exist in three forms depending on the pH of the medium. If the molecular formula of (A) is $C_3H_7NO_2$ write
 - (i) Structure of compound (A) in aqueous medium. What are such ions called?
 - (ii) In which medium will the cationic form of compound (A) exist?
 - (iii) In alkaline medium, towards which electrode will the compound (A) migrate in electric field?

TOPIC: VITAMINS

1. Vitamins are Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.
2. **Classification of Vitamins**
 - Fat soluble vitamins:** Insoluble in water. These are **vitamins A, D, E and K**. They are stored in liver and adipose (fat storing) tissues.
 - ☐ **Water soluble vitamins: B group vitamins and vitamin C.** Water soluble vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot be stored (*except vitamin B12*) in our body.
3. **Hypervitaminosis:** Excess intake of vitamins.
4. **Avitaminosis:** Condition of vitamin deficiency.
5. **Some important Vitamins, their Sources and their Deficiency Diseases**

S No.	Name of vitamin	Source	Deficiency disease
1	Vitamin A	Fish liver oil, carrots, butter and milk	Xerophthalmia i.e cornea hardening of eye , Night blindness
2	Vitamin B1 (thiamine)	Yeast, milk, green vegetables and cereals	Beri beri (loss of appetite, retarded growth)system)
3	Vitamin B2 (riboflavin)	Milk, eggwhite, liver,Kidney	Cheilosis (fissuring at corners of mouth and lips), digestive disorders and burning sensation of the skin.
4	Vitamin B6 (pyridoxine)	Yeast, milk, egg yolk, cereals and grams	Convulsions(Body muscles contract and relax rapidly & Repeatedly resulting in uncontrolled actions of body.)
5	Vitamin B12	Meat, fish, egg and Curd	Pernicious anaemia (RBC deficient in haemoglobin)
6	Vitamin C (Ascorbic acid)	Citrus fruits, amla and green leafy vegetables	Scurvy (bleeding gums)
7	Vitamin D	Exposure to sunlight, fish and egg yolk	Rickets (bone deformities in children) and osteomalacia

			(soft bones and joint pain in adults)
8	Vitamin E	Vegetable oils likewheat germ oil, sunflower oil, etc.	Sterility, Increased fragility of RBCs and muscular Weakness
9	Vitamin K	Green leafy vegetables	Increased blood clotting ,time Hemorrhagic conditions

QUESTION RELATED TO VITAMIN

1. Define vitamins. How are vitamins classified?
2. Name the deficiency diseases caused due to lack of vitamin A, C, E, B1, B2, B6, B12 E & K.
3. Write the chemical name of vitamin A, C, E, B1, B2, B6, B12 E & K.
4. Write the name of Vitamin responsible for the : (a) Pernicious anaemia (b) Increased blood clotting time (c) Xerophthalmia (d) Rickets (e) Muscular weakness (f) Night blindness (g) Beri Beri (h) Bleeding gums (i) Osteomalacia
5. Which of the following B group vitamins can be stored in our body? Vitamin B1, Vitamin B2, Vitamin B6 Vitamin B12
6. Why Vitamin B & C essential for us.

TOPIC : ENZYMES & NUCLEIC ACIDS

1. **Enzymes** are Biocatalyst produced by living cells which catalysis the biological reactions. Enzymes are mainly globular proteins. They are very specific in nature. They are needed in very small quantity. The various steps involve in the enzyme catalyzed reaction are as follows:--
 - Binding of the enzymes (E) to substrate (S) to form a complex.

$$E + S \rightarrow ES \text{ (complex)}$$
 - Product formation in the complex:

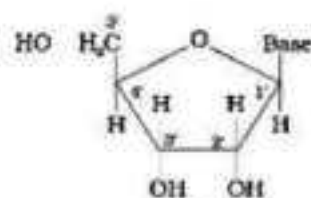
$$ES \rightarrow E + P$$
 - Release of product from the complex.: $E + P \rightarrow E + P$
2. **NUCLEIC ACIDS:** The particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called **nucleic acids**. These are of two types, the **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)**. Since nucleic acids are long chain polymers of **nucleotides**, so they are also called polynucleotides.
3. Complete hydrolysis of DNA (or RNA) yields a pentose sugar, phosphoric acid and nitrogen containing heterocyclic compounds (called bases).

4. DNA (DEOXYRIBOSE NUCLEIC ACIDS) & RNA (RIBOSE NUCLEIC ACIDS)

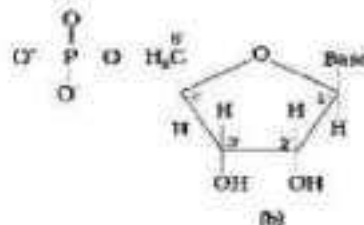
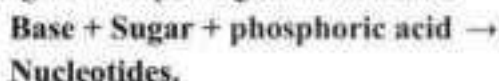
DNA	RNA
It contains β -D-2-deoxyribose sugar.	It Contains β -D-ribose sugar.
It Contains adenine (A), guanine (G), cytosine (C) and thymine (T) as bases.	It Contains adenine (A), guanine (G), cytosine (C), uracil (U), as bases
It has double helix structure	It has single helix structure
It Can replicate	It Cannot replicate
It is responsible for inheritance of character	It is responsible for protein synthesis.
It is present in the nucleus cell.	It is present in the cytoplasm of the cell.

STRUCTURE OF NUCLEIC ACIDS

5. **NUCLEOSIDES:** A unit formed by the attachment of a base to 1' position of sugar is known as nucleoside



6. **NUCLEOTIDES:** When nucleoside is linked to phosphoric acid at 5'-position of sugar moiety, we get a nucleotide.



7. **PHOSPHODIESTER LINKAGE:** Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of the pentose sugar.

10. **PRIMARY STRUCTURE OF A NUCLEIC ACID:** Information regarding the sequence of nucleotides in the chain is of a nucleic acid is called its primary structure.

11. SECONDARY STRUCTURE OF A NUCLEIC ACID :

- Two nucleic acid chains are wound about each other and held together by hydrogen bonds between pairs of bases. **The two strands are complementary to each other because the hydrogen bonds are formed between specific pairs of bases. Adenine forms hydrogen bonds with thymine whereas cytosine forms hydrogen bonds with guanine.**
- In secondary structure of RNA, helices are present which are only single

stranded. RNA molecules are of three types and they perform different functions.

12. DIFFERENT TYPES OF RNA: RNA molecules are of three types and they perform different functions. They are named as **messenger RNA (m-RNA)**, **ribosomal RNA (r-RNA)** and **transfer RNA (t-RNA)**.

13. DNA FINGERPRINTING: A sequence of bases on DNA is unique for a person and information regarding this is called DNA fingerprinting. It is same for every cell and cannot be altered by any known treatment.

DNA fingerprinting is now used (i) in forensic laboratories for identification of criminals. (ii) to determine paternity of an individual. (iii) to identify the dead bodies in any accident by comparing the DNA's of parents or children. (iv) to identify racial groups to rewrite biological evolution.

Questions related to Enzymes & Nucleic acids

1. What are biocatalysts? Give an example.
2. Define Nucleic acids. How are they classified? Mention their two important sources.
3. Write the full forms of DNA and RNA.
4. Write the important differences between DNA and RNA.
5. Of the two bases named below which one is present in RNA and which one is present in DNA? (i) Thymine (ii) Uracil
6. Out of the four bases name those which are common to both DNA
7. Which of the following are purine bases? Guanine, Adenine Thymine & Uracil
8. What is the difference between a nucleoside and a nucleotide?
9. What is phosphodiester linkage?
10. The two strands in DNA are not identical but are complementary. Explain
11. What are different types of RNA molecules which perform different functions?
12. What products would be formed when a nucleotide from DNA containing thymine is hydrolyzed?
13. Write a note on DNA fingerprinting.

TOPIC: HORMONES

1. **Hormones:** Hormones are biomolecules that are produced in the ductless (endocrine) glands and transported by the bloodstream to various parts of the body where they control various metabolic processes. These are required in minute amounts and, unlike fats and carbohydrates, are not stored in the body but are constantly produced.

QUESTION BANK-CHAPTER- BIOMOLECULES

SECTION A (MCQ/ASSERTION REASON)

Question 1.

The number of tripeptide formed by 3 different amino acids.

- (a) Three
- (b) Four
- (c) Five
- (d) Six.

Answer: (d) Six.

Question 2.

The functional group which is found in amino acids is

- (a) COOH
- (b) -NH₂
- (c) -CH₃
- (d) both (a) and (b).

Answer: (d) both (a) and (b).

Question 3.

The vitamins absorbed from intestine along with fats are

- (a) A and D
- (b) A, B
- (c) A, C
- (d) D, B

Answer: (a) A and D

Question 5.

Which of the following biomolecules is insoluble in water?

- (a) α -Keratin
- (b) haemoglobin
- (c) ribonuclease
- (d) adenine

Answer: (a) α -Keratin

Question 6.

The protein responsible for blood clotting is

- (a) Albumins
- (b) Globulins
- (c) Fibroin
- (d) Fibrinogen

Answer: (d) Fibrinogen

Question 7.

Which one of them is not a protein?

- (a) Wool
- (b) Nail

- (c) Hair
- (d) DNA

Answer: (d) DNA

Question 8.

The helical structure of protein is stabilized by:

- (a) Peptide band
- (b) Dipeptide band
- (c) Hydrogen bands
- (d) vander Waal's forces

Answer: (c) Hydrogen bands

Question 9.

Which of the following has a branched chain structure

- (a) Amylopectin
- (b) Anylose
- (c) Cellulose
- (d) Nylon

Answer: (a) Amylopectin

Question 10.

Glucose reacts with acetic anhydride to form

- (a) Monoacetate
- (b) Tetraacetate
- (c) Penta-acetate
- (d) Hexa-acetate

Answer: (c) Penta-acetate

Assertion and Reason Questions

Directions: These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.

Q.1. Assertion : D(+)- Glucose is dextrorotatory in nature.

Reason : 'D' represents its dextrorotatory nature.

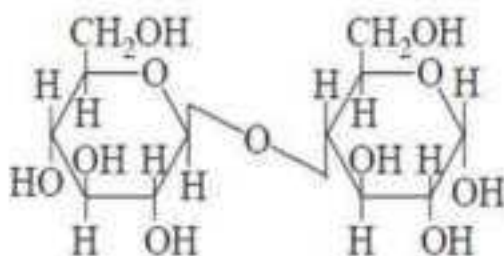
Answer c

Q.2. Assertion : Sucrose is called an invert sugar.

Reason : On hydrolysis, sucrose bring the change in the sign of rotation from dextro (+) to laevo(-).

Answer(a) The hydrolysis of sucrose brings about a change in the sign of rotation from dextro (+) to laevo (-) and the product is named as invert sugar.

Q.3. Assertion : β -glycosidic linkage is present in maltose



Reason : Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.

Answer d

Q.4. Assertion : At isoelectric point, the amino group does not migrate under the influence of electric field.

Reason : At isoelectric point, amino acid exists as a zwitterion.

Answer a

Q.5. Assertion : Vitamin D cannot be stored in our body

Reason : Vitamin D is fat soluble vitamin and is excreted from the body in urine

Answer (d) Vitamin D is a fat soluble vitamin and can be stored in the body since it is not excreted out of the body.

SECTION –B SHORT ANSWER (2 MARKS)

1. Differentiate between fibrous and globular proteins.

Ans.

Fibrous Proteins	Globular Proteins
1. Their molecules have long thread like structure.	1. They have folded ball – like structure
2. they have helical or sheet structures	2. They may have three dimensional Shapes.
3. They are in soluble in water but soluble in strong acids and bases. e.g. Keratin, fibroin etc.	3. They are soluble in water, acids and Bases and salts. e.g. Egg albumin, casein insulin.

2. Differentiate between α – helical and β – pleated sheet structure.

Ans.

α – helical structure	β – pleated sheet structure
1. In this structure, formation of hydrogen Bonding between amide groups within the same chain causes the peptide chains to coil up into a spiral structure like a right handed screw. e.g. α – keratin, skin, wool etc.	1. In this structure, the long peptide chains lie side by side in a zig-zag manner to form a flat sheet. Each chain is held to the two neighboring Chains by hydrogen bonds. These sheets can slide upon one another in three dimensional structures. e.g. fibroin present in silk etc.

3. What is denaturation of proteins? Explain with examples.

Ans. Disruption of the native conformation of a protein by changing its environment like PH value, temperature etc. resulting into loss of its biological activity is called denaturation of proteins. During denaturation, secondary and tertiary structures get destroyed while primary structure remains same e.g., coagulation of egg albumin by boiling..

4. Give an example of enzyme catalysed reaction.

Ans. Example of enzyme catalysed reaction –



5. Write the disease caused by deficiency of vitamins A, B_2 , B_6 , B_{12} , C, D E and K.

Ans.

Vitamin	Deficiency disease
A	Xerophthalmia, Night blindness
B_2	digestive disorders
B_6	Convulsions
B_{12}	Pernicious anaemia
	Scurvy

C	Rickets
D	Muscular weakness
E	Increased blood clotting time.
K	

6. What are essential and non-essential amino acids? Give two examples of each type.

Ans. Essential amino acids are required by the human body, but they cannot be synthesised in the body. They must be taken through food. For example: valine and leucine

7. What are the different types of RNA found in the cell?

Ans. (i) Messenger RNA (m-RNA)

(ii) Ribosomal RNA (r-RNA)

(iii) Transfer RNA (t-RNA)

SECTION-C SHORT ANSWER (3 MARKS)

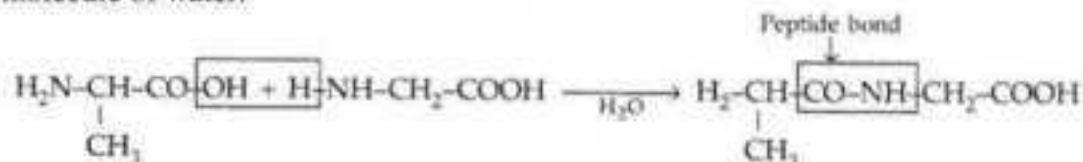
1. Explain what is meant by

(i) a peptide linkage

(ii) a glycosidic linkage.

Answer:

(i) **Peptide linkage:** A peptide linkage is an amide linkage formed between – COOH group of one α -amino acid and NH_2 group of the other α -amino acid by loss of a molecule of water.

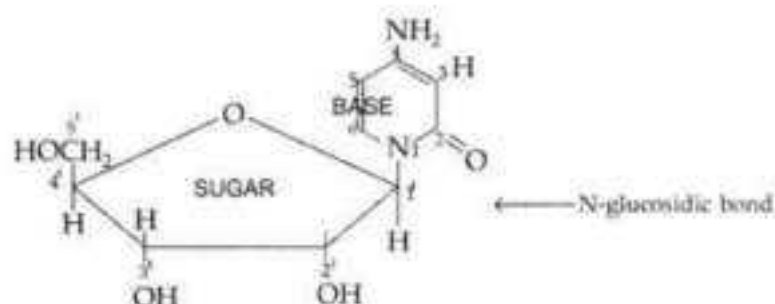


(ii) **Glycosidic linkage:** The two monosaccharide units are joined together through an ethereal or oxide linkage formed by loss of a molecule of water. Such a linkage between two monosaccharide units through oxygen atom is called glycosidic linkage.

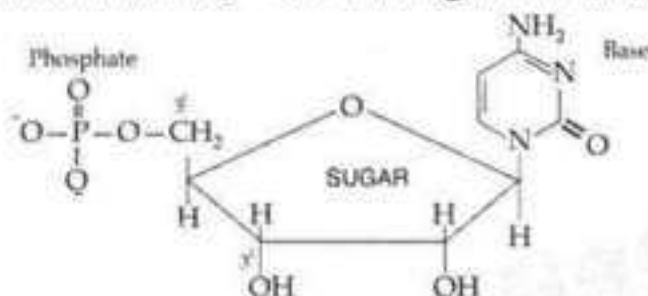
2. What are nucleosides and nucleotides?

Answer:

Nucleoside : A nucleoside contains only two basic components of nucleic acids i.e. a pentose sugar and a nitrogenous base. During their formation 1-position of the pyrimidine or 9-position of the purine moiety is linked to C_1 of the sugar (ribose or deoxyribose) by a β -linkage.



Nucleotides : A nucleotide contains all the three basic components of nucleic acids, i.e. a phosphoric acid group, a pentose sugar and a nitrogenous base. These are formed by esterification of $C_5' - OH$ of the sugar of the nucleoside with phosphoric acid.

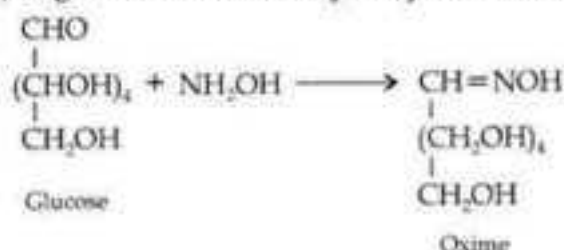


3. Write down the structures and names of the products formed when D-glucose is treated with

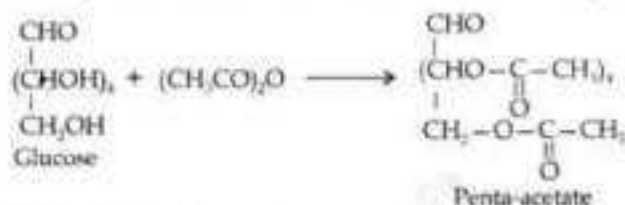
- Hydroxylamine
- Acetic anhydride,

Answer:

- D-glucose reacts with hydroxylamine to form oxime.



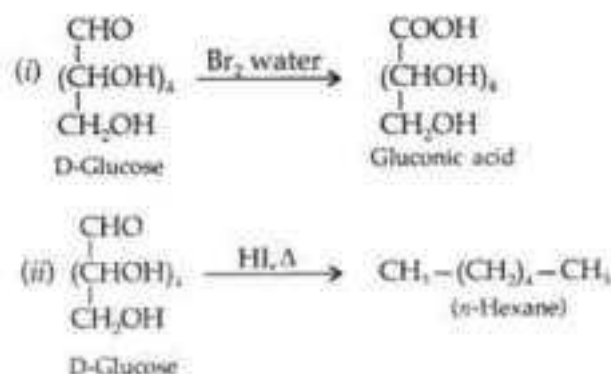
- D-glucose reacts with acetic anhydride to give penta-acetate.



4. Write down the structures and names of the products formed when D-glucose is treated with

- Bromine water
- Hydrogen Iodide (Prolonged heating). (Comptt. All India 2012)

Answer:



5.(a) Write the structural and functional differences between DNA and RNA

(b) Name two components of starch.

Answer:

(a) Structural difference :

DNA	RNA
1. The sugar present in DNA is 2-deoxy-(-) ribose.	1. The sugar present in RNA is D-(-) ribose
2. DNA contains cytosine and thymine as pyrimidine bases.	2. RNA contains cytosine and uracil as pyrimidine bases.
3. DNA has double stranded α -helix structure.	3. RNA has single stranded α -helix structure.

Adenine (A) The base which are common to both DNA and RNA are :

1. Guanine (G)
2. Cytosine (C)

Functional difference : DNA's main function is to control cell activities like telling each organ what to make and what to do. RNA's main function is to make protein.

(b) Components of starch : Amylose and amylopectin.

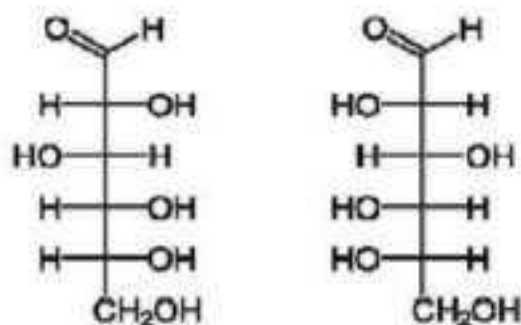
SECTION-D CASE BASED QUESTIONS

1. Read the given passage and answer the questions that follow

Monosaccharides containing an aldehyde group are called aldoses while those containing a keto group are called ketoses. All monosaccharides containing five and six carbon atoms have cyclic structures, furanose (five-membered) and pyranose (six-membered). During ring formation, C_1 aldoses and C_2 in ketoses becomes chiral and hence all these monosaccharides exist in two forms called the α -anomer and β -anomer while C_1 and C_2 are called glycosidic or anomeric

carbon atoms. In contrast, stereoisomers, which differ in configuration at any other chiral carbon other than the glycosidic carbon, are called epimers. Two molecules of the same or different monosaccharides combine together through glycosidic linkage to form disaccharides

Q 1. Which of the following compounds show furanose structures?



- a) Mannose
- b) Galactose
- c) Fructose

Ans 1. (c)

Q 2. What is the relation between two molecules?

- (a) Enantiomers
- (b) Epimers
- (c) Functional groups
- (d) Anomers

Ans 2. (b)

Que 3. In disaccharides, the linkage connecting monosaccharide units is called

- (a) Glycogen linkage
- (b) Nucleoside linkage
- (c) Glycosidic linkage
- (d) Peptide linkage.

Ans 3. (c)

2. Read the given passage and answer the questions that follow

Proteins are the most abundant biomolecules of the living system. The chief sources of proteins are milk, cheese, pulses, fish, meat, peanuts, etc. They are found in every part of the body and form a fundamental basis of the structure and functions of life. These are also required for the growth and maintenance of the body. The word protein is derived from the Greek word, 'proteios' meaning 'primary' or of 'prime importance'. Chemically, proteins are the polymers in which the monomeric units are the α -amino acids. Amino acids contain an amino ($-\text{NH}_2$) and carboxylic ($-\text{COOH}$) functional groups. Depending upon the relative position of the amino group with respect to the carboxylic group, the amino acids can be classified as α , β , and γ -amino acids. Amino acids which are synthesised by the body are called non-essential amino acids. On the

other hand, those amino acids which cannot be synthesized in the human body and are supplied in the form of diet (because they are required for proper health and growth) are called essential amino acids.

Q 1. Amino acids show amphoteric behavior. Why?

- a) They have an amino group
- b) They have a carboxylic group
- c) Both (a) and (b)
- d) none of the above

Ans 1. (c)

Q2. The name of linkage joining two amino acids

- a) Hydrogen bonding
- b) Peptide linkage
- c) Amino linkage
- d) Imino joints

Ans 2. (b)

Q3. What are polypeptides?

- a) 10 < α -amino acids joined together
- b) amino acids joined together
- c) 20 < β -amino acids joined together
- d) None of the above

Ans 3. (a)

Que 4. What type of bonding helps in stabilizing the α -helix structure of proteins?

- a) Peptide linkage
- b) Hydrogen bonding
- c) Amino linkage
- d) Van der waals force

Ans 4. (b)