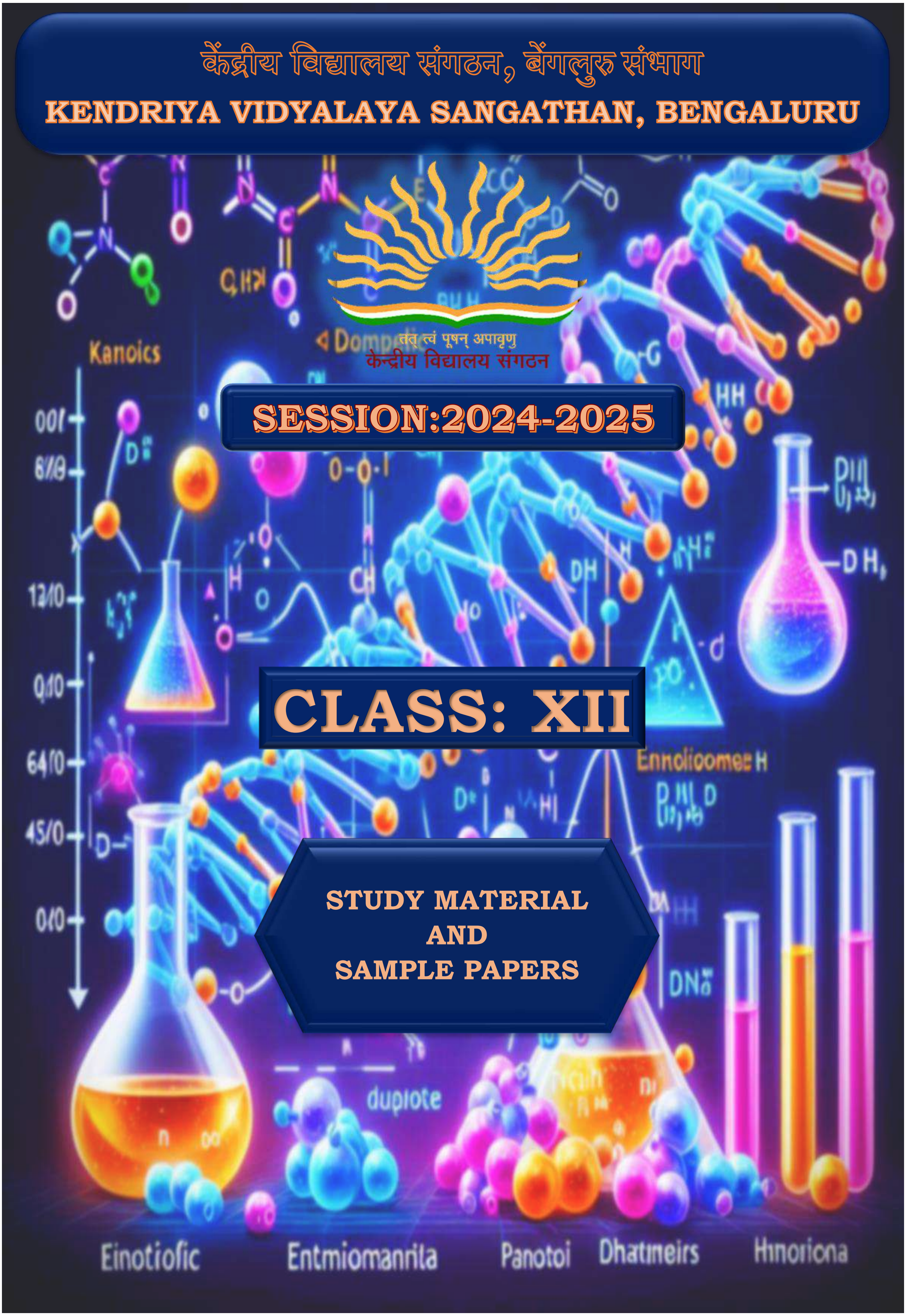
केंद्रीय विद्यालय संगठन, बेंगलुरु संभाग

KENDRIYA VIDYALAYA SANGATHAN, BENGALURU



तत् त्वं पूषन् अपावृणु
केन्द्रीय विद्यालय संगठन

SESSION:2024-2025

CLASS: XII

STUDY MATERIAL
AND
SAMPLE PAPERS

Message from Honorable Deputy Commissioner

Sh. Dharmendra Patle
Deputy Commissioner

ಕೇಂದ್ರೀಯ ವಿದ್ಯಾಲಯ ಸಂಘಟನೆ, ಪ್ರಾದೇಶಿಕ ಕಛೇರಿ ಬೆಂಗಳೂರು
(ಸಂಸ್ಥೆ, ಭಾರತ ಸರ್ಕಾರದ ಶಿಕ್ಷಣ ಸಚಿವಾಲಯದ ಅಡಿಯಲ್ಲಿ, ಸ್ವಾಯತ್ತ)
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MESSAGE FROM THE DEPUTY COMMISSIONER

Dear students and teachers !

It is a matter of great pride and delight that KVS Bengaluru Region is putting forward the Students' Support Material (SSM) for class .12th. subject.Chemistry...for the session 2024-25. I believe firmly that, the subject experts have left no stone unturned to enable our students to add on more to their quality of performance by deep rooting more towards accessing required understating in the subject. Certainly, use of this SSM will help students in empowering themselves as one of the tools and will lead in bringing success.

With devotion, dedication & persistent hard work the team of experts has crafted out this SSM meticulously to complement the classroom learning experience of the students as well as to cope up with the Competency Based Questions as per the new pattern of examinations aligned with NEP-2020 and NCFSE-2023. This SSM, being well-structured and presented in a manner which makes it to be comprehended easily, will definitely serve as a precious supplement for self-study of students.

I am pleased to place on record my appreciation and commendation for the commitment and dedication of the team comprising of the subject experts in carving out such a useful edition of Students' Support Material for the students.

Wishing all the best !

(DHARMENDRA PATLE)
DEPUTY COMMISSIONER
KVS BENGALURU REGION

OUR SUPPORT, GUIDANCE & MOTIVATION

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DEPUTY COMMISSIONER KVS RO BENGALURU

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SYLLABUS FOR SESSION 2024-25

Unit I: Solutions (7 marks) 10 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 (9 marks) 12 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 (7 marks) 10 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 (7 marks) 12 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 property, interstitial compounds, alloy formation, preparation and properties of $K_2Cr_2O_7$ and $KMnO_4$. Lanthanoids – Electronic configuration, oxidation states, chemical reactivity and lanthanoid contraction and its consequences. Actinoids - Electronic configuration, oxidation states and comparison with lanthanoids.

Unit V: Coordination Compounds (7 marks) 12 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. (6 marks) 10 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 (6 marks) 10 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 (8 marks) 10 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 (6 marks) 10 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 (7 marks) 12 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.

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1. SOLUTIONS

QUICK REVISION POINTS:

It is a homogenous mixture of solute and solvent. (Solute + Solvent=Solution)

Types of solutions: -

Sl.No.	Solute	Solvent	Types of Solutions	Examples
1.	Solid	Solid	**Solid solutions**	alloys like brass, bronze, an alloy of copper and gold
2.	Liquid	Solid		Mercury with Sodium(amalgams)
3.	Gas	Solid		Solution of H_2 in Pd, dissolved gases in minerals
4.	Solid	Liquid	**Liquid Solutions**	Sugar solution, salt solution
5.	Liquid	Liquid		Benzene in toluene, alcohol in water.
6.	Gas	Liquid		CO_2 in water, NH_3 in water
7.	Solid	Gas	**Gaseous Solutions**	Iodine vapours in air, camphor in N_2
8.	Liquid	Gas		Water vapours in air, $CHCl_3$ mixed with N_2 gas
9.	Gas	Gas		Air (O_2 + N_2),any non-reacting gases together

EXPRESSING CONCENTRATION OF SOLUTIONS

Some basic formulae: -

Mass percentage. **w/w%** $\frac{\text{mass of solute} W_B}{\text{mass of solution}(W_A+W_B)} \times 100$ **For liquid solutions** % v/v= $\frac{Volume\ of\ solute(V_B)}{Volume\ of\ solution(V_A + V_A)}$	**Mole fraction** For solvent X_A=n_A/$n_{A+}n_B$ For solute X_B=n_B/$n_{A+}n_B$ X_A+ X_B = 1 **ppm (parts per million)=** mass of solute (W_B)x10^6/total mass of solution (W_A+W_B)	**Molarity (**M) = no. of moles of solute/volume of solution (L) Unit=mole/litre [mol/L] **Molality (m)** = no. of moles of solute/mass of solvent(kg) Unit=mole/Kilogram [mol/kg]

NOTE:, mole fraction, mass percentage, ppm and molality are independent of temperature, whereas molarity depends on temperature. This is because volume depends on temperature.

SOLUBILITY (maximum amount of solute present in a specific amount of solvent at a specified temperature) of gas depends on:

Nature of gas	Pressure	Temperature and Solubility of gas
Easily liquefiable, Easy to dissolve	Increases with increase in pressure (HENRY'S LAW)	increases with decrease in temperature, aquatic species are more comfortable in cold water rather than in warm water and prefer to stay at lower level away from the upper layer of water in summers.

Henry's law: -

Statement: - Mole fraction of gas in the solution is directly proportional to partial pressure of gas in the vapour phase.

p α **X_B** **p= $K_H X_B$** (**K_H= Henry's constant**)(greater the **K_H** value lower the solubility)

APPLICATIONS: Soft drinks are sealed under high pressure to increase solubility of CO_2.

To avoid **BENDS**, the tanks used by scuba divers are filled with air diluted with helium (less soluble than N_2)
ANOXIA problem at higher altitudes due to low pressure low concentration of O_2 in Blood cells.

Vapour pressure: -The pressure exerted by the vapours in the equilibrium with liquid at a given temperature.

For two volatile liquids	**For one non-volatile and one volatile liquid**
$P_A = P^0{}_A X_A$ $P_B = P^0{}_B X_B$	$P_A = P^0{}_A X_A$ $P_B = 0$
Dalton's partial pressure $P_{Total} = P^0{}_A X_A + P_B{}^0 X_B$ $P_{Total} = P^0{}_A(1-X_B) + P_B{}^0 X_B$	**Dalton's partial pressure** $P_{Total} = P^0{}_A X_A + 0$ $P_{Total} = P^0{}_A X_A$
Composition of **vapour phase** in equilibrium with the solution: $P_A = P_{total} Y_A$ $P_B = P_{total} Y_B$	

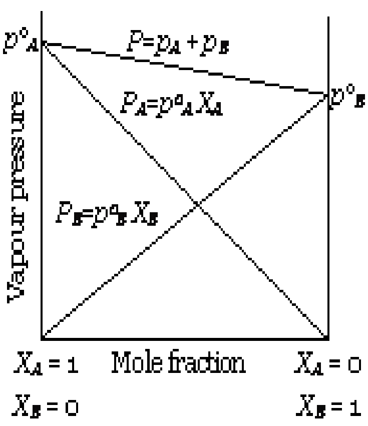
Raoult's law: - The partial vapour pressure of each component in the solution is directly proportional to its mole fraction. [$P_A \propto X_A$ *and* $P_B \propto X_B$]

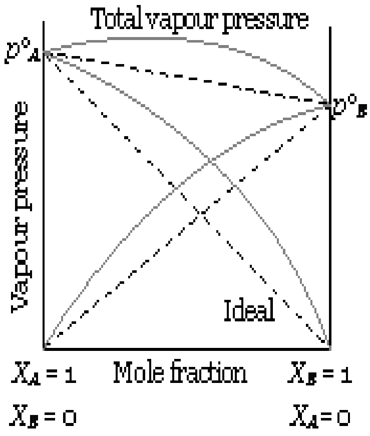
Ideal solutions	**Non-Ideal solutions**
Obeys **Raoult's law** over the entire range of concentration e.g. Solution of n-hexane and n-heptane	Don't Obey **Raoult's law**
A-A , B-B = A-B interactions	A-A , B-B ≠ A-B interactions
$P_{Total} = P_A + P_B$ $P_{Total} = P^0{}_A X_A + P_B{}^0 X_B$	$P_{Total} \neq P_A + P_B$ $P_{Total} \neq P^0{}_A X_A + P_B{}^0 X_B$
$\Delta_{mix} H = 0$ $\Delta_{mix} V = 0$	$\Delta_{mix} H \neq 0$, $\Delta_{mix} V \neq 0$
Can be separated by fractional distillation	Cannot be separated by fractional distillation

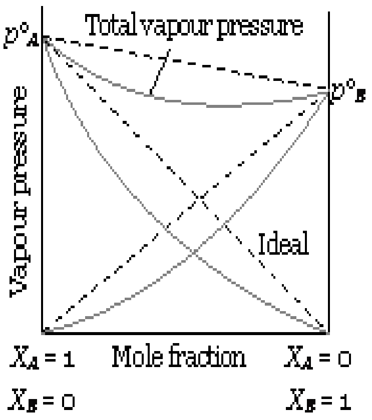
Non-Ideal solutions

Positive deviation	**Negative deviation**
$P_{Total} > P_A + P_B$ $\Delta V_{mix} = +ve$ $\Delta H_{mix} = +ve$	$P_{Total} < P_A + P_B$ $\Delta V_{mix} = -ve$ $\Delta H_{mix} = -ve$
A – B interaction is weaker than A – A and B – B interactions.	A – B interaction is stronger than A – A and B – B interaction
Minimum boiling **Azeotrope***	Maximum boiling **Azeotrope**
e.g. water + alcohol	**e.g.** water+ HNO_3

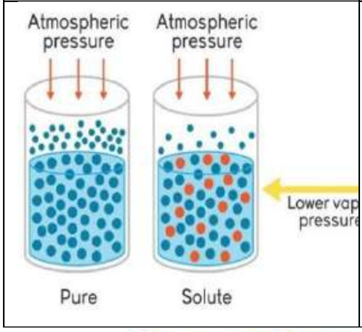
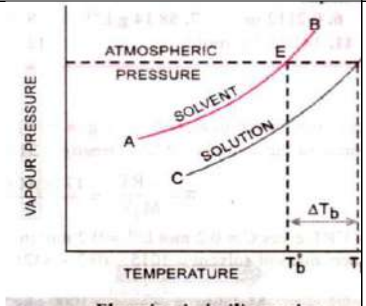
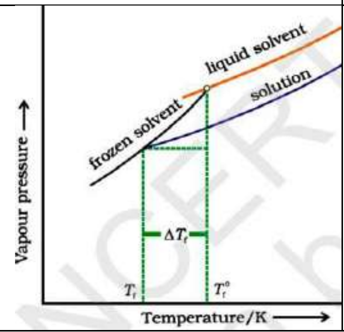
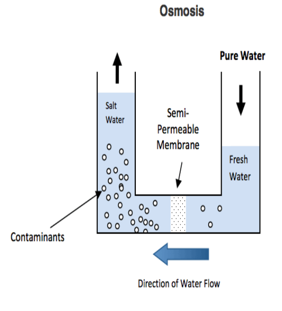
Azeotrope* (Greek: boiling without change) Mixtures having same composition in liquid and vapour phase, boil at a constant temperature and cannot be separated by fractional distillation.

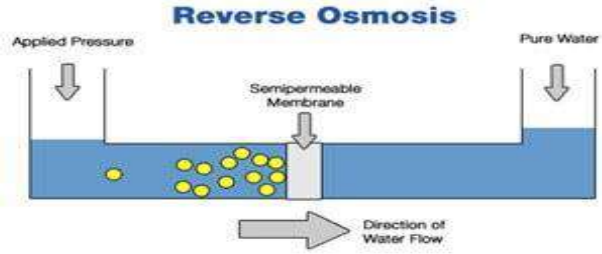

Ideal solution


Positive deviation


Negative deviation

Colligative properties: - The properties of solutions which depend only on the number of particles of the solute (molecules or ions) dissolved in a definite amount of the solvent and do not depend on the nature of solute.

Relative lowering in vapour pressure	**Elevation in boiling point**	**Depression in freezing point**	**Osmosis**
$p^o_A - p_s / p^o_A = X_B$	**$\Delta T_b = T_b - T_b^o$**	**$\Delta T_f = T_f - T_f^o$**	**$\pi = CRT$**
$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2$ $\frac{p_1^0 - p_1}{p_1^0}$ = Relative lowering of vapour pressure x_2 = mole fraction of the solute = $\frac{n_2}{n_1 + n_2}$ [for a very dilute solution $n_B << n_A$] $\frac{p_1^o - p_1}{p_1^o} = \frac{n_2}{n_1} = \frac{w_{2/M_2}}{w_{1/M_1}}$	**$\Delta T_b = K_b\ m$** $\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$ **K_b** = molal elevation or EBULLIOSCOPIC constant. It is the elevation in boiling point of 1 molal solution. $K_b = MRT_b^2 \big/ 1000X\ \Delta H_{vap}$	**$\Delta T_f = K_f\ m$** $\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$ **K_f** = molal depression or CRYOSCOPIC constant. It is the depression in freezing point of 1 molal solution. $K_f = MRT_f^2 \big/ 1000X\ \Delta H_{fus}$	**$\pi = n/V \times RT$** The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a semipermeable membrane is called **OSMOSIS.** The excess pressure on solution side which just prevents the flow of solvent molecules is called **OSMOTIC PRESSURE.**
	 Elevation in boiling point		

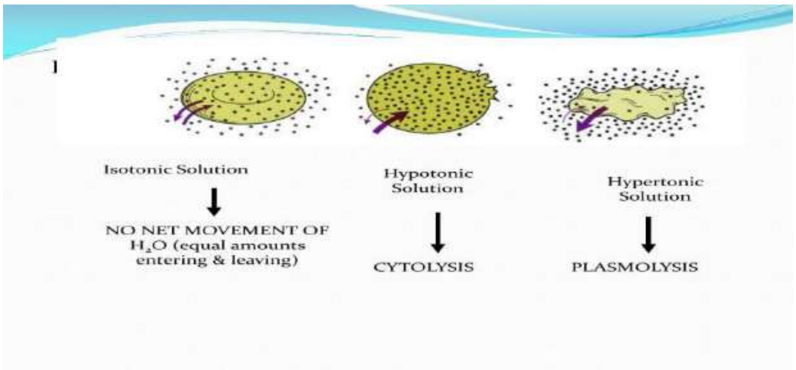


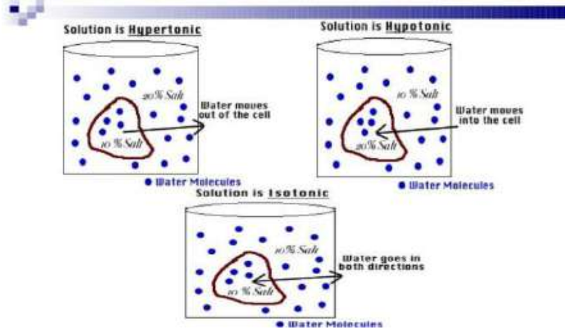
Condition: pressure higher than the osmotic pressure is applied on the solution
The solvent will flow from the solution into the pure solvent through the semi-permeable membrane(**cellulose acetate**)
Used in **desalination of sea water**,

Osmosis in plants and animal cells:

Two solutions having same osmotic pressure at a given temperature are called **isotonic** solutions.
When such solutions are separated by semipermeable membrane **no osmosis** occurs between them.

Two solutions having different osmotic pressure at a given temperature, the one with lower osmotic pressure is called **hypotonic** solution and another one with higher osmotic pressure is *called* ***hypertonic*** *solution*





IMPORTANT POINTS:

Antifreeze agent: **ethylene glycol used in car radiators at hill stations (Depression in freezing point)**

De-icing agents: common salt (NaCl) or calcium chloride ($CaCl_2$) is scattered on the roads to melt ice in cold countries (**Depression in freezing point)**

Biological and Industrial importance of osmosis:

- In animals, circulation of water to all parts of body takes place due to osmosis.
- Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.
- Water absorbed by plant roots is circulated in the entire plant body and reaches to the top of a tall tree due to osmosis.
- Osmosis helps in plant growth and germination of seeds.
- Red blood cells burst when placed in water; it is due to endosmosis.
- Various functions of plants are controlled by osmosis, e.g., stretching of leaves and flowers, opening and closing of flowers.
- Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.
- Dead bodies swell under water due to endosmosis.
- When dried fruits and vegetables are placed in water, they slowly swell and return to the original form. It is again due to the endosmosis of water into the fruits and vegetables.
- **Edema:** Due to excess intake of salt by a person, the tissues become puffy, it is called edema. It is due to retention of water in the tissue owing to osmosis.
- The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

The **osmotic pressure** method has got **advantages** over other colligative properties:

The measurement of osmotic pressure is around the room temperature, gives large measurable values for molar masses and molarity of the solution is used instead of molality.

Conditions for normal molar mass (Accurate value)

Solute must be non-volatile, Solution must be dilute and solute should not undergo any association or dissociation in the solution (non-electrolyte solution).

Abnormal molar mass: ELECTROLYTIC SOLUTIONS: - When the molar mass of a substance (solute) become higher or lower after its association or dissociation in the solution it is called abnormal molar mass.

Van't Hoff factor: i = normal molar mass/abnormal(observed)molar mass

Colligative property after abnormal molar masses: -

Lowering of vapour pressure: -

$\mathbf{X_B = i\ p^o_A - p_s/p^o_A}$

Elevation in boiling point**: -**

$\mathbf{\Delta T_b = i\ K_b\ m}$

Depression in freezing point: -

$\mathbf{\Delta T_f = i\ K_f\ m}$

Osmotic pressure**: -** **π=iCRT**

PROPERTY	ASSOCIATION	DISSOCIATION
No. of molecules	Less	more
Colligative property	Lowers	Increases
Molar mass	Greater than theoretical value	lesser
i=1	i Less than 1	i More than 1
α(extent) =degree of dissociation / association	$\frac{i-1}{\frac{1}{n}-1}$ [n = no. of particles associated]	$\frac{i-1}{n-1}$ [n = no. of dissociated particles.]

MULTIPLE CHOICE QUESTIONS (1 MARK)

1 K_H value for Ar(g), CO_2(g), HCHO (g) and CH_4(g) are 40.39, 1.67, 1.83 × 10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.
a) HCHO < CH_4 < CO_2 < Ar b) HCHO < CO_2 < CH_4 < Ar
c) Ar < CO_2 < CH_4 < HCHO d) Ar < CH_4 < CO_2 < HCHO

2 When a non-volatile solid is added to pure water it will:
a) boil above 100°C and freeze above 0°C b) boil below 100°C and freeze above 0°C
c) boil above 100°C and freeze below 0°C d) boil below 100°C and freeze below 0°C

3 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 III
c) I and IV d) III and IV

4 An azeotropic solution of two liquids has boiling point lower than either of them when solute solvent interactions are:
a) Equal to solute solute and solvent solvent interactions
b) Stronger than solute solute and solvent solvent interactions
c)Weaker than solute solute and solvent solvent interactions
d)None of the above

5 Molarity of a solution at 60°C is-------- than molarity at 30°C
a) More b) less c) same d) no effect of temperature

6 For isotonic solutions which of the following is not equal
a) concentration b) temperature c) osmotic pressure d) vapour pressure

7 For non-electrolyte solute value of Van't Hoff factor is
a)0 b) 1 c) >1 d) <1

8 In reverse osmosis:
a) a pressure greater than osmotic pressure is applied on pure water side
b) a pressure lesser than osmotic pressure is applied on pure water side
c)a pressure greater than osmotic pressure is applied on salt water side
d)a pressure lesser than osmotic pressure is applied on salt water side

9 Which of the following salt will have same value of Van't Hoff's factor (i) as that of $K_4[Fe(CN)_6]$

(a) $Al_2(SO_4)_3$ (b) NaCl (c) $Al(NO_3)_3$ (d) Na_2SO_4

10 Pure benzene has vapour pressure three times that of pure toluene. They form nearly ideal solution. What would be the ratio of their mole fractions in the vapour phase of a solution having equal mole fractions of benzene and toluene.

a) 1 b) 2/3 c) 3 d) 1/3

ANSWERS

1 (a), 2 (a), 3 (d), 4 (c), 5 (b), 6 (d), 7 (b), 8 (c), 9 (a) , 10 (c)

ASSERTION REASON TYPE QUESTIONS (1 MARK)

Note: In the following questions (1-5) 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 statements and reason is the correct explanation for assertion.

(b) Assertion and reason both are correct statements but the reason is not a correct explanation for assertion.

(c) Assertion is a correct statement but the reason is the wrong statement.

(d) Assertion is a wrong statement but the reason is a correct statement.

1 **Assertion:** When methyl alcohol is added to water, the boiling point of water decreases.

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

2 **Assertion**: Cooking time in pressure cooker is reduced

Reason: Boiling point inside the pressure cooker is raised

3 **Assertion**: Vapour pressure of a liquid is constant at a constant temperature

Reason: At equilibrium rate of evaporation becomes equal to the rate of condensation.

4 **Assertion**: The components of azeotropic mixture can be separated by distillation

Reason: At a particular composition azeotropic mixture boil at the same temperature.

5 **Assertion**: The shrinking of cells is called hemolysis.

Reason: Hemolysis occurs when cell comes in contact with solution of lower osmotic pressure than that of cell

ANSWERS

1 (c), 2 (a) , 3 (a) , 4 (d) , 5 (d)

VERY SHORT ANSWER QUESTIONS 1 mark Type:

Q1 Give an example of a solid solution in which solute is a liquid

Ans Amalgam of mercury with sodium

Q 2 Suggest the most important type of intermolecular attractive interaction between methanol and acetone

Ans Both methanol and acetone are polar. So, the intermolecular interactions between them are dipole – dipole interactions

Q 3 X and Y liquids on mixing produces cold solution. What type of deviation is shown by them?

Ans Positive deviation

Q 4 Aquatic species are more comfortable in cold waters rather than in warm waters. Give reason.

Ans Solubility of gases increases with decrease in temperature as it is an exothermic process.

Q 5 If is **α** the degree of dissociation of Na_2SO_4, calculate Van't Hoff factor to determine the molecular mass.

Ans $1+2\alpha$

Q 6 Give an example of a substance that can be used as a SPM.

Ans Pig's bladder or parchment or cellophane.

Q 7. What happens when blood cells are placed in a solution containing more than 0.9% (mass/volume) sodium chloride?

Ans Water will flow out of the cells and they would shrink

Q 8 People taking lot of salt experience puffiness or swelling of the body. Why ?

Ans People taking lot of salt experience puffiness or swelling of the body due to water retention in tissue cells and intercellular spaces because of osmosis.

Q 9 What are hypotonic solutions?

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

Q 10 How can the direction of osmosis be reversed?

Ans The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side.

VERY SHORT ANSWER QUESTIONS (2 MARKS)

1	a) Common salt and Calcium chloride are used to clear snow on the roads, both are of almost same cost but sodium chloride is preferred. Why? b) How the freezing point changes when mercuric iodide is added to the aqueous solution of potassium iodide?
Ans	a) NaCl is needed in lesser quantity. b) Freezing point is raised as no. of particles decreases which results in decrease in colligative property.
2	a) Write the expression for degree of dissociation of a weak electrolyte AxBy in terms of Van't Hoff factor. b) Name a substance that can be used in radiators of vehicles in places where the temperature is less than zero.
Ans	a) $\alpha = i-1/(x+y-1)$ b) Ethylene glycol
3	a) How the osmotic pressure of 5 % aqueous solution of glucose (π_1) is related to that of 5 % aqueous solution of urea (π_2)? b) Why do salt water fish die when they are suddenly transferred to a fresh water aquarium?
Ans	a) $\pi_1 < \pi_2$ b) Water from aquarium enters in cell causing them to expand and get ruptured.
4	a) Two 500 ml beakers were taken. One filled with 400ml water marked 'X' and another with 400ml of 2M NaCl solution marked 'Y'. At the same temperature both were placed in closed containers of same material and same capacity, in which container the vapour pressure is less. b) Out of 1M sucrose and 1M urea solution which has more osmotic pressure?
Ans	a) Y b) Both have osmotic pressure.
5	a) Sia's father is suffering from high blood pressure but he is advised to consume less quantity of common salt. Why? b) Two solutions A and B are separated by semi-permeable membrane. If the liquid flows from A to B then which solution is more concentrated?
Ans	a) More salt use will increase ions in the body fluid which increases blood pressure b) B
6	a) Why the colligative property of an electrolyte solution is always greater than that of a non-electrolyte solution?

	b) Mohit wants to put an egg with outer shell removed in a bottle but he is unable to do so as mouth of bottle is slightly smaller. Suggest one method to help him putting the peeled egg in the bottle
Ans	a) Due to dissociation of electrolyte the number of ions increases b) Peeled egg shrinks in saturated brine solution.
7	a) Out of 1M and 2M sugar solutions which one has a lower boiling point? b) While performing practical it is directed that the bottle of liquid ammonia is to be cooled before opening the seal but Suman forgot to cool it before opening. What consequence she faced?
Ans	a)1M (higher the concentration of solute added higher is the colligative property) b) It is cooled to lower down the pressure of ammonia else the gas will bump out of the bottle.
8	a) What is the effect of temperature on the process when shrunk and dried vegetables are placed in water? b) The boiling point of 0.2 mol kg^{-1} solution of X in water is greater than equimolal solution of Y in water. Which one is undergoing dissociation in water?
Ans	a) Process will be accelerated with increase in temperature as osmosis becomes faster with increase in temperature. b) X
9	a) What is the unit of Ebullioscopic constant? b) Which type of deviation is shown by Carbon tetrachloride and chloroform mixture?
Ans	a) K kg mol^{-1} or K $(molality)^{-1}$ b) positive deviation
10	a) What is the significance of Henry's Law constant K_H? b) How the colligative properties change if the solute undergo dissociation in solution?
Ans	a) Henry's Law constant (K_H) helps in comparing the relative solubilities of different gases in the same solvent (e.g. water). In general, the lesser the value of K_H, the more the solubility of a gas. b) increases due to increase in number of particles on dissociation.
SHORT ANSWER TYPE QUESTIONS (3 MARKS)	
1	a) If the elevation in boiling point of a solution for which i = 1 in a solvent (K_f =x K kg mol^{-1} and K_b=y K kg mol^{-1}) is z K,then calculate the depression in freezing point of the same concentration. b) Give two examples of materials used for making semi permeable membrane for carrying out reverse osmosis.
Ans	a) z x/y b) Cellulose acetate, potassium ferrocyanide
2	a) What is the degree of dissociation for 0.1M $Ba(NO_3)_2$ if i(Van't Hoff factor) is 2.74 b) Arrange the following solutions in increasing order of Van't Hoff factor. 0.1M $CaCl_2$, 0.1M KCl, 0.1M $C_{12}H_{22}O_{11}$, 0.1 M $Al_2(SO_4)_3$
Ans	a) $\alpha = \frac{i-1}{n-1}$ $\alpha = 87\%$ b) 0.1M $C_{12}H_{22}O_{11}$ < 0.1M KCl < 0.1M $CaCl_2$ < 0.1 M $Al_2(SO_4)_3$
3	a) Molal elevation constant for benzene is 2.52 K/m. A solution of some organic substance in benzene boils at 0.126°C higher than benzene. What is the molality of the solution? b) What are the values of Van't Hoff factor for NaCl and K_2SO_4, respectively?
Ans	a) $\Delta T_b = K_b m$, molality=0.05m b) 2 and 3

4	a) State Henry's law. b) Which cold drink you prefer one chilled or other one at room temperature and why? c)At the same temperature hydrogen is more soluble in water than Helium. Which of them will have higher value of K_H and why?
Ans	a) Mole fraction of gas in the solution is directly proportional to partial pressure of gas in the vapour phase b) Chilled as solubility of CO_2 is more at low temp. c) Helium as greater the K_H value lower the solubility
5	a) Account for the reason, marine life like fish prefers to stay at lower level and stay away from the upper layer of water. b) Why freezing/melting point of a substance used as a criterion for testing the purity of a substance? c) Account for the reason for preservation of fruits against bacterial action by adding sugar.
Ans	a) Temperature is higher in upper layer so solubility of oxygen is less b) M.P./F.P. changes due to impurities. c) Bacterium in canned fruit loses <u>water</u> through the process of osmosis, shrivels and dies.
LONG ANSWER TYPE QUESTIONS (5 MARKS)	
1	a) If boiling point of an aqueous solution containing a non-volatile solute is 100.15°C. What is its freezing point? Given latent heat of fusion and vapourisation of water are 80cal/g and 540 cal/g respectively. b) Electrolyte A gives 4 ions and B is a non-electrolyte. If 0.1 molar solution of solute B produces an osmotic pressure 'p', then 0.02 molar solution of A will produce how much osmotic pressure?
Ans	a) $\Delta T_b = K_b\, m$, $\Delta T_f = K_f\, m$ $K_f = \frac{R\times M_1\times T_f^2}{1000\times\Delta_{fus}H}$ $K_b = \frac{R\times M_1\times T_b^2}{1000\times\Delta_{vap}H}$ $K_f/K_b = \frac{T_f^2\ X\ latent\ heat\ of\ fusion}{T_b^2 X\ latent\ heat\ of\ vapourisation} = \Delta T_f/\ \Delta T_b$ $\Delta T_f = 0.542$ $T_f = 0-0.542 = -0.542^{o}C$ b) 0.8p
2	a) 0.6 mL of acetic acid CH_3COOH, having density 1.06 g/mL, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid. K_f= 1.86 K kg /mol. b) How does Raoult's law become a special case of Henry's law?
Ans	a) First find out number of moles of acetic acid, mass of acetic acid =volume x density mass of acetic acid=0.6 X 1.06= 0.636 g and molar mass of acetic acid = 60 g/ mol $no.\ of\ moles\ of\ acetic\ acid = \frac{mass\ of\ acetic\ acid}{molar\ mass\ of\ acetic\ acid}\frac{0.636}{60} = 0.0106$ $molality = \frac{No.\ of\ moles}{mass\ of\ solvent} = \frac{0.0106}{1} = 0.0106\, m$ (As density of water = 1 g/cm^3) $\therefore 1\,L = 1kg$) $\Delta T_f = i\,K_f\,m$ $i = \frac{0.0205}{1.86\times0.0106} = 1.04$ $\alpha = \frac{i-1}{n-1} = \frac{1.04-1}{2-1} = 0.04$ As n=2, $CH_3COOH \leftrightharpoons CH_3COO^- + H^+$ Dissociation constant $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{c\alpha\times c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} = \frac{0.0106\times0.04\times0.04}{1-0.04} = 1.76\times10^{-5}$ b) In two laws only the proportionality constant K_H differs from P_A^0. Thus, Raoult's law becomes a special case of Henry's law in which $K_H = P_A^0$

CASE BASED QUESTIONS (4 MARKS)

Read the passage given below and answer the following case-based questions:

Q1. Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure solvent crystals. According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution. Freeze concentration is a high-quality liquid food concentration method where water is removed by forming ice crystals. This is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapor pressure relative lowering, boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity.

(Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). Freezing point depression of different Sucrose solutions and coconut water.)

a What is the relation between vapour pressure of solid and liquid states at freezing point?

b Why freezing point of 0.1m solution of acetic acid in benzene is less than freezing point of 0.01m solution?

c Out of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression? KCl , $C_6H_{12}O_6$, $Al_2(SO_4)_3$, K_2SO_4

OR

c If K_f for water is 1.86 °C/m, explain why 1m NaCl in water does not have a freezing point equal to a) -1.86 °C b) -3.72°C

ANS Q1

a Equal

b Depression in FP in 0.1m solution is more than 0.01 solution so FP of first is less.

c $C_6H_{12}O_6$

OR

c a) as there are 2 moles of ions per mol of NaCl

b) degree of ionisation is not 100% at freezing point due to stronger interactions for 1m solution.

Q2 1. Henna is investigating the melting point of different salt solutions. She makes a

S.No	Mass of the salt used in g	Melting point in °C	
		Readings Set 1	Reading Set 2
1	0.3	-1.9	-1.9
2	0.4	-2.5	-2.6
3	0.5	-3.0	-5.5
4	0.6	-3.8	-3.8
5	0.8	-5.1	-5.0
6	1.0	-6.4	-6.3

salt solution using 10 mL of water with a known mass of NaCl salt. She puts the salt solution into a freezer and leaves it to freeze. She takes the frozen salt solution out of the freezer and measures the temperature when the frozen salt solution melts. She repeats each experiment.

Assuming the melting point of pure water as 0°C, answer the following questions:

(a) One temperature in the second set of results does not fit in the pattern. Which temperature is that? Justify your answer. 1

(b) Why did Henna collect two sets of results? 1

(c) In place of NaCl, if Henna had used glucose, what would have been the melting point of the solution with 0.6 g glucose in it? 2

OR

(c) What is the predicted melting point if 1.2 g of salt is added to 10 mL of water? Justify your answer.

Ans-Q2

a) 3rd reading for 0.5 g there has to be an increase in depression of freezing point and therefore decrease in freezing point so also decrease in melting point when amount of salt is increased but the trend is not followed in this case.

b) Two sets of reading help to avoid error in data collection and give more objective data.

c.) ΔT_f (glucose) = 1 x K_f x 0.6 x 1000 /180x 10 ……….. (1)

ΔT_f (NaCl) = 2 x K_f x 0.6 x 1000 / 58.5x10

3.8 = 2 x K_f x 0.6 x 1000 /58.5x 10 ……………. (2)

Divide equation 1 by 2

ΔT_f (glucose)/ 3.8 = 58.5/ 2 x 180

ΔT_f (glucose) = 0.62

Freezing point or Melting point = - 0.62 °C

OR

depression in freezing point is directly proportional to molality (mass of solute when

the amount of solvent remains same)

0.3 g depression is 1.9 °C

0.6 g depression is 3.8 °C

1.2 g depression will be 3.8 x2 = 7.6 °C

Q3

Aarav Sharma is very fond of a special drink made by his grandmother using different fruits available in their hometown. It has an outstanding taste and also provides great health benefits of natural fruits. He thought of utilizing his grandmother recipe to create a new product in the beverage market that provide health benefits and also contain fizziness of various soft drinks available in the market. Based on your understanding of solutions chapter, help Aarav Sharma to accomplish his idea by answering following:

(a) How he can add fizz to the special drink made by his grandmother? 1

(b) What is the law stated in the chapter that can help Aarav to make his drink fizzy? 1

(c) What precautions he should take while bottling so that his product does not lose fizz during storage and handling across long distances? 2

OR

(c)The mole fraction of helium in a saturated solution at 20°C is 1.2×10^{-6}. Find the pressure of helium above the solution. Given Henry's constant at 20°C is 144.97 kbar.

Ans-Q3

a) Carbon dioxide is a gas which provides fizz and tangy flavour. He can dissolve Carbon dioxide gas in the drink.

b) Henry's law which states that solubility of a gas in liquid is directly proportional to partial pressure of the gas.

(c) Bottles should be sealed under high pressure of CO and capping should be done perfectly to avoid leakage of CO_2 as any loss of partial pressure will result into decrease in solubility.

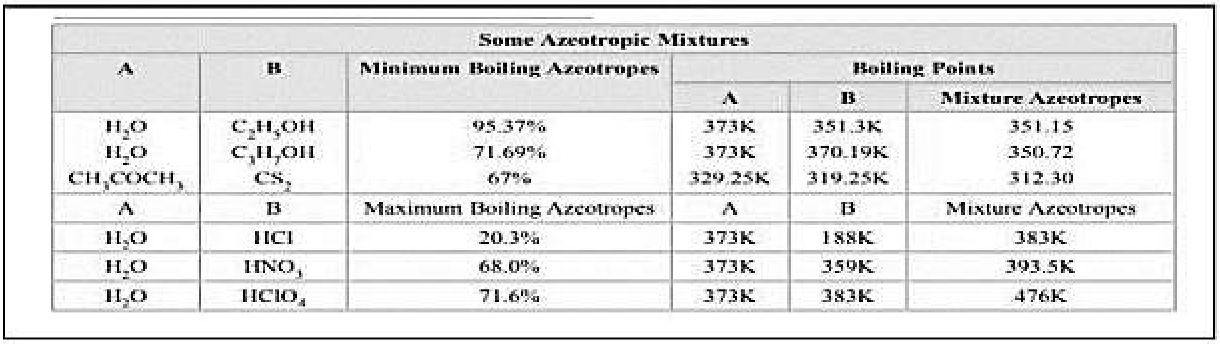
OR

(c) $p_{He} = K_H \times X_{He}$

$= (144.97 \times 10^3 bar)(1.2 \times 10^{-6})$
$= 0.174$ bar

Q4

Observe the table in which azeotropic mixtures are given along with their boiling points of pure Components and azeotropes and answer the questions that follow.



Some Azeotropic Mixtures

A	B	Minimum Boiling Azeotropes	Boiling Points		
			A	B	Mixture Azeotropes
H_2O	C_2H_5OH	95.37%	373K	351.3K	351.15
H_2O	C_3H_7OH	71.69%	373K	370.19K	350.72
CH_3COCH_3	CS_2	67%	329.25K	319.25K	312.30
A	B	Maximum Boiling Azeotropes	A	B	Mixture Azeotropes
H_2O	HCl	20.3%	373K	188K	383K
H_2O	HNO_3	68.0%	373K	359K	393.5K
H_2O	$HClO_4$	71.6%	373K	383K	476K

(a) What type of deviation is shown by minimum boiling azeotropes? 1

OR

(a) Why does H_2O and HCl mixture form maximum boiling azeotropes? 1

(b) What are azeotropes?

(c) Give one example of ideal solution. What type of liquids form ideal solutions? 2

Ans-Q4

(a) Positive deviation from Raoult's law.

OR

(a) It is because force of attraction between H_2O and HCl is more than H_2O-H_2O and HCl-HCl.

(b) Azeotropes- Binary mixtures having same composition in liquid and vapour phase and boil at a constant temperature.

(c) Hexane and heptane form ideal solution. Those compounds of same family having similar forces of attraction form ideal solution.

Q5

Boiling point or freezing point of liquid solution would be affected by the dissolved solids in the liquid phase. A soluble solid in solution has the effect of raising its boiling point and depressing its freezing point. The addition of non-volatile substances to a solvent decreases the vapor pressure and the added solute particles affect the formation of pure solvent crystals According to many researches the decrease in freezing point directly correlated to the concentration of solutes dissolved in the solvent. This phenomenon is expressed as freezing point depression and it is useful for several applications such as freeze concentration of liquid food and to find the molar mass of an unknown solute in the solution.

Freeze concentration is a high-quality liquid food concentration method where water is removed by forming ice crystals, this is done by cooling the liquid food below the freezing point of the solution. The freezing point depression is referred as a colligative property and it is proportional to the molar concentration of the solution (m), along with vapour pressure lowering boiling point elevation, and osmotic pressure. These are physical characteristics of solutions that depend only on the identity of the solvent and the concentration of the solute. The characters are not depending on the solute's identity.

(Source: Jayawardena, J. A. E. C., Vanniarachchi, M. P. G., & Wansapala, M. A. J. (2017). Freezing point depression of different Sucrose solutions and coconut water)

a. Four samples $BaCl_2$, NaCl, $ZnCl_2$ and $AICI_3$ of 0.5 M are being boiled Which of the among will show highest elevation in boiling point?

b. How does sprinkling of salt help in clearing the snow-covered roads in hilly areas?

c. The freezing point of nitrobenzene is 278.8 K. When 2.8 g of an unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found 276.8 K. If the freezing point depression of nitrobenzene is 8.0 K kg mol^{-1}, what is the molar mass of unknown substance? [K_f=8 $KKgmol^{-1}$for nitrobenzene]

OR

C.A solution prepared by dissolving 2g of oil of wintergreen (methyl salicylate) in 100.0 g of benzene has a boiling point of 80. 31° C. Determine the molar mass of this compound. (B.P. of benzene - 80.10°C and K_b for benzene 2.52^0 C kg mol^{-1})

Ans Q5

a. $AlCl_3$

b. By depression of freezing point (it lowers freezing point of water less than 0 C)

c. $\Delta T_f = i\ k_f\ m$

$2=1x\ 8\ x\ (2.8/M_b)x1000/100 =8x2.8x10/M_b$

$M_b=8x28/2=8x14=112g/mol$

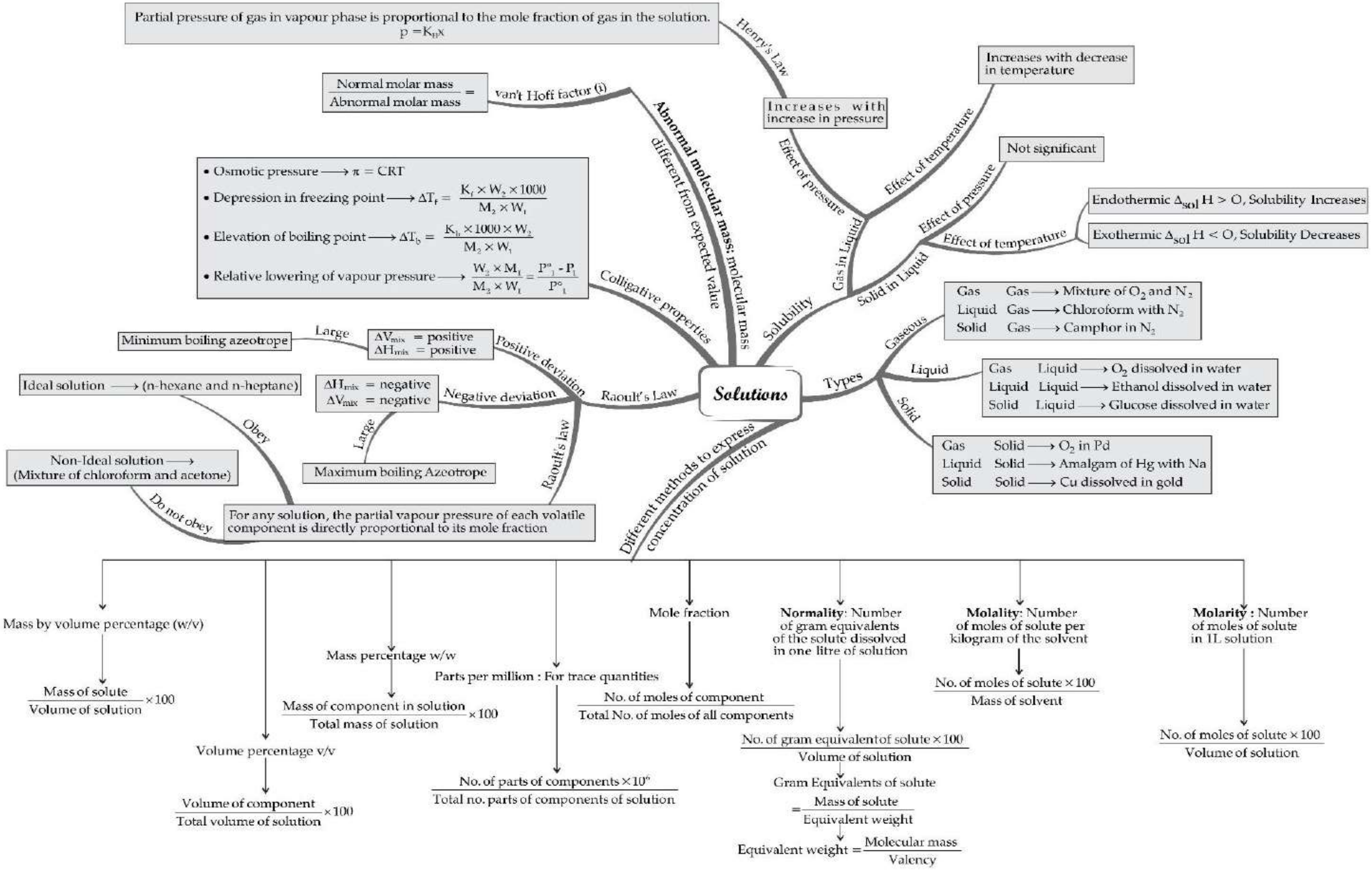
OR

$\Delta T_b = i\ k_b\ m$

$0.21= 1x\ 2.52x2x1000/100xM_b$

$M_b= 2.52x2x10/0.21=240$ g/mol

MIND MAP : LEARNING MADE SIMPLE



2. ELECTROCHEMISTRY

Quick Revision Points

Electrochemistry: the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical reactions.

Differences Between

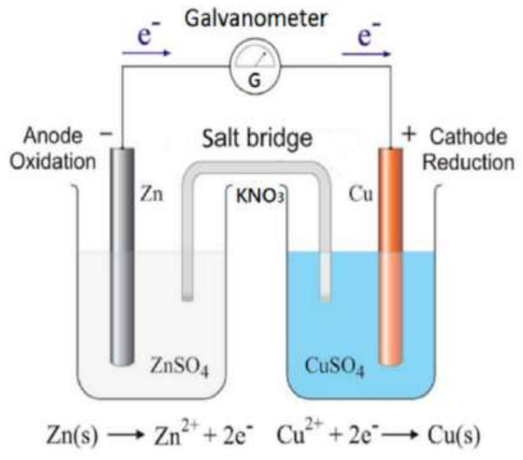
Galvanic cell or Voltaic cell or electrochemical cell	**Electrolytic cell**
A device in which electric current (electrical energy) is generated from spontaneous redox chemical reaction (chemical energy)	A device in which a nonspontaneous chemical reaction is carried with the help of electric current (electrical energy).
eg: Daniel cell, dry cell, lead storage battery	eg : electrolysis of molten NaCl, electrolysis of dilute aq.H_2SO_4 solution using Pt electrode

.

Electrochemical cell e.g., Daniel cell

The overall cell reaction is:

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$



The Daniel cell is represented as :

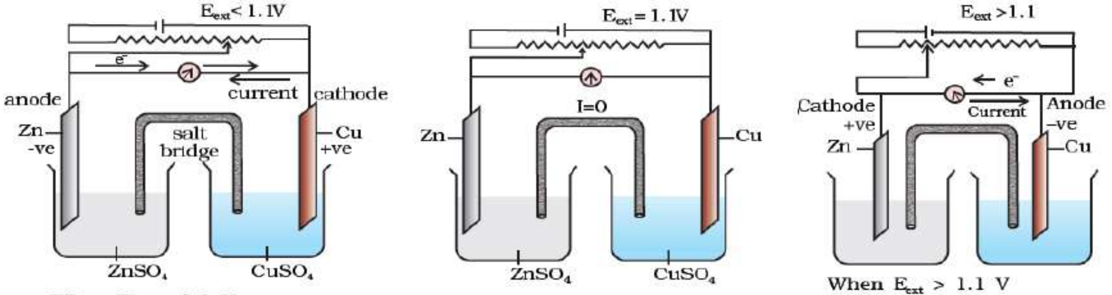
$Zn(s) | Zn^{2+}(aq)(C_1) || Cu^{2+}(aq)(C_2) | Cu(s)$
Left side Salt bridge Right side
Oxidation half reaction Reduction half reaction
Anode Cathode
Negative terminal Positive terminal

Salt Bridge and Its Functions: It consists of a glass U-tube containing semi-solid paste of either KCl, KNO_3 or NH_4Cl (inert electrolytes) in gelatine or agar-agar jelly. It helps in flow of ions by completing the circuit and maintains electrical neutrality.

Electrode potential and standard electrode potential	**Cell potential (E_{cell})**	**Electromotive force(emf)**
Electrode potential ($E_{electrode}$) A potential difference which develops between the electrode (Metal rod) and the electrolyte (solution containing metal ion). **standard electrode potential ($E°_{electrode}$)** When concentrations of all the species involved in a half-cell is unity and temperature is at 298 K, then the electrode potential is known as standard electrode potential	Difference between the electrode potential of the cathode and anode. (Measured in Volts $E_{cell} = E_{right} – E_{left}$ $Ecell = E_{cathode} – E_{anode}$ **standard cell potential** $E^0cell = E^0_{cathode} – E^0_{anode}$	Cell potential when no current is drawn through the cell

Note: It is a common practice to express all the electrode potentials as reduction potentials.
Reduction potential = - Oxidation potential.

Reversibility of Daniel Cell:



When E_{ext} < 1.1 V
(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.
(ii) Zn dissolves at anode and copper deposits at cathode.

When E_{ext} = 1.1 V
(i) No flow of electrons or current.
(ii) No chemical reaction.

When E_{ext} > 1.1 V
(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.
(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

Functioning of Daniell Cell when External Voltage (E_{ext}) Opposing the Cell Potential is Applied.

Measurement of electrode potential: SHE (Standard Hydrogen electrode) is used as a reference electrode to measure the standard electrode potential of other electrodes by assigning standard electrode potential of SHE is zero. It consists of Pt electrode coated with Pt black, in acidic solution of 1M H^+ ion concentration at 1 bar Pressure and 298 K temperature.

Example: (i) When SHE is coupled with Zn, Pt(s) | H_2(g, 1bar) || Zn^{2+}(aq, 1M) | Zn(s)
EMF of the above cell = 0.76 V so E° Zn^{+2} / Zn =-0.76V
(ii) When SHE is couples with Cu, Pt(s) | H_2(g, 1bar) || Cu^{2+}(aq, 1M) | Cu(s)
EMF of the above cell = 0.34 V so E° Cu^{+2}/ Cu = +0.32V

Nernst equation: It is an equation which gives the relationship between electrode potential and the concentration of ions in electrolytic solution. For an electrode reaction (reduction reaction),
M^{n+} (aq) + ne^- → M(s), Nernst equation can be written as:

$$E_{\mathrm{M}^{n+}/\mathrm{M}} = E^{o}_{\mathrm{M}^{n+}/\mathrm{M}} - \frac{RT}{nF}\ln\frac{[\mathrm{M}]}{[\mathrm{M}^{n+}]}$$

$$E_{\mathrm{M}^{n+}/\mathrm{M}} = E^{o}_{\mathrm{M}^{n+}/\mathrm{M}} - \frac{2.303RT}{nF}\log\frac{1}{[\mathrm{M}^{n+}]}$$

where, $E_{\mathrm{M}^{n+}/\mathrm{M}}$ = Electrode potential, $E^{o}_{\mathrm{M}^{n+}/\mathrm{M}}$ = Standard electrode potential R = 8.314JK /mol,
T = Temperature in kelvin, n = No. of electrons gained, F = Faraday constant (96500 C /mol)

Substituting the value of R and F we get

$$E_{\mathrm{M}^{n+}/\mathrm{M}} = E^{o}_{\mathrm{M}^{n+}/\mathrm{M}} - \frac{0.0591}{n}\log\frac{1}{[\mathrm{M}^{n+}]} \quad \text{at 298 K}$$

Thus, the electrode potential increases with increase in concentration of ions.
For electrochemical cell , Nernst equation can be given as:

$$\text{at 298 K,} \quad E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n}\log\frac{[\text{Product}]}{[\text{ Reactant}]}$$

For example, (i) **Nernst equation for Daniel cell (Zn – Cu cell)** can be written as:

$$E_{(\text{cell})} = E^{\text{o}}_{(\text{cell})} - \frac{0.059}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

(ii) **Nernst equation for Ni – Ag cell**

$$\text{Ni(s)}|\text{Ni}^{2+}\text{(aq)} \parallel \text{Ag}^{+}\text{(aq)}|\text{Ag(s)}$$

The cell reaction is $\text{Ni(s)} + 2\text{Ag}^{+}\text{(aq)} \rightarrow \text{Ni}^{2+}\text{(aq)} + 2\text{Ag(s)}$

The Nernst equation can be written as

$$E_{(\text{cell})} = E^{\text{o}}_{(\text{cell})} - \frac{0.059}{2}\log\frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

Equilibrium Constant from Nernst Equation:

At equilibrium, $E_{\text{cell}} = 0$, then $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_c$

In general, $E^{\circ}_{\text{cell}} = \frac{0.0591}{n}\log K_c$ or, $\log K_c = \frac{n}{0.0591}E^{\circ}_{\text{cell}}$

Electrochemical cell and Gibbs Free Energy:

The work done by a reversible galvanic cell is equal to decrease in its free energy.
Mathematically, $\Delta_{\text{r}}G = -nFE_{\text{cell}}$
If concentration of all the reacting species is unity, then,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} \text{ and we get, } \Delta_r G^o = -nFE^{\circ}_{\text{cell}}$$

From $\Delta_r G^o$, we can calculate the equilibrium constant of a reaction,

$$\Delta_r G^o = -RT\ln K_c \text{ or } \Delta_r G^o = -2.303RT\log K_c$$

$$\text{Maximum work} = \Delta_r G^o$$

Electrochemical Series: The arrangement of various standard half-cells/electrodes in the order of their decreasing standard reduction potential values is known as electrochemical series.

Metallic and Electrolytic Conductance

S. No.	Metallic Conductance	Electrolytic Conductance
(i)	Movement of electrons is responsible for conduction.	Movement of ions is responsible for conduction.
(ii)	Does not involve transfer of matter.	Matter moves in the form of ions.
(iii)	Decreases with increase in temperature as kernels start vibrating which produce hindrance in the flow of electrons.	Increases with increase in temperature due to decrease in interionic attraction or increase in movement of ions
iii)	**Metallic conductance depends upon** - Nature and structure of the metal, Number of valence electrons per atom and Temperature	**Electrolytic or ionic conductance depends upon** - Nature of electrolyte or interionic attractions, Solvation of ions, Nature of solvent and its viscosity, and Temperature

Conductance of Electrolytic solutions:
Resistance (R) - Obstruction to the flow of current, R = ρ l/A, Its SI unit is ohm.

Resistivity (ρ) - electrical resistance of a conductor of unit cross-sectional area and unit length.
ρ = R A /l, Its SI unit is ohm metre.

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R}=\frac{A}{\rho l}=\frac{\kappa A}{l}$	$\text{Ohm}^{-1}(\Omega^{-1})$/ Siemens (S)	Increases as larger number of ions are produced or due to increase in movement of ions
Specific conductance (κ, kappa) or conductivity	$\frac{1}{\rho}$ or $G\frac{l}{A}$	Sm^{-1}	Decreases as number of ions per unit volume of solution decreases.
Molar conductivity (Λ_m)	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	S cm^2 mol^{-1}	Increases with dilution due to large increase in V.

Conductivity(κ)=conductance(G) X cell constant (G*)

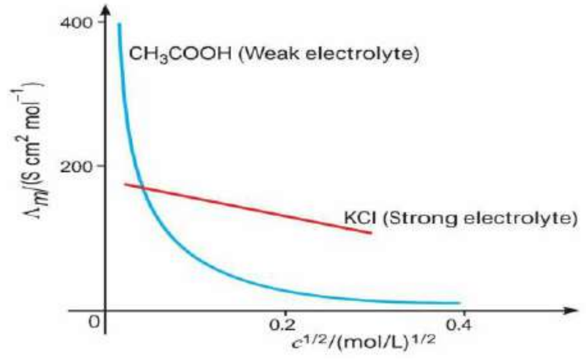
Coductivity is defined as conductance of unit volume of electrolytic solution.

Molar conductivity is defined as conductance of sufficient volume of the electrolytic solution that contains one mole of the electrolyte.

Cell Constant is defined as the ratio of the distance between the two electrodes to their area of cross section. Its SI unit is m^{-1}

Limiting molar conductivity: When concentration approaches zero i.e., at infinite dilution, the molar conductivity is known as limiting molar conductivity ($\Lambda^\circ{}_m$).

Variation Molar Conductivity with Concentration:
For a strong electrolyte it is shown by Debye–Huckel Onsager equation:
$\Lambda_m = \Lambda^\circ{}_m - AC^{1/2}$, Here, $\Lambda^\circ{}_m$ = Molar conductivity at infinite dilution (Limiting molar conductivity)
Λ_m = Molar conductivity at given concentration, A = Constant which depends upon nature of solvent and temperature, C = Concentration.



For weak electrolytes: molar conductivity increases steeply on dilution or decrease in concentration due to increase in the number of ions or increase in degree of dissociation.

For a strong electrolyte: molar conductivity increases slowly on dilution or decrease in concentration due to increase in the movement of ions. There is only a small increase in conductance with dilution. (This is because a strong electrolyte is completely dissociated in solution, so the number of ions remain constant and on dilution, interionic attractions decrease as ions move far apart.)

Kohlrausch's Law: It states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.
In general, if an electrolyte on dissociation gives v_+cations and v_-anions then its limiting molar conductivity is given by $\Lambda_m^0 = v_+\lambda_+^0 + v_-\lambda_-^0$
Here, λ_+° and λ_-° are the limiting molar conductivities of cations and anions, respectively.

Applications of Kohlrausch's law:
(a) Calculation of molar conductivities of weak electrolyte at infinite dilution: For example, molar conductivity of acetic acid (weak acid) at infinite dilution can be obtained from the knowledge of molar conductivities at infinite dilution of strong electrolytes like $\mathrm{HCl}, \mathrm{CH_3COONa}$ and NaCl as illustrated below:
$\Lambda^\circ_{\mathrm{m(CH_3COOH)}} = \lambda^\circ_{\mathrm{CH_3COO^-}} + \lambda^\circ_{\mathrm{H^*}}$
$= \left[\lambda^0_{\mathrm{CH_3COO^-}} + \lambda^0_{\mathrm{Na^+}}\right] + \left[\lambda^0_{\mathrm{H^+}} + \lambda^0_{\mathrm{Cl^-}}\right] - \left[\lambda^0_{\mathrm{Na^+}} + \lambda^0_{\mathrm{Cl^-}}\right]$
i.e., $\Lambda^0_{m\mathrm{(CH_3COOH)}} = \Lambda^o_{\mathrm{m(CH_3COONa)}} + \Lambda^0_{\mathrm{m(HCl)}} - \Lambda^0_{\mathrm{m(NaCl)}}$
(b) Determination of degree of dissociation of weak electrolytes:
Degree of dissociation $(\alpha) = \frac{\Lambda_m^c}{\Lambda_m^o}$
(c) Determination of dissociation constant (K) of weak electrolytes:

$$K = \frac{c\alpha^2}{1-\alpha}$$

Electrolytic cell and electrolysis: Electrolysis is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.
Criteria for product formation: At cathode, when there is competition between many cations or many reduction reactions, then the reduction reaction with higher E^0 value is preferred. Similarly at anode, the oxidation reaction with lower E^0 value is preferred.

Products of Electrolysis:

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	$\mathrm{Cl_2}$ gas	$\mathrm{Na^+_{(l)}} + e^- \rightarrow \mathrm{Na_{(l)}}$	$\mathrm{Cl^-_{(l)}} \rightarrow \frac{1}{2}\mathrm{Cl_{2(g)}} + e^-$
Aqueous NaCl	$\mathrm{H_2}$ gas	$\mathrm{Cl_2}$ gas	$\mathrm{H_2O_{(l)}} + e^- \rightarrow \frac{1}{2}\mathrm{H_{2(g)}} + \mathrm{OH^-_{(aq)}}$	$\mathrm{Cl^-_{(aq)}} \rightarrow \frac{1}{2}\mathrm{Cl_{2(g)}} + e^-$
Dil. $\mathrm{H_2SO_4}$	$\mathrm{H_2}$ gas	$\mathrm{O_2}$ gas	$\mathrm{H^+_{(ag)}} + e^- \rightarrow \frac{1}{2}\mathrm{H_{2(g)}}$	$2\mathrm{H_2O_{(l)}} \rightarrow \mathrm{O_{2(g)}} + 4\mathrm{H^+_{(aq)}} + 4e^-$

Conc. H_2SO_4	H_2 gas	$S_2O_8^{2-}$	$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$	$2SO^{2-}_{4(aq)} \rightarrow S_2O_8^{2-}(aq) + 2e^-$
$AgNO_3$(aq)-Ag electrode	Ag	Ag+	Ag^+(aq) + e^- → Ag(s)	Ag(s) → Ag^+(aq) + e^-
$AgNO_3$(aq)-Pt electrode	Ag	O_2 gas	Ag^+(aq) + e^- → Ag(s)	$2H_2O$(l) → O_2(g) + 4H+(aq) + $4e^-$
$CuCl_2$(aq)-Pt electrode	Cu	O_2 gas	Cu^{+2}(aq) + $2e^-$ → Cu(s)	$2H_2O$(l) → O_2(g) + 4H+(aq) + $4e^-$

Overvoltage/Over potential: Oxidation of H_2O is relatively slow process and thus needs extra potential. This extra potential needed to oxidise H_2O is called overvoltage/over potential. Due to overvoltage, the oxidation of chloride ion occurs at anode in preference to H_2O.

Faraday's first law of electrolysis: The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte. m=ZQ,
m = Z × I × t, where Z = Electrochemical equivalent =M/nF where n= no of electrons or valency, F=96487, M= molar mass of the metal

Faraday's second law of electrolysis: Amount of various substances liberated by the same quantity of electricity passed through the electrolytic solution is proportional to their chemical equivalent weights. $W_1/E_1 = W_2/E_2$

Battery: Combination of galvanic cells in series and used as a source of electrical energy.
(i)Primary batteries are non-chargeable batteries such as Leclanche cell and Dry cell.
(ii) Secondary batteries are chargeable cells involving reversible reaction. Example, Lead storage battery and Nickel-cadmium cells.

Dry cell (Leclanche cell): The anode consists of a zinc container and the cathode is a graphite electrode surrounded by powdered MnO_2 and C. The space is filled with paste of NH_4Cl and $ZnCl_2$.
At anode: Zn(s) → Zn^{2+}(aq) + $2e^-$ At cathode: MnO_2 (s) + NH_4^+(aq)+ $2e^-$ → MnO(OH) + NH_3
The net reaction: Zn + NH_4^+(aq) + MnO_2 → Zn^{2+} + MnO(OH) +NH_3

Mercury cell: consists of zinc–mercury amalgam as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The electrode reactions are:
Anode: Zn(Hg) + $2OH^-$→ ZnO(s) + H_2O + $2e^-$ Cathode: HgO(s) + H_2O + $2e^-$ → Hg (l) + $2OH^-$
The cell potential is approximately 1.35 V and remains constant as the ionic concentration of the solution is not changed during its life

Lead storage battery: Anode - Spongy lead Cathode - Lead packed with Lead dioxide Electrolyte -Aqueous solution of H_2 SO_4 (38%)
Discharge reaction of cell:
At anode : Pb(s) +SO_4^{2-}(aq) → $PbSO_4$ (s) +$2e^-$

At cathode: PbO_2 filled in lead grid gets reduced to Pb^{2+} ions which combines with SO4 $^{2-}$ ions to form $PbSO_4$ (s). The reaction is PbO_2 (s) + $4H^+$(aq) + SO_4^{2-}(aq) + $2e^-$ → $PbSO_4$ (s) + $2H_2O$(l)
Complete cell reaction: Pb(s) + PbO_2 (s) + $2H_2$ SO_4 (aq) → $2PbSO_4$ (s) + $2H_2O$(l)
Recharge reaction of cell (charging): It changes the direction of electrode reaction. $PbSO_4$ accumulated at cathode gets reduced to Pb.
Overall Reaction: $PbSO_4$ (s) + $2H_2O$(l) → Pb(s) + PbO_2 (s) + $2H_2SO_4$ (aq)

Nickel–cadmium cell which has longer life than the lead storage cell but is costly. Here, the overall reaction during discharging: Cd(s) + $2Ni(OH)_3$ (s)→ CdO(s) + $2Ni(OH)_2$ (s) + H_2O(l)

Fuel cells: Electrical cells that are designated to convert the energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called fuel cells. the cell reactions are:
Anode: $2H_2$ (g) + $4OH^-$ (aq) → $4H_2$ O (l) + $4e^-$, Cathode: O_2 (g) + $2H_2$ O(l) + $4e^-$ → $4OH^-$ (aq)
Net reaction: $2H_2$ (g) + O_2 (g) →$2H_2O$ (l)
Advantages: high efficiency, free from pollution (eco-friendly),continuous source of energy

Corrosion: The process of slow conversion of metals into their undesirable compounds (usually oxide) by reaction with moisture and other gases present in the atmosphere. Rusting of iron:
Oxidation: Fe(s) → Fe^{+2} (aq) + $2e^-$, Reduction: O_2(g) + $4H^+$(aq) + $4e^-$→ $2H_2O$(l)
Atmospheric oxidation: $2Fe^{+2}$(s) + ½ O_2 (g) + $2H_2O$(l) → Fe_2O_3 + $4H^+$(aq)
Fe_2O_3 + xH_2O → $Fe_2O_3.xH_2O$(rust)
Prevention of Corrosion:
(i)Barrier protection: By covering the surface with paint or a thin film of grease or by some chemicals (eg-bisphenol).
(ii) Sacrificial protection: Sn, Zn (by galvanization), sacrificial anode- Mg, Zn (iii) Alloying

MULTIPLE CHOICE QUESTIONS (1 MARKS)

Q1. Which metal is used as electrode which do not participate in the reaction but provides surface for conduction of electrons? (a) Cu (b) Pt (c) Zn (d) Fe

Q2. An electrochemical cell can behave like an electrolytic cell when
(a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$ (c) $E_{ext} > E_{cell}$
(d) $E_{cell} = E_{ext}$

Q3. 4. Which cell will measure standard electrode potential of copper electrode?
(a) Pt(s)| H_2 (g, 0.1 bar)| H^+ (aq., 1 M) | | Cu^{2+} (aq., 1M)| Cu(s)
(b) Pt(s)| H_2 (g, 1 bar) | H^+ (aq., 1 M) | | Cu^{2+} (aq., 2M)| Cu(s)
(c) Pt(s)| H_2 (g, 1 bar) | H^+ (aq., 1 M) | | Cu^{2+} (aq., 1M)| Cu(s)
(d) Pt(s)| H_2 (g, 1 bar) | H^+ (aq., 0.1 M)| | Cu^{2+} (aq., 1M)| Cu(s)

Q4. The positive value of the standard electrode potential of Cu^{2+}/Cu indicates that
(a) this redox couple is a stronger reducing agent than the H^+/H_2 couple.
(b) this redox couple is a stronger oxidising agent than H^+/H_2.
(c) Cu can displace H_2 from acid.
(d) Cu can displace H_2 from acid

Q5. On increasing temperature,
(a) ionic conductance increases and electronic conductance decreases.

(b) ionic conductance decreases and electronic conductance increases.
(c) both ionic and electronic conductance increase.
(d) both ionic and electronic conductance decrease.

Q6. The electrolyte used in the mercury cell is
(a) paste of NH_4Cl and $ZnCl_2$ (b) paste of HgO and carbon
(c) paste of KOH and ZnO (d) paste of PbO and H_2SO_4

Q7. A device that converts energy of combustion of fuels like hydrogen and methane directly into electrical energy is known as:
(a) dynamo (b) Ni-Cd cell (c) fuel cell (d) electrolytic cell

Q8. Which one of the following is always true about the spontaneous cell reaction in a galvanic cell?
(a) $E^\circ_{cell} > 0, \Delta G^\circ < 0, Q > K_C$ (b) $E^\circ_{cell} < 0, \Delta G^\circ < 0, Q < K_C$
(c) $E^\circ_{cell} > 0, \Delta G^\circ > 0, Q > K_C$ (d) $E^\circ_{cell} > 0, \Delta G^\circ < 0, Q < K_C$

Q9. Charge carried by 1 mole of electrons is
(a) 6.023×10^{23} coulomb (b) 9.65×10^4 coulomb
(c) 1.6×10^{-19} coulomb (d) 6.28×10^{19} coulomb

Q10. To calculate the standard emf of the cell, which of the following options is correct if E° is reduction potential values?
(a) emf = $E^\circ_{cathode} - E^\circ_{anode}$ (b) emf = $E^\circ_{anode} - E^\circ_{cathode}$
(c) emf = $E^\circ_{anode} + E^\circ_{cathode}$ (d) None of these

Answers : 1(b), 2(c), 3(c), 4(b), 5(a), 6(c), 7(c), 8(d), 9(b), 10(a)

ASSERTION REASON TYPE QUESTIONS(1MARKS)

Given below are two statements labelled as Assertion (A) and Reason (R)
Select the most appropriate answer from the options given below:
a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

Q1. Assertion (A) : E_{cell} should have a positive value for the cell to function.
Reason(R) : $E_{cathode} < E_{anode}$

Q2. Assertion (A) : Copper sulphate cannot be stored in zinc vessel.
Reason (R) : Zinc is less reactive than copper.

Q3. Assertion (A) : Current stops flowing when $E_{cell} = 0$.
Reason (R) : Equilibrium of the cell reaction is attained.

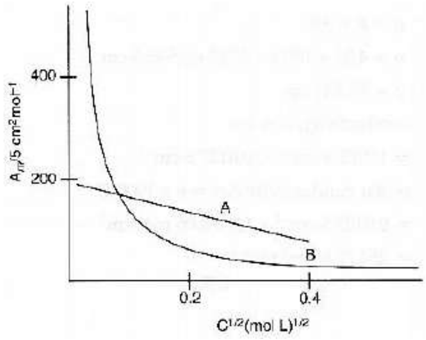
Q4. Assertion (A) : Conductivity of all electrolytes decreases on dilution.
Reason (R) : On dilution number of ions per unit volume decreases.

Q5. Assertion (A) : Conductivity decreases for weak electrolyte and increases for strong electrolyte with decrease in concentration.
Reason (R) : On dilution, the number of ions per unit volume that carry the current decreases.

Answers: 1(c), 2(c), 3(a), 4(a), 5(d)

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

Q1. In the plot of molar conductivity (Λ_m) vs square root of concentration ($C^{1/2}$), following curves are obtained for two electrolytes A and B.



Answer the following:

(i) Predict the nature of electrolytes A and B.

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes A and B?

Ans. (i) A is a strong electrolyte while B is a weak electrolyte.

(ii) For electrolyte A, the plot becomes linear near high dilution and thus can be extrapolated to zero concentration to get the molar conductivity at infinite dilution.

For weak electrolyte B, Λ_m increases steeply on dilution and extrapolation to zero concentration is not possible. Hence, molar conductivity at infinite dilution cannot be determined.

Q2. Calculate $\Delta_r G^\circ$ and log K_c for the following reaction at 298 K :

$$2\text{Cr}\,(s) + 3\text{Fe}^{2+}(aq) \longrightarrow 2\text{Cr}^{3+}(aq) + 3\text{Fe}(s)$$

Given: $E^0_{\text{cell}} = 0.30$ V

Ans. n=6, log $K_c = \frac{n}{0.059} E^0_{\text{cell}}$ = 3.224 x 10 ^{30}, ΔG° = -nFE°$_{\text{cell}}$ = -1737.7KJ/mol, or log Kc = 30.5084

Q3. Three iron sheets have been coated separately with three metals A, B and C whose standard electrode potentials are given below. Identify in which rusting will takes place faster when coating is damaged.

Metal	A	B	C	Iron
E^0	-0.46 V	-0.66 V	-0.20 V	-0.44 V

Ans. As iron (-0.44 V) has lower standard reduction potential than C(-0.20 V) only and therefore when coating is broken, rusting will take place faster.

Q4. Can you store copper sulphate solutions in a zinc pot?

Ans. For this we have to check whether the following reaction will take place or not.

$$\text{Zn}(s) + \text{CuSO}_4(aq) \longrightarrow \text{ZnSO}_4(aq) + \text{Cu}(s)$$
$$E^o_{\text{cell}} = E^o_{\text{Cu}^{2+}/\text{Cu}} - E^o_{\text{Zn}^{2+}/\text{Zn}} = 0.34 - (-0.76) = 1.10 \text{ V}$$

As E°_{cell} is positive, the reaction will take place so No.

Q5. Suggest a way to determine the Λ^0_m value of water.

Ans.

$$\Lambda^o_{m(\text{H}_2\text{O})} = \lambda^o_{(\text{H}^+)} + \lambda^o_{(\text{OH}^-)}$$
$$= \lambda^o_{(\text{H}^+)} + \lambda^o_{(\text{OH}^-)} + \lambda^o_{(\text{Cl}^-)} - \lambda^0_{(\text{Cl}^-)} + \lambda^0_{(\text{Na}^+)} - \lambda^0_{(\text{Na}^+)}$$

Rearranging we get

$$\Lambda^o_{m(\text{H}_2\text{O})} = \left[\lambda^o_{(\text{H}^+)} + \lambda^o_{(\text{Cl}^-)}\right] + \left[\lambda^o_{(\text{Na}^+)} + \lambda^o_{(\text{OH}^-)}\right] - \left[\lambda^o_{(\text{Na}^+)} + \lambda^o_{(\text{Cl}^-)}\right]$$
$$\Lambda^o_{m(\text{H}_2\text{O})} = \Lambda^o_{m(\text{HCl})} + \Lambda^o_{m(\text{NaOH})} - \Lambda^o_{m(\text{NaCl})}$$

Thus, the molar conductivity of water at infinite dilution can be determined from the knowledge of $\Lambda^{o}_{m(\mathrm{HCl})}, \Lambda^{o}_{m(\mathrm{NaOH})}$ and $\Lambda^{o}_{m(\mathrm{NaCl})}$.

Q6. Why on dilution the Λm of CH_3COOH increases drastically while that of CH_3COONa increases gradually?

Ans. Ans. CH_3COOH is a weak electrolyte, the number of ions increase on dilution due to an increase in degree of dissociation.

Q7. (a) What is the role of $ZnCl_2$ in a dry cell

(b) Unlike dry cell, the mercury cell has a constant cell potential throughout its useful life. why?

Ans (a) $ZnCl_2$ combines with the NH_3 produced to form the complex salt $[Zn(NH_3)_2\,Cl_2]$ otherwise the pressure developed due to NH_3 would crack the seal of the cell

(b) Ions are not involved in the overall cell reaction of mercury cells

Q8. **(a)** Value of standard electrode potential for the oxidation of Cl^- ions is more positive than that of water, even then in the electrolysis of aqueous sodium chloride, why is Cl^- oxidised at anode instead of water?

(b) How will the pH of brine (aq. NaCl solution) be affected when it is electrolysed?

Ans. (a) On electrolysis of aqueous sodium chloride, oxidation of water at anode requires over potential hence Cl^- is oxidised instead of water.

(b) The pH of the solution will increase as NaOH is formed in the electrolytic cell.

Q9. (a) Which type of a metal can be used in cathodic protection of iron against rusting?

(b) Write the name of the electrolyte used in fuel cell

Ans. (a) More electropositive than iron such as Al, Zn, Mg etc. (b) Conc. Aq. KOH solution

Q10. Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place. **Further show: (i)** Which of the electrode is negatively charged?

(ii) The carriers of the current in the cell.

Ans. Cell can be represented as $Zn \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag$.

(i) zinc electrode is negatively charged (anode)

(ii) Ions are the current carriers within the cell

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

Q1. (a) Calculate the cell emf and ΔG° for the cell reaction at 25°C for the cell :

$\mathrm{Zn}_{(s)}|\mathrm{Zn}^{2+}(0.0004\mathrm{M}) \parallel \mathrm{Cd}^{2+}(0.2\mathrm{M})|\mathrm{Cd}_{(s)}$ E° values at 25°C: $\mathrm{Zn}^{2+}/\mathrm{Zn} = -0.763$ V

$\mathrm{Cd}^{2+}/\mathrm{Cd} = -0.403$ V; $F = 96500\mathrm{Cmol}^{-1}$; $R = 8.314\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1}$.

(b) If E° for copper electrode is 0.34 V, how will you calculate its emf value when the solution in contact with it is 0.1M in copperions? How does emf for copper electrode change when concentration of Cu^{2+} ions in the solution is decreased?

Ans. (a) $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}} \quad = 3.36\mathrm{V}$

The net cell reaction is, $\mathrm{Zn}_{(s)} + \mathrm{Cd}^{2+}_{(\mathrm{aq})} \rightarrow \mathrm{Zn}^{2+}_{(\mathrm{aq})} + \mathrm{Cd}_{(s)}$, n=2

$$E_{\mathrm{cell}} = E^\circ_{\mathrm{cell}} - \frac{0.0591}{2}\log\frac{[Zn^{2+}]}{[Cd^{2+}]} = 0.44\ V,$$

$$\Delta \mathrm{G} = -\mathrm{nFEcell} = -84920\mathrm{J/mol}$$

(b) $\mathrm{Cu}^{2+}_{(\mathrm{aq})} + 2e^- \rightarrow \mathrm{Cu}_{(s)}$

$$E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = E^\circ_{\mathrm{Cu}^{2+}/\mathrm{Cu}} - \frac{0.059}{2}\log\frac{[\mathrm{Cu}]}{[\mathrm{Cu}^{2+}]} = 0.34 - \frac{0.059}{2}\log\frac{1}{0.1} = 0.34 - \frac{0.059}{2}\log\ 10$$

$$= 0.34 - \frac{0.059}{2} \times (1) = 0.34 - 0.0295 = 0.3105 \text{ V}$$

When the concentration of Cu^{2+} ions is decreased, the electrode potential for copper decreases.

Q2. The molar conductivity of sodium acetate, sodium chloride and hydrochloric acid are 83,127 and 426 mho cm^2mol^{-1} at 250°C respectively. Calculate the molar conductivity of acetic acid solution.

Ans. Given : $\Lambda^\circ_m(CH_3COONa) = 83 \text{ mho } cm^2mol^{-1}$

$\Lambda^\circ_m(NaCl) = 127 \text{ mho } cm^2mol^{-1}$

$\Lambda^\circ_m(HCl) = 426 \text{ mho } cm^2mol^{-1}$

$\Lambda^\circ_m(CH_3COOH) = ?$

Using Kohlrausch law of independent migration of ions

$\Lambda^\circ_m(CH_3COOH) = \Lambda^\circ_m(CH_3COONa) + \Lambda^\circ_m(HCl) - \Lambda^\circ_m(NaCl)$ or $\Lambda^\circ_m(CH_3COOH) = 83 + 426 - 127$
$= 382 \text{ mho } cm^2mol^{-1}$

Q3. A strip of nickel metal is placed in a 1 molar solution of $Ni(NO_3)_2$ and a strip of silver metal is placed in a 1 molar solution of $AgNO_3$. An electrochemical cell is created when the two solutions are connected by a salt bridge and the two strips are connected by wires to a voltmeter.

(i) Write the balanced equation for the overall reaction occurring in the cell and calculate the cell potential.

(ii) Calculate the cell potential, E, at 25°C for the cell if the initial concentration of $Ni(NO_3)_2$ is 0.100 molar and the initial concentration of $AgNO_3$ is 1.00 molar.

$\left[E^0_{Ni^{2+}/Ni} = -0.25 \text{ V}; E^0_{Ag^+/Ag} = 0.80 \text{ V}, \log 10^{-1} = -1\right]$

Ans. Cell reaction: $Ni + 2Ag^+ \rightarrow Ni^{2+} + 2Ag$, $E^\circ_{Cell} = E^\circ_{cathode} - E^\circ_{anode}$, $E^\circ_{Cell} = 1.05V$

(ii)$E_{cell} = E^o_{cell} - \frac{0.059}{n}\log\frac{[Ni^{2+}]}{[Ag^+]^2} \quad = 1.0795V$

Q4. The electrochemical cell given alongside converts the chemical energy released during the redox reaction to electrical energy: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

It gives an electrical potential of 1.1 V when concentration Zn^{2+} and Cu^{2+} ions is unity. State the direction of flow of current and also specify whether zinc and copper are deposited or dissolved at their respective electrodes when:

(i) an external opposite potential of less than 1.1 V is applied.

(ii) an external potential of 1.1 V is applied.

(iii) an external potential of greater than 1.1 V is applied.

Ans. (i) Reaction continues to take place. Electrons flow from Zn electrode to copper electrode, current flows from Cu to Zn. Zn dissolves and copper deposits at their respective electrodes.

(ii) The reaction stops and no current flows. (iii) Reaction takes place in opposite directions.

Electrons flow from copper electrode to zinc electrode, current flows from Zn to Cu. cell functions as an electrolytic cell.

Q5. Explain redox potential. Reduction potentials of some ions are given below. Arrange them in decreasing order of oxidizing power.

Ion	ClO_4^-	IO_4^-	BrO_4^-
Reduction potential $E^\ominus$/V	$E^0 = 1.19$ V	$E^0 = 1.65$ V	$E^0 = 1.74$ V

Ans. It is a measure of the tendency of a chemical species to acquire electrons from or lose electrons to an electrode and thereby be reduced or oxidized respectively. The more positive the reduction potential of a species, the greater the species' affinity for electrons and tendency to be reduced the higher the reduction potential, the higher is its tendency to get reduced. Hence, the order of oxidizing power is:

$BrO_4^- > IO_4^- > ClO_4^-$

LONG ANSWER TYPE QUESTIONS (5 MARKS)

Q1. (i) State two advantages of H_2—O_2 fuel cell over ordinary cell.

(ii) Silver is electrodeposited on a metallic vessel of total surface area 500 cm^2 by passing a current of 0.5 amp for two hours. Calculate the thickness of silver deposited. [Given: Density of silver = 10.5 g cm^{-3}, Atomic mass of silver = 108 amu, F = 96,500 C mol^{-1}]

Ans. (i) pollution free, 75% efficiency, continuous source of energy.

(ii) m=ZIt = 4.029g, V=m/d = 0.3837 cm^3, thickness of Ag deposited is x, V= A. x = 7.67×10^{-4}cm

Q2. (i) Define limiting molar conductivity and fuel cell.

(ii) Resistance of a conductivity cell filled with 0.1 mol L^{-1} KCl solution is 100 ohm. If the resistance of the same cell when filled with 0.02 mol L^{-1} KCl solution is 520 ohm, calculate the conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. The conductivity of 0.1 molL^{-1} KCl solution is 1.29×10^{-2} ohm^{-1} cm^{-1}.

Ans (i) Limiting Molar conductivity -limiting value of molar conductivity when concentration approaches to zero. Fuel cell - device which converts energy produced during the combustion of fuels directly into electrical energy.

(ii) cell constant = conductivity x resistance = 1.29 cm^{-1}, Conductivity, k = Cell constant/Resistance = 0.00248 ohm^{-1} cm^{-1}, Λ_m = k X 1000/M = 124 ohm^{-1} cm^2 mol^{-1}

CASE BASED QUESTIONS

Read the passage carefully and answer the questions.

Redox reactions play an important role in chemistry. Whenever a redox reaction takes place directly in a single beaker, chemical energy in the form of heat is produced. By suitable means, it is possible to bring about the redox reactions indirectly so as to convert the chemical energy into electrical energy. A device used to convert the chemical energy produced in a redox reaction into electrical energy is called an electrochemical cell. If a redox reaction is allowed to take place in such a way that oxidation half reaction takes place in one beaker and the reduction half reaction in another beaker, the electrons given out by the former will be taken by the latter and the current will ow. The two portions of the cell are called half cells. The values of standard redox potential (E^0) of two half cell reactions decides in which way the reaction will proceed. A redox reaction is feasible when the substance having higher reduction potential gets reduced and the one having lower reduction potential gets oxidised. For example, In Daniel cell, zinc goes into solution and copper gets deposited.

1.Formulate the galvanic cell for: $Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$

Ans. The cell is represented as: $Zn(s)|Zn^{2+}(aq) \parallel Ag^+(aq)|Ag(s)$

2. Is it safe to stir $AgNO_3$ solution with a copper spoon? Why or why not?

Given: $E^0_{Ag^+/Ag} = 0.80$ volt and $E^0_{Cu^2+/Cu} = 0.34$ volt

Ans. No, because copper is more reactive than Ag and can displace Ag from $AgNO_3$ solution.

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

$$\mathrm{MnO_4^-}(aq) + 8\mathrm{H^+}(aq) + 5e^- \longrightarrow \mathrm{Mn^{2+}}(aq) + 4\mathrm{H_2O}(l), \quad E^0 = +1.51\ \mathrm{V}$$

$$\mathrm{Sn^{2+}}(aq) \longrightarrow \mathrm{Sn^{4+}}(aq) + 2e^-, \quad E^0 = +0.15\ \mathrm{V}$$

Construct the redox reaction from the two half-cell reactions and predict if this reaction favours formation of reactants or products shown in the equation.

Ans.

$$2\mathrm{MnO_4^-}(aq) + 16\mathrm{H^+}(aq) + 5\mathrm{Sn^{2+}}(aq) \longrightarrow 2\mathrm{Mn^{2+}}(aq) + 5\mathrm{Sn^{4+}}(aq) + 8\mathrm{H_2O}(l)$$

$$E^o_{\mathrm{Cell}} = E^\circ_{\mathrm{Cathode}} - E^\circ_{\mathrm{Anode}} = 1.51\ \mathrm{V} - 0.15\ \mathrm{V} = 0.36\ \mathrm{V},\ \text{product forms}$$

OR

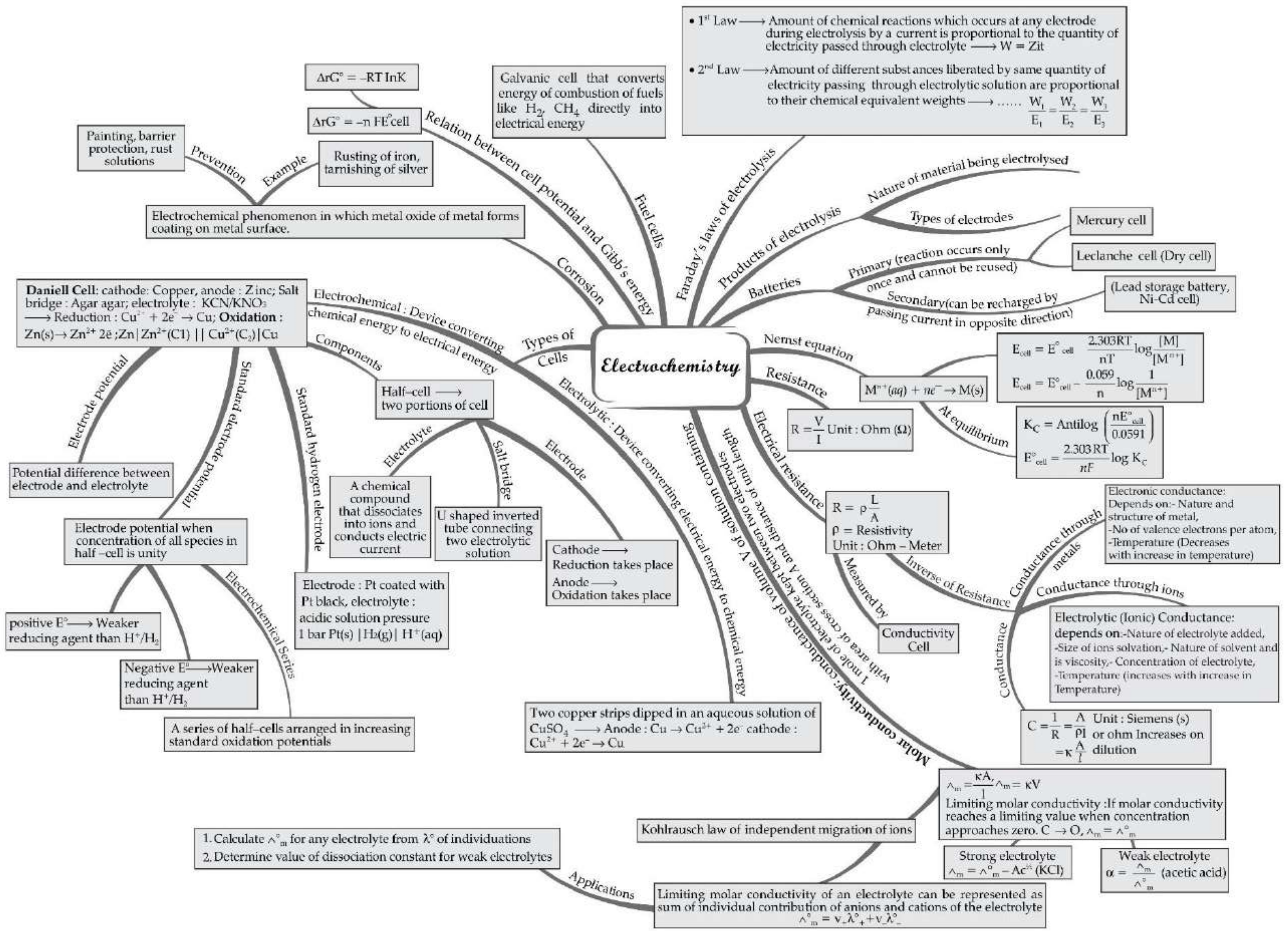
(i) State the factors affecting cell potential of: $\mathrm{Mg}\,(s)|\mathrm{Mg^{2+}}(aq) \parallel \mathrm{Ag^+}(aq)|\mathrm{Ag}(s)$

(ii) Can E^0_{cell} or $\Delta_r G^0$ for cell reaction ever be equal to zero?

Ans.(i) concentration of Mg^{2+} and Ag^+ions in the solution and temperature.

(iii) No, E°_{cell} or $\Delta_r G^0$ for cell reaction can never be zero. $\Delta G° = -nFE°$

MIND MAP : LEARNING MADE SIMPLE



Electrochemistry

Faraday's laws of electrolysis

- 1st Law ⟶ Amount of chemical reactions which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte ⟶ $W = Zit$
- 2nd Law ⟶ Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights ⟶ …… $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$

Products of electrolysis

- Nature of material being electrolysed
- Types of electrodes

Batteries

- Primary (reaction occurs only once and cannot be reused)
  - Mercury cell
  - Leclanche cell (Dry cell)
- Secondary (can be recharged by passing current in opposite direction)
  - (Lead storage battery, Ni-Cd cell)

Nernst equation

$M^{n+}(aq) + ne^- \rightarrow M(s)$

$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log\frac{[M]}{[M^{n+}]}$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}$

At equilibrium

$K_C = \text{Antilog}\left(\frac{nE^\circ_{cell}}{0.0591}\right)$

$E^\circ_{cell} = \frac{2.303RT}{nF}\log K_C$

Resistance

$R = \frac{V}{I}$ Unit : Ohm (Ω)

Electrical resistance

$R = \rho\frac{L}{A}$

ρ = Resistivity

Unit : Ohm – Meter

Measured by: Conductivity Cell

Inverse of Resistance: Conductance

Conductance through metals

Electronic conductance:
Depends on:- Nature and structure of metal,
-No of valence electrons per atom,
-Temperature (Decreases with increase in temperature)

Conductance through ions

Electrolytic (Ionic) Conductance:
depends on:-Nature of electrolyte added,
-Size of ions solvation,- Nature of solvent and is viscosity,- Concentration of electrolyte,
-Temperature (increases with increase in Temperature)

Conductance

$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$ Unit : Siemens (s) or ohm Increases on dilution

Molar conductivity: conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length

$\wedge_m = \frac{\kappa A}{l}, \wedge_m = \kappa V$

Limiting molar conductivity :If molar conductivity reaches a limiting value when concentration approaches zero. $C \rightarrow O, \wedge_m = \wedge^\circ_m$

Strong electrolyte
$\wedge_m = \wedge^\circ_m - Ac^{1/2}$ (KCl)

Weak electrolyte
$\alpha = \frac{\wedge_m}{\wedge^\circ_m}$ (acetic acid)

Kohlrausch law of independent migration of ions

Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte
$\wedge^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$

Applications

1. Calculate $\wedge^\circ_m$ for any electrolyte from λ° of individuations
2. Determine value of dissociation constant for weak electrolytes

Types of Cells

Electrolytic : Device converting electrical energy to chemical energy

Two copper strips dipped in an aqueous solution of $CuSO_4$ ⟶ Anode : $Cu \rightarrow Cu^{2+} + 2e^-$ cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Electrochemical : Device converting chemical energy to electrical energy

Daniell Cell: cathode: Copper, anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO₃ ⟶ Reduction : $Cu^{2+} + 2e^- \rightarrow Cu$; **Oxidation** : $Zn(s) \rightarrow Zn^{2+} 2e^-$; $Zn|Zn^{2+}(C1) || Cu^{2+}(C_2)|Cu$

Components

Half–cell ⟶ two portions of cell

- Electrolyte: A chemical compound that dissociates into ions and conducts electric current
- Salt bridge: U shaped inverted tube connecting two electrolytic solution
- Electrode: Cathode ⟶ Reduction takes place; Anode ⟶ Oxidation takes place

Standard hydrogen electrode

Electrode : Pt coated with Pt black, electrolyte : acidic solution pressure 1 bar $Pt(s) | H_2(g) | H^+(aq)$

Standard electrode potential

Electrode potential when concentration of all species in half –cell is unity

- positive E° ⟶ Weaker reducing agent than H^+/H_2
- Negative E° ⟶ Weaker reducing agent than H^+/H_2

Electrochemical Series

A series of half–cells arranged in increasing standard oxidation potentials

Electrode potential

Potential difference between electrode and electrolyte

Corrosion

Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.

- Example: Rusting of iron, tarnishing of silver
- Prevention: Painting, barrier protection, rust solutions

Relation between cell potential and Gibb's energy

$\Delta rG^\circ = -nFE^\circ cell$

$\Delta rG^\circ = -RT\ln K$

Fuel cells

Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy

3. CHEMICAL KINETICS

QUICK REVISION POINTS

Rate of a Chemical Reaction: It is the change in concentration of a reactant or product in unit time (or) it is the rate of change of concentration of reacting species.

Consider a reaction,

$$R \rightarrow P$$

Rate of a Chemical Reaction = $\frac{-\Delta[R]}{-\Delta t} = \frac{\Delta[P]}{\Delta t}$

Units of rate of a reaction: mol $L^{-1}s^{-1}$.

NOTE: Rate of reaction always expressed for every one mole.

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

Rate of reaction $= -\frac{1}{a}$[Rate of disappearance of A] $= -\frac{1}{b}$[Rate of disappearance of B]

$= \frac{1}{c}$[Rate of disappearance of C] $= \frac{1}{d}$[Rate of disappearance of D]

Factors Influencing Rate of a reaction:

(i)effect of concentration of reactants (pressure in case of gases),
(ii) effect of temperature and (iii) effect of catalyst.

Average Rate	Instantaneous Rate
It is the change in concentration of reactants in a given interval of time	It is the change in concentration of reactants at instantaneous time

Rate Law Expression: It is a mathematical expression in which rate of reaction is expressed in terms of molar concentration of reactants with each term raised to power, which may or may not be equal to the stoichiometric coefficient of the reacting species in a balanced chemical equation.

Consider a general reaction: $aA + bB \rightarrow cC + dD$, then
Rate Law = $k [A]^x [B]^y$, where,
'x' may/ may not be equal to 'a' and 'y' may/ may not be equal to 'b'

Order of a Reaction: It is the sum of powers of concentrations of reactants expressed in rate law.

Consider a general reaction: $aA + bB \rightarrow cC + dD$, then
Rate Law = $k [A]^x [B]^y$, overall order of reaction = (x+y) and x and y represent the order with respect to the reactants A and B respectively.

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 (k)

REACTION	ORDER	UNITS OF RATE CONSTANT
Zero order reaction	0	mol $L^{-1}S^{-1}$
first order reaction	1	S^{-1}
Second order reaction	2	$mol^{-1} LS^{-1}$
nth order of reaction	nth	$mol^{(1-n)}L^{(n-1)}S^{-1}$

Difference between order of reaction and molecularity of reaction:

	Order of reaction	**Molecularity of reaction**
1	It is the sum of powers of concentrations of reactants expressed in rate law.	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
2	Order of a reaction is an experimental quantity.	Molecularity of a reaction is a theoretical quantity.
3	It can be zero and even a fraction	Molecularity cannot be zero or a non-integer.
4	Order is applicable to elementary as well as complex reactions	Molecularity is applicable only for elementary reactions.

Integrated Rate Equations

(i) Zero Order Reactions: Consider zero order reaction

$$R \rightarrow \text{products}$$

Let $[R]_o$ be the initial concentration of reactant and [R] be the final concentration at time‘t’. For zero order reaction, the rate of the reaction is proportional to zero power of the concentration of reactants.

Rate = $-\frac{d[R]}{dt}$ = k $[R]^o$⇒ Rate = $-\frac{d[R]}{dt}$=k ⇒ d[R] = – k dt

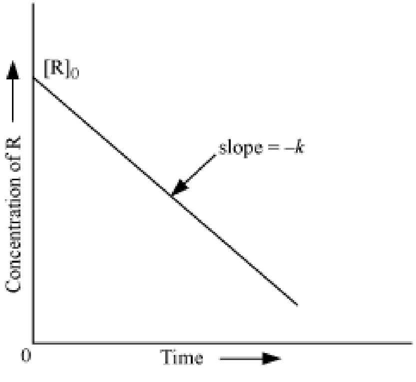
Integrating on both sides

[R] = – k t + I, where, I is the constant of integration.

when t = 0, the concentration of the reactant R becomes $[R]_0$, where $[R]_0$ is initial concentration of the reactant.

$[R]_0 = -k \times 0 + I$ ⇒ $[R]_0 = I$ ⇒ $[R] = -kt + [R]_0$ ⇒ $k = \frac{[R]o-[R]}{t}$

Comparing with equation of a straight line, y = mx + c, a graph is drawn between [R] against t, it gives a straight line with slope = –k and intercept equal to $[R]_0$.



Some enzyme catalysed reactions and reactions which occur on metal surfaces (metal catalyst) are a few examples of zero order reactions.

(ii) First Order Reactions

Consider first order reaction

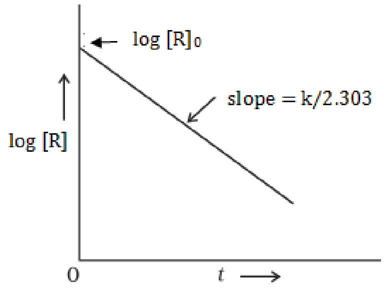
$$R \rightarrow P$$

Let $[R]_o$ be the initial concentration of reactant and [R] be the final concentration at time‘t’. For zero order reaction, the rate of the reaction is proportional to the first power of the concentration of the reactant R.

Rate =$-\frac{d[R]}{dt}$ = k R ⇒ $\frac{d[R]}{R} = -kdt$

Integrating on both sides, $\ln [R] = -kt + I$, I is the constant of integration.
When $t = 0$, R becomes $[R]_0$, where $[R]_0$ is the initial concentration of the reactant.
Therefore, $\ln [R]_0 = -k \times 0 + I \Rightarrow \ln [R]_0 = I$
Substituting the value of I, $\ln[R] = -kt + \ln[R]_0$
Rearranging this equation, $\ln\frac{[R]}{[R]o} = kt$ Or, $k = \frac{1}{t}\ln\frac{[R]o}{R}$ $\Rightarrow$ $k = \frac{2.303}{t}\log\frac{[R]o}{R}$

A graph is drawn between log [R] against 't' gives a straight line with slope = –k and intercept equal to log $[R]_0$



Half-Life of a Reaction: It is the time required to reduce the concentration of reactant to half of its initial concentration.

Case 1: For a zero order reaction, rate constant is given by equation

$$K = \frac{[R0 - R]}{t}$$

when $t = t_{½}$, then $[R] = ½ [R_0]$

The rate constant at $t_{½}$ becomes $k = \frac{[R0 - \frac{1}{2}R0]}{t\frac{1}{2}} \Rightarrow t_{½} = \frac{[Ro]}{2k}$

$t_{½}$for a zero-order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.

Case 2:For the first order reaction,

$$k = \frac{2.303}{t}\log\frac{[Ro]}{[R]}$$

At $t = t_{½}$, then $[R] = ½ [R_0] \Rightarrow k = \frac{2.303}{t}\log\frac{[Ro]}{[Ro]/2}$

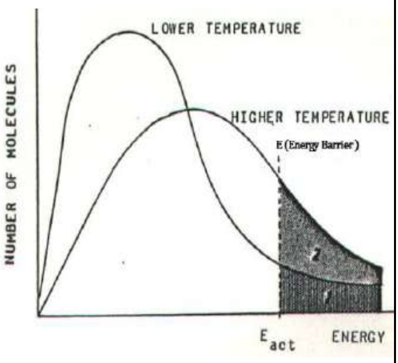
$t_{½} = \frac{2.303}{t}\log 2 \Rightarrow t_{½} = \frac{0.693}{k}$

For a first order reaction, half-life period is constant, i.e., it is independent of initial concentration of the reacting species.

For zero order reaction $t_{½} \propto [R]_0$.
For first order reaction $t_{½}$ is independent of $[R]_0$.
In general, for nth order, $t_{½} = 1/ [R]_0^{(n-1)}$

Pseudo First Order Reaction: A reaction which appear to follow higher order but follows lower order kinetics.

Effect of temperature on rate of a reaction



Rate of a reaction always increases with increase of temperature

(i) According to Kinetic theory of Molecular gases, the average kinetic energy of reacting gaseous molecules is directly proportional to absolute temperature.

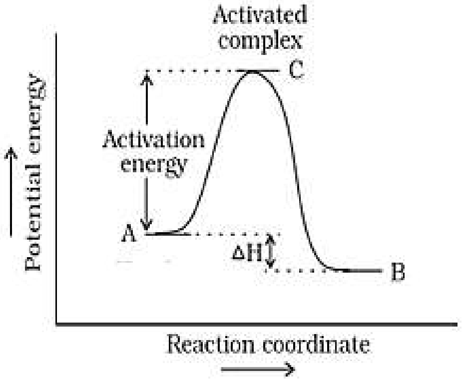
$K.E \ \alpha\ T \Rightarrow ½ mv^2 \alpha\ T$

As temperature increases, speed of reacting molecules increases. Thereby, the frequency of collisions also increases and hence rate of reaction increases.

(ii) Experimental evidence shows that for every 10 degree rise in temperature, the rate of a reaction will be doubled.

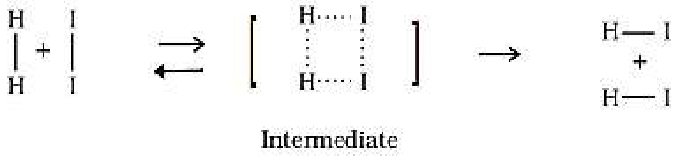
(iii) If 'E' is the energy barrier, then the number of molecules that crosses over the energy barrier is more at higher temperature than at low temperature.

Activated complex (Transition State theory):It is the reaction intermediate possessing energy that correspond to top of energy barrier.



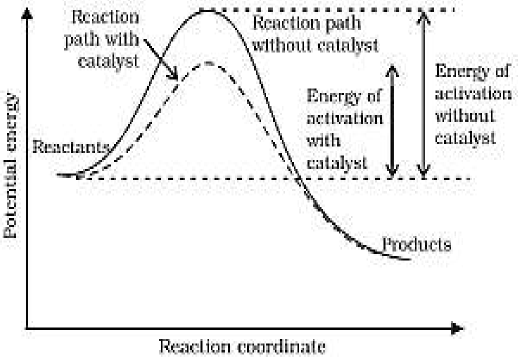
Activated complex state is highly energy state and hence it is highly unstable state. It is always reversible state.

Consider a reaction: $H_2 (g) + I_2 (g) \rightarrow 2HI (g)$



If the total energy of reacting species are equal or higher than threshold energy then the reaction proceed in forward direction and hence gives the products otherwise it retain as reactants only.

Effect of Catalyst: A catalyst is a substance which alters the rate of a reaction without itself undergoing any permanent chemical change.



Catalyst help to increase the rate of chemical reaction. It carries the reaction through the path of lower activation energy.

MULTIPLE CHOICE QUESTIONS:

1. For a given rate, the unit of rate and the rate constant are the same.
   (A) zero order reaction (B) first order reaction
   (C) second order reaction (D) third order reaction
2. If concentration of reactant 'A' is increased 10 times and the rate of reaction becomes 100 times. What is the order with respect to 'A'?
   (A) 1 (B) 2 (C) 3 (D) 4

3. Which of the following is not a direct factor affecting the rate of a reaction?
(A) Temperature (B) Presence of catalyst
(C) Order of reaction (D) Molecularity

4. In the reaction $2A + B \rightarrow A_2B$, if the concentration of A is doubled and that of B is halved, then the rate of the reaction will
(A) increase 2 times (B) increase 4 times
(C) decrease 2 times (D) remain the same

5. A first order reaction has a half-life length of 10 minutes. In 100 minutes, what proportion of the response will be completed?
(A) 25% (B) 50% (C) 99.9% (D) 75%

6. What is the order of reaction decomposition of Ammonia on platinum surface is
(A) Zero order reaction (B) First order reaction
(C) Second order reaction (D) Fractional order reaction

7. In the rate equation, when the concentration of reactants is unity then the rate is equal to:
(A) Specific rate constant (B) Average rate constant
(C) Instantaneous rate constant (D) None of the above

8. The rate constant of zero order reactions has the unit
(A) s^{-1} (B) mol $L^{-1}s^{-1}$
(C) L^2 mol^{-2} s^{-1} (D) L $mol^{-1}s^{-1}$

9. Radioactive disintegration is an example of
(A) first order reaction (B) zero order reaction
(C) second order reaction (D) third order reaction

10. A catalyst alters, which of the following in a chemical reaction?
(A) Entropy (B) Enthalpy
(C) Internal energy (D) Activation energy

ASSERTION – REASON BASED QUESTIONS

Read the Assertion and Reason statements and choose the appropriate option from below:

A) Both A and R are true and R is the correct explanation of A
B) Both A and R are true and R is not the correct explanation of A
C) A is true but R is false
D) A is false but R is true

1. Assertion: Increasing the pressure of reactants can increase the rate of a reaction.
Reason: Higher pressure can increase the frequency of collisions between reactant molecules

2. Assertion: The presence of a catalyst increases the activation energy of a reaction.
Reason: Catalysts provide an alternative reaction pathway with a lower activation energy.

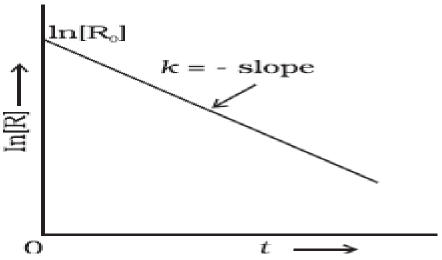
3. Assertion: Hydrolysis of methyl ethanoate is a pseudo-first-order reaction.
Reason: Water is present in large excess and therefore its concentration remained constant throughout the reaction.

4. Assertion: Average rate and instantaneous rate of a reaction have the same unit.
Reason: Average rate becomes an instantaneous rate when the time interval is too small.

5. Assertion: All collision of reactant molecules lead to product formation.
Reason: Only those collisions in which molecules have correct orientation and sufficient kinetics energy lead to compound formation.

VERY SHORT ANSWER QUESTIONS (1 MARK)

1. In some cases, it is found that a large number of colliding molecules have energy more than threshold value, yet the reaction is slow. Why?
2. For a reaction R→P, half-life ($t_{½}$) is observed to be independent of the initial concentration of reactants. What is the order of reaction?
3. Why does the rate of a reaction not remain constant throughout the reaction process?
4. What is elementary reaction?
5. Express the rate of the following in terms of ammonia.
   $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
6. Mention the factors that affect the rate of a chemical reaction.
7. In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?
8. A graph is drawn between ln[R] and *t* for a reaction. What is order of reaction?



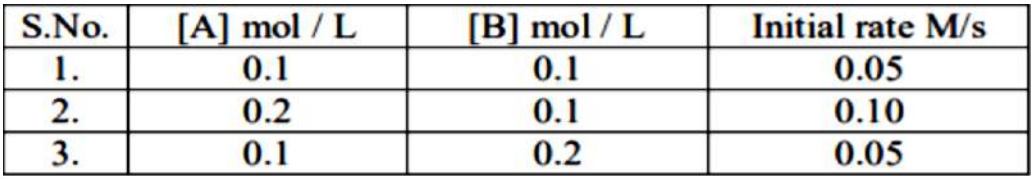
9. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.
10. How catalyst increase the rate of reaction?

SHORT ANSWER QUESTIONS TYPE-1 (2 MARKS)

1. What is the effect of temperature on the rate constant of a reaction?
2. Define each of the following:
   (i) Specific rate of a reaction. (ii) Energy of activation of a reaction.
3. Bring out the difference between order and molecularity of reaction.
4. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate Ea.
5. The rate for the decomposition of NH_3 on platinum surface is zero order. What are the rate of production of N_2 and H_2 if $K=2.5\times10^{-4}$mol $litre^{-1}s^{-1}$.

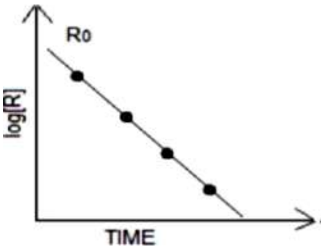
SHORT ANSWER QUESTIONS TYPE-2 (3 MARKS)

1. For the reaction A + B →products, the following initial rates were obtained at various given initial concentrations. Determine the overall order of a reaction



S.No.	[A] mol / L	[B] mol / L	Initial rate M/s
1.	0.1	0.1	0.05
2.	0.2	0.1	0.10
3.	0.1	0.2	0.05

2. Observe the graph in diagram and answer the following questions.



(i) If slope is equal to -2.0 x10^{-6} sec^{-1}, what will be the value of rate constant?
(ii) How does the half-life of zero order reaction relate to its rate constant?

3. (a) Consider a certain reaction A → Products with k = 2.0 × 10^{-2} s^{-1}. Calculate the concentration of a remaining after 100 s if the initial concentration of A is 1.0 mol l^{-1}
(b) The half-life for radioactive decay of C -14 is 5730 years. An archaeological artefact containing wood had only 80% of the C -14 found in a living tree. Estimate the age of the sample**.**

4. If a zero-order reaction starts with the concentration of 10 mol/L, it's half-life is 2 minutes, what will be the half-life of the same reaction, if it is started with 20 mol/L?

5. (i) What will be the effect of temperature on rate constant?
(ii) State a condition under which a biomolecular reaction is kinetically first order reaction.
(iii) For a zero-order reaction, will the molecularity be equal to zero? Explain.

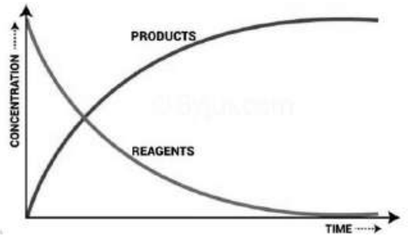
LONG ANSWER QUESTIONS (5 MARKS)

1. (a) (i) For the reaction 2X →X_2, the rate of reaction becomes three times, when concentration of X is increased 27 times. What is the order of the reaction?
(ii) Write the rate equation for the reaction
2A + B →2C, if the order of the reaction is zero.
(iii) Oxygen is available in plenty in air, yet fuels do not burn by themselves at room Temperature. Explain.
(b) Rate constant for first order reaction has been found to be 2·54 ×10^{-3} s^{-1}. Calculate its three- fourth life. [log 2 = 0·3010].

2. (a) (i) A reaction is 50% complete in 2 hours and 75% complete in 4 hours. What is the order of the reaction?
(ii) A first order reaction is 50% completed in 1.26 × 10^{14} s. How much time would it take for 100% completion?
(iii) The activation energy of a reaction is zero. Will the rate constant depend upon temperature? Explain.
(b) A reaction is first order in A and second order in B. Write the differential rate equation and calculate how the rate is affected when
(i) concentration of B is tripled, (ii) concentration of both A and B is doubled.

CASE BASED QUESTIONS / INTEGRATED BASED QUESTIONS (4 MARKS)

1. **Read the passage carefully and answer the questions that follow**
Rate of the Reaction
Speed of any event is measured by the change that occurs in any interval of time. The speed of a reaction (reaction rate) is expressed as the change in concentration of a reactant or product over a certain amount of time. Sometimes it is more convenient to express rates as numbers of molecules formed or consumed in unit time.



We could also look at the rate of appearance of a product. As a product appears, its concentration increases. The rate of appearance is a positive quantity. We can also say the rate of appearance of a product is equal to the rate of disappearance of a reactant.

Answer the following questions:

(a) Write the rate of the chemical reaction with respect to the variables for the given equation.

$$2A+3B \rightarrow C+2D$$

(b) In a reaction, 2A → Products, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

(c) In the reaction $H_2O_{2(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2} O_{2(g)}$, the initial concentration of H_2O_2 is 0.2546 M, and the initial rate of reaction is 9.32×10^{-4} M s^{-1}. What will be $[H_2O_2]$ at $t = 35$ s?

OR

(c) How is the rate of disappearance of ozone related to the rate of appearance of oxygen in the following equation?

$$2O_{3\ (g)} \rightarrow 3O_{2\ (g)}$$

If the rate of appearance of O_2 is 60.0×10^{-5} M/s at a particular instant, what is the value of the rate of disappearance of O_3 at this same time?

2. **Read the passage carefully and answer the questions that follow**

Order of the Reaction

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction, aA + bB→ C with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction. The rate law is given by $r = k\,[A]^x\,[B]^y$ where [A] and [B] express the concentrations of A and B in moles per litre. Exponents x and y vary for each reaction and are determined experimentally. The value of k varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reaction has constant rate that is independent of the concentration of the reactants. A first order reaction depends on the concentration of only reactant. A reaction is said to be of second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug one set of our initial values and solve for k.

Answer the following questions:

(a) Calculate the overall order of the reaction which has the following rate expression:

$$\text{Rate} = k[A]^{1/2}[B]^{3/2}$$

(b) What is the effect of temperature on rate of the reaction?

(c) What is meant by the rate of reaction?

(d) A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of the reaction. (log 10= 1, log 7=0.8450)

OR

A first order reaction has a rate constant 1×10^{-3} s^{-1}. How long will 5 gm of this reactant take to reduce to 3 gm? (log 3= 0.4771, log 5=0.6990)

3. **Read the passage carefully and answer the questions that follow**

Radio Activity

There are nuclear reactions constantly occurring in our bodies, but these are very few of them compared to the chemical reactions, and they do not affect our bodies much. All of the physical processes that take place to keep a human body running are chemical processes. Nuclear reactions can lead to chemical damage, which the body may notice and try to fix. The nuclear reaction occurring in our bodies is radioactive decay. This is the change of a less stable nucleus to a more stable nucleus. Every atom has either a stable nucleus or an unstable nucleus, depending on how big it is and on the ratio of protons to neutrons. The ratio of neutrons to protons in a stable nucleus is thus around 1:1 for small nuclei ($Z<20$). Nuclei with too many neutrons, too few neutrons, or that are simply too big are unstable. They eventually transform to a stable form through radioactive decay. Wherever there are atoms with unstable nuclei (radioactive atoms), there are nuclear reactions occurring naturally. The interesting thing is that there are small amounts of radioactive atoms everywhere: in your chair, in the ground, in the food you eat, and yes, in your body. The most common natural radioactive isotopes in humans are carbon-14 and potassium-40. Chemically, these isotopes behave exactly like stable carbon and potassium. For this reason, the body uses carbon-14 and potassium-40 just like it does normal carbon and potassium; building them into the different parts of the cells, without knowing that they are radioactive. In time, carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium atoms. Half-life of C-14 is 6000 years Chemicals in the body that relied on having a carbon14 atom or potassium-40 atom in a certain spot will suddenly have a nitrogen or calcium atom. Such a change damages the chemical. Normally, such changes are so rare, that the body can repair the damage or filter away the damaged chemicals.

Answer the following questions:

(a) Why is Carbon -14 radioactive while Carbon -12 not?
(Atomic number of Carbon: 6)
(b) Which are the two most common radioactive decays happening in human body?
(c) Suppose an organism has 20 g of Carbon -14 at its time of death. Approximately how much Carbon -14 remains after 10,320 years? (Given antilog 0.517 = 3.289)

OR

(c) Approximately how old is a fossil with 12 g of Carbon -14 if it initially possessed 32 g of Carbon -14? (Given log 2.667 = 0.4260)

4. **Read the passage carefully and answer the questions that follow**

Temperature Dependence of Rate of a Reaction

Temperature influences the rate of a reaction. As the temperature increases, the rate of a reaction increases. For example, the time taken to melt a metal will be much higher at a lower temperature but it will decrease as soon as we increase the temperature. It has been found that the rate constant is nearly *doubled* for a chemical reaction with a rise in temperature by 10°. The dependence of the rate of a chemical reaction on temperature can be explained by Arrhenius equation.

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

According to the Arrhenius equation, a reaction can only take place when a molecule of one substance collides with the molecule of another to form an unstable intermediate. This intermediate exists for a very short time and then breaks up to form product. The energy required to form this intermediate is known as activation energy (E_a). The fraction of molecules with kinetic energy equal to or greater than E_a at a given temperature may lead to the product. As the temperature rises, the proportion of molecules with energies equal to or greater than activation energy ($\geq E_a$) increases. As a result, the reaction rate would increase.

Answer the following questions:

(a) How does the half life period of a first order reaction vary with temperature?

OR

For an endothermic reaction, the activation energy of forward reaction will be equal to or less than or more than activation energy of backward reaction.

(b)The slope of Arrhenius Plot (ln k vs 1/T) of first order reaction is $-5\times10^3 K$. Calculate the value of E_a of the reaction. [Given R = $8.314 JK^{-1}mol^{-1}$]

(c) The rate constant of a reaction is 6×10^{-3} s^{-1} at 50° and 9×10^{-3} s^{-1} at 100° C. Calculate the energy of activation of the reaction.

5. Read the passage carefully and answer the questions that follow:

The Arrhenius equation, developed by Swedish chemist Svante Arrhenius, is a fundamental equation in chemical kinetics that relates the rate constant (k) of a reaction to temperature (T) and the activation energy (Ea). The equation is given by:

$$k = A\, e^{-Ea/RT}$$

Here, A is the pre-exponential factor or frequency factor, Ea is the activation energy, R is the ideal gas constant, and T is the absolute temperature.

The Arrhenius equation helps explain the temperature dependence of reaction rates. As temperature increases, the exponential term $e^{-Ea/RT}$ becomes smaller, leading to a higher rate constant and consequently, a faster reaction. Conversely, lower temperatures result in a decrease in the rate constant and a slower reaction.

In summary, the Arrhenius equation provides valuable insights into the relationship between temperature and reaction rates, aiding in the understanding and prediction of chemical reactions under different temperature conditions.

a) Calculate the activation energy for a reaction if the rate constant is known at two different temperatures.

b) Define activation energy?

c) Calculate the activation energy of a reaction if the slope of its ln k vs 1/T plot is -3166 K.

OR

c) The activation energy for the reaction 2 HI(g) → H_2 + I_2 (g) is 209.5 kJ mol^{-1} at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

ANSWERS

MULTIPLE CHOICE QUESTIONS:

1	2	3	4	5	6	7	8	9	10
A	B	D	A	C	A	A	B	A	D

ASSERTION – REASON BASED QUESTIONS

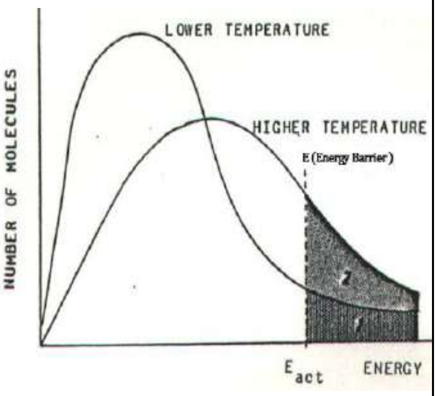
1	2	3	4	5
A	D	A	B	D

VERY SHORT ANSWER QUESTIONS (1 MARK)

1. because of the orientation of the molecules which are colliding.
2. first order reaction
3. A reaction depends upon change in the amount of chemical substances varies with time and hence the reaction rate does not remain constant throughout.
4. A reaction which occur in single step
5. $\text{Rate} = \frac{-d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$
6. concentration of reactants (pressure in case of gases), temperature and catalyst.
7. $\text{Rate} = \frac{1}{2}\frac{[A_0] - [A]}{t} = \frac{1}{2}\frac{[0.5] - [0.4]}{10} = 5 \times 10^{-3}\ \text{mol L}^{-1}\ \text{min}^{-1}$
8. First order reaction
9. $t_{1/2} = \frac{0.693}{k}$ $\quad k = \frac{0.693}{3600} = 0.0001925 = 1.925 \times 10^{-4}\ s^{-1}$
10. Catalyst takes the reaction through the path of lower activation energy.

SHORT ANSWER QUESTIONS TYPE-1 (2 MARKS)

1. Rate of a reaction always increases with increase of temperature
   (i) According to Kinetic theory of Molecular gases, the average kinetic energy of reacting gaseous molecules is directly proportional to absolute temperature.
   $K.E \ \alpha\ T \Rightarrow \frac{1}{2} mv^2 \alpha\ T$
   As temperature increases, speed of reacting molecules increases. Thereby, the frequency of collisions also increases and hence rate of reaction increases.
   (ii) Experimental evidence shows that for every 10-degree rise in temperature, the rate of a reaction will be doubled.
   (iii) If 'E' is the energy barrier, then the number of molecules that crosses over the energy barrier is more at higher temperature than at low temperature.



2. (i) A given temperature, rate is equal to the rate constant of reaction when concentration of the reactant in unity. Thus rate constant is also known as specific reaction rate.
   (ii) Additional energy required by the reacting molecules to attain Threshold energy is called Activation energy.

3.

	Order of reaction	**Molecularity of reaction**
1	It is the sum of powers of concentrations of reactants expressed in rate law.	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
2	Order of a reaction is an experimental quantity.	Molecularity of a reaction is a theoretical quantity.
3	It can be zero and even a fraction	Molecularity cannot be zero or a non-integer.
4	Order is applicable to elementary as well as complex reactions	Molecularity is applicable only for elementary reactions.

4. let us take the value of k1 = k and that of k2 = 2k

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \log\frac{2}{1} = \frac{E_a}{2.303 \times 8.314}\left(\frac{1}{298} - \frac{1}{308}\right)$$

$$E_a = 52.9\text{kJ mol}^{-1}$$

5. $\text{Rate of reaction} = -\frac{1}{2}\frac{d}{dt}[NH_3] = \frac{d}{dt}[N_2] = \frac{1}{3}\frac{d}{dt}[H_2] = k$

For a zero order reaction, $\text{Rate} = k = 2.5 \times 10^{-4}$ M/s

$\text{Rate of production of } N_2 = \frac{d}{dt}[N_2] = 2.5 \times 10^{-4}$ M/s

$\text{Rate of production of } H_2 = \frac{d}{dt}[H_2] = 3 \times 2.5 \times 10^{-4}$ M/s $= 7.5 \times 10^{-4}$ M/s

SHORT ANSWER QUESTIONS TYPE-2 (3 MARKS)

1. For A, Rate $=k[A]^x$ For B, Rate $=k[B]^y$
From case 1 and 2 ⇒ 2× Rate $=k[2A]^x$ From case 1 and 3, Rate $=k[2B]^y$
x=1 y=0
Order n = x+y =1+0 =1

2. (i) SLOPE = -K - $2.0\text{x}10^{-6}$ sec^{-1} = -K Hence k = $2.0\text{x}10^{-6}$ sec^{-1}
(ii) t ½= $R_0/2k$

3. (a) The integrated rate expression for the first order reaction is as follows:
k=2.303/t log$[A]^0$/ [A] ⇒2.0×10−2=2.303tlog1.0[A]
⇒log1.0[A]=0.868 ⇒[A]=0.135M
(b) Decay constant k=0.693t1/2=0.6935730year=1.209×10^{-4}/years
The rate of counts is proportional to the number of C-14 atoms in the sample. N_0=100, N=80 The age of the sample t=2.303/k log(N_0/N)
t=2.303/1.209×10^{-4} × log(10080)=1846years

4. For zero order reaction-$t_{1/2}$=$[R_0]$/2k (half-life is directly proportional to initial concentration)
So $t_{1/2}$ for 20 mol/L will be 4 minutes.

5. a) The rate constant of a reaction is nearly doubled with rise in temperature by 10
b) Bimolecular reactions become kinetically first order when one of the reactants is present in excess
c) No, the molecularity can never be zero or a fractional number. As it represents the total number of reactants taken in a reaction

LONG ANSWER QUESTIONS (5 MARKS)

1. (a) (i)Rate $=k(x)^n$; 3Rate $=k(27x)^n$

Solving then, n =1/3, so order of reaction =1/3

(ii)Rate $=k[A]^0[B]^0=k$

(iii)The activation energy for combustion of fuels is generally very high, and not achieved at room temperature.

(b) $t = \frac{2.303}{k} \log\frac{[R_0]}{[R]}$

$t_{3/4} = \frac{2.303 \log[R_0]}{\frac{1}{4}[R_0]}$

$=5.46 \times 10^2$ s

2. (a)(i) First order

(ii)Infinite, because no first order reaction is 100% completed.

(iii)$k= Ae^{-Ea/RT}$, if $E_a=0$ then k =A, so the rate constant does not depend on temperature.

(b)$Rate(R)=k[A][B]^2$

(i)$Rate(R_1) =k[A][B]^2$

$(R_1) =9R$, so the rate increases 9 times.

(ii) $R_2= k[A][B]^2$

$R_2=8R$, rate increases 8 times

CASE BASED QUESTIONS / INTEGRATED BASED QUESTIONS (4 MARKS)

1. (a) Rate $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\frac{\Delta[B]}{\Delta t} = \frac{\Delta[C]}{\Delta t} = \frac{1}{2}\frac{\Delta[D]}{\Delta t}$

(b) Rate $= -\frac{1}{2}\frac{[A]-[Ao]}{t}$

Rate $= -\frac{1}{2}\frac{[0.4]-[0.5]}{10}$

Rate = 5×10^{-3} mol L^{-} min^{-}

(c) Rate = 9.32×10^{-4} Ms^{-1} = $-\frac{\Delta[H_2O_2]}{\Delta t}$

9.32×10^{-4} Ms^{-1} = $-\frac{[H_2O_2]-0.2546\ M}{(35-0)s}$

H_2O_2 = 0.2220 M

OR

Rate $= -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$

$= -\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}$ $(60.0 \times 10^{-5}\ M/s) = 4.0 \times 10^{-5}\ M/s$

2. (a) Rate = $k[A]^{1/2}[B]^{3/2}$, as it is an elementary reaction,

Order of reaction = 1/2 + 3/2 = 2

(b) Rate of reaction increases with increase in temperature.

(c) Rate of reaction is the rate of change in concentration of a reactant per unit time.

(d) For first order reaction

$R = 0.693/t_{1/2} = (0.693)/(77.78min) = 8.90 \times 10^{-3}$ min

Time required to complete 30% reaction,

$t = (2.303)/k \times \log a / (a - x) = (2.303) / (8.9 \times 10^{-3}\ min^{-1}) \times \log (100 / (100 - 30))$

$= ((2.303 \times 10^3 \times 0.155)/(8.9)$ = 40minutes

OR

For a first order reaction
$t = (2.303)/k \times \log a/(a - x) = 2.303/1\times10^{-3} \times \log 5/3 = 2.303\times 10^3 \times 0.2219$ s
= 511 s

3. (a) Ratio of neutrons to protons in C-14 is 1.3: 1 which is not the stable ratio of 1:1 while ratio of neutrons to protons in C-12 is 1:1 which is the stable ratio.
(b) carbon-14 atoms decay to stable nitrogen atoms and potassium-40 atoms decay to stable calcium
(c) $t = 2.303/ k \log (C_o/C_t)$
$C_o = 20$ g $C_t = ?$ t = 10320 years
k = 0.693/6000 (half-life given in passage)
Substituting in equation:
$10320 = 2.303 / (0.693/6000) \log 20/ C_t$ $0.517 = \log 20 / C_t$
Antilog $(0.517) = 20/C_t$ $3.289 = 20/C_t$ $C_t = 6.17$ g

OR

$t = 2.303/ k \log (C_o/C_t)$ $C_o = 32$ g $C_t = 12$ t = ?
k = 0.693/6000 (half-life given in passage)
Substituting in equation:
$t = 2.303 / (0.693/6000) \log 32/ 12$
$t = 2.303 \times 6000/0.693 \log 2.667 = 2.303\times6000\times0.4260 /0.693$ = 8494 years

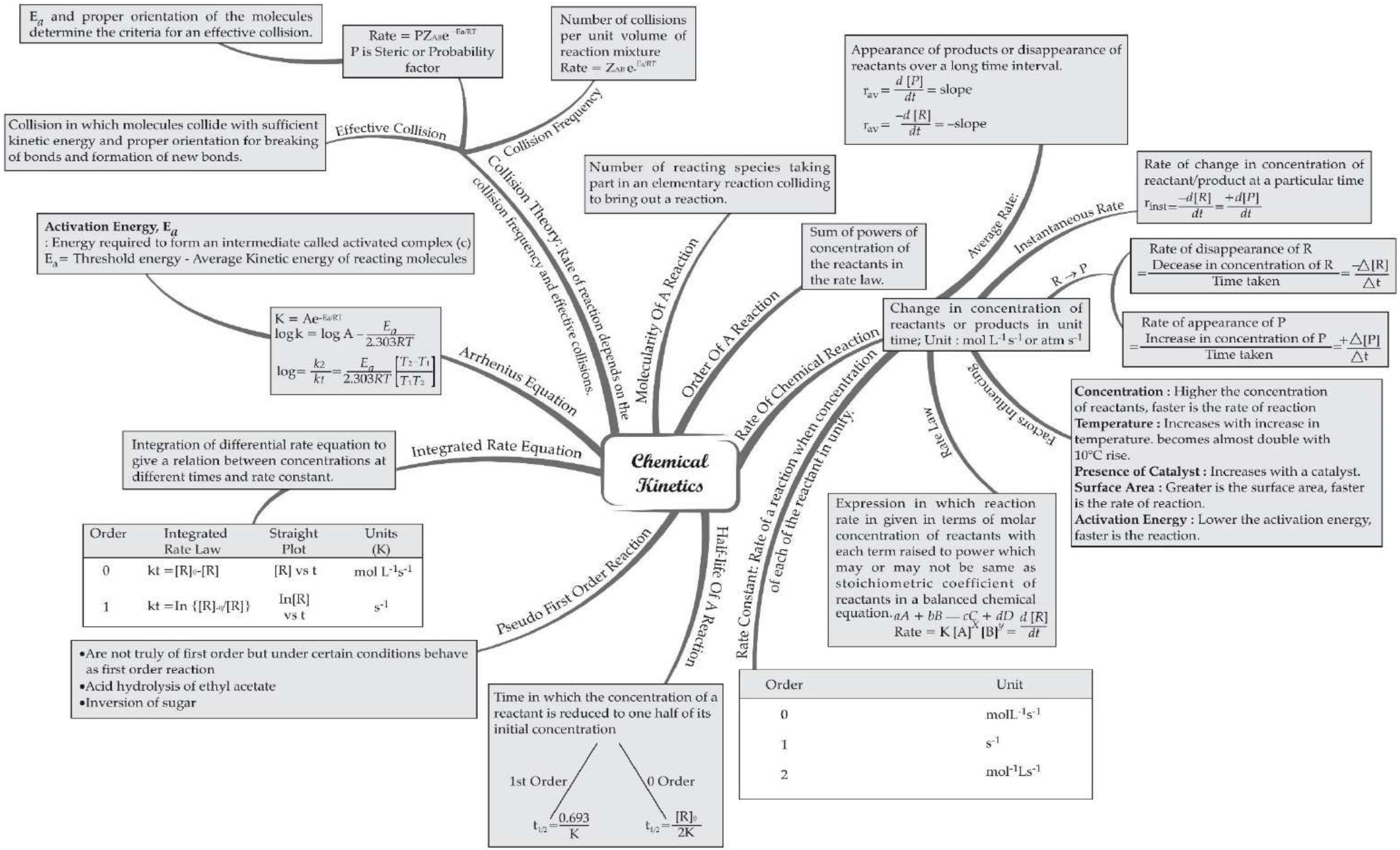
4. (a) Half-life period increases with temperature.

OR

The activation energy of forward reaction will be more than activation energy of backward reaction.
(b) $k = Ae^{-E_a/RT}$ $\ln k = \ln A – E_a/RT$ *Slope* = $-E_a/R = - 5 \times 10^3$
$Ea = 5 \times10^3 \times8.314 = 41.57\times10^3$ J/mol
(c) $k_1 = 6 \times 10^{-3}$ s^{-1} $T_1 = 50 + 273 = 323$ K
$k_2 = 9 \times 10^{-3}$ s^{-1} $T_2 = 100 + 273 = 373$ K
Substituting these values in the equation:
$\log (k_2 / k_1) = (E_a / 2.303 R) \times ((T_2 – T_1) / T_1 T_2)$
$\log (9 \times 10^{-3} s^{-1} / 6 \times 10^{-3} s^{-1}) = ((E_a / (2.303 \times 8.314)) \times ((373 – 323) / (373 \times 323))$
$\log (9 / 6) = ((E_a / (2.303 \times 8.314)) \times (50 / (373 \times 323))$ $E_a = 8.124$ kJ mol^{-1}.

5. (a) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$
(c) Additional energy required by the reacting molecules to attain Threshold energy is called Activation energy.
(d) 110.115 kJ/mol   OR
The fraction of molecules of reactants having energy equal to or greater than activation energy is 1.471×10^{-19}

MIND MAP : LEARNING MADE SIMPLE



E_a and proper orientation of the molecules determine the criteria for an effective collision.

Rate = $PZ_{AB}e^{-Ea/RT}$
P is Steric or Probability factor

Number of collisions per unit volume of reaction mixture
Rate = $Z_{AB}e^{-Ea/RT}$

Collision in which molecules collide with sufficient kinetic energy and proper orientation for breaking of bonds and formation of new bonds.

Activation Energy, E_a
: Energy required to form an intermediate called activated complex (c)
E_a = Threshold energy - Average Kinetic energy of reacting molecules

$K = Ae^{-Ea/RT}$
$\log k = \log A - \frac{E_a}{2.303RT}$
$\log = \frac{k_2}{k_1} = \frac{E_a}{2.303RT}\left[\frac{T_2 - T_1}{T_1T_2}\right]$

Integration of differential rate equation to give a relation between concentrations at different times and rate constant.

Order	Integrated Rate Law	Straight Plot	Units (K)
0	$kt = [R]_0 - [R]$	[R] vs t	mol $L^{-1}s^{-1}$
1	$kt = \ln\{[R]_0/[R]\}$	In[R] vs t	s^{-1}

- Are not truly of first order but under certain conditions behave as first order reaction
- Acid hydrolysis of ethyl acetate
- Inversion of sugar

Time in which the concentration of a reactant is reduced to one half of its initial concentration

1st Order: $t_{1/2} = \frac{0.693}{K}$

0 Order: $t_{1/2} = \frac{[R]_0}{2K}$

Number of reacting species taking part in an elementary reaction colliding to bring out a reaction.

Sum of powers of concentration of the reactants in the rate law.

Change in concentration of reactants or products in unit time; Unit : mol $L^{-1}s^{-1}$ or atm s^{-1}

Appearance of products or disappearance of reactants over a long time interval.
$r_{av} = \frac{d[P]}{dt} = \text{slope}$
$r_{av} = \frac{-d[R]}{dt} = -\text{slope}$

Rate of change in concentration of reactant/product at a particular time
$r_{inst} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$

Rate of disappearance of R
$= \frac{\text{Decease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$

Rate of appearance of P
$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$

Concentration : Higher the concentration of reactants, faster is the rate of reaction
Temperature : Increases with increase in temperature. becomes almost double with 10°C rise.
Presence of Catalyst : Increases with a catalyst.
Surface Area : Greater is the surface area, faster is the rate of reaction.
Activation Energy : Lower the activation energy, faster is the reaction.

Expression in which reaction rate in given in terms of molar concentration of reactants with each term raised to power which may or may not be same as stoichiometric coefficient of reactants in a balanced chemical equation. $aA + bB \longrightarrow cC + dD$ Rate = $K[A]^x[B]^y = \frac{d[R]}{dt}$

Order	Unit
0	$molL^{-1}s^{-1}$
1	s^{-1}
2	$mol^{-1}Ls^{-1}$

4. THE d- AND f-BLOCK ELEMENTS

QUICK REVISION POINTS:

1. d-block elements

(a) DEFINITION: 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. Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. Their Outer electronic configuration is (n -1) d^{1-10} ns $^{1-2}$

(b) MELTING AND BOILING POINTS: High MP & BP which is due to their strong metallic bond (strong interatomic bonding) due to unpaired electrons in (n-1) d orbitals.In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc.

(c) ENTHALPIES OF ATOMIZATION: High enthalpies of atomization Because of large number of unpaired electrons in their atoms they have stronger interatomic interaction (metal-metal bonding). The metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series due to occurrence of much more frequent metal – metal bonding.

(d) VARIATION IN ATOMIC AND IONIC SIZES : In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number The atomic radii decreases from group 3 to 6 because of increase in effective nuclear charge gradually, The atomic radii of group 7,8,9 &10 elements is almost same because Screening effect counter balances increased effective nuclear charge, Group 11 &12 elements have bigger size due to increase inter-electronic repulsion as result electron cloud expands and size increases. Members of second(4d) and the third (5*d*) series in each group of transition elements have similar radii and shows similar properties because lanthanoid contraction essentially compensates for the expected increase in atomic size with increasing atomic number.

(e) DENSITY: The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus, from titanium (22) to copper (29) the significant increase in the density may be noted.

(f) VARIATION IN IONISATION ENTHALPIES OF TRANSITION METALS: There is an increase in ionisation enthalpy along each series of the transition elements from left to right due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals. Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3*d*-configurations (e.g., d^0, d^5, d^{10} are exceptionally stable).

(g) OXIDATION STATES: The transition elements show variable oxidation state due to small energy difference between (n-1) d & ns orbital as a result both (n-1) d & ns electrons take part in bond formation. The highest oxidation state of an element is equal to number of unpaired e^- present in (n-1) d & ns orbital.

(h) MAGNETIC PROPERTIES : Most of the transition metal ions are paramagnetic. due to the presence of unpaired electrons in d-orbitals. Magnetic moment is given by

$$\mu = \sqrt{n(n+2)}\ \text{B.M.}$$

Where, n = number of unpaired electrons and BM = Bohr magneton (unit of magnetic moment).

(i) FORMATION OF COLOURED IONS: Due to the presence of unpaired electrons in d-orbitals of the transition metal ions & because of d– d transitions occurring in a transition metal ions by the absorption of visible light.

(j) FORMATION OF COMPLEX COMPOUNDS :- Due to smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.

(k) CATALYTIC PROPERTIES: Due to Variable oxidation states & Large surface area.

(l) FORMATION OF INTERSTITIAL COMPOUNDS: Transition elements form interstitial compounds because size of C, N, O, and B is similar to size of interstitial voids of transition metals.

(m) ALLOY FORMATION: As the atomic sizes are very similar, one **metal** can replace the other **metal** from its lattice and **form** a solid solution which is the **alloy**.

(n) STANDARD ELECTRODE POTENTIALS: Transition elements have lower negative value of **Standard Electrode Potentials** due to high ionization potential, high heat of sublimation & low enthalpy of hydration. The E^0 (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionization enthalpies and also the sublimation enthalpies which are relatively much less for manganese and vanadium.

(o) Oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in effective nuclear charge.e.g. MnO (basic), Mn_3O_4 (amphoteric), Mn_2O_7 (acidic).

2. LANTHANOIDS

(a) The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids. The general electronic configuration of these elements is [Xe] $4f^{1-14}$, $5d^{0-1}$,$6s^2$.

(b) **LANTHANOID CONTRACTION (ATOMIC AND IONIC SIZES):** The overall decrease in atomic and ionic radii from lanthanum to lutetium is due to poor shielding of 4f electrons is known as lanthanoid contraction. **Due to lanthanoid contraction:-**
(a)**basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$**,
(b) Sizes of 4d and 5d metal pairs like Zr and Hf; Nb and Ta are almost similar.

(c) **OXIDATION STATES:** Most common oxidation state of these elements is +3, However, occasionally +2 (Eu^{+2} and Yb^{+2})and +4 ions (Ce^{+4} and Tb^{+4}) in solution or in solid compounds are also obtained.

(d) **COLOUR FORMATION** :Many trivalent lanthanoid ions are coloured both in the solid state and in aqueous solutions. Colour of these ions may be attributed to the presence of ***unpaired*** **electrons** in f subshell.

(e) **MAGNETIC BEHAVIOUR**: The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.

(f) **USES** : A well-known alloy is *mischmetall* which consists of a lanthanoid metal(~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A good deal of *mischmetall* is used in Mg-based alloy to produce bullets, shell and lighter flint.

3. ACTINOIDS

(a) The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids

(b) The actinoids are radioactive elements These facts render their study more difficult.

(c) **Electronic Configurations:** The general electronic configuration of these elements is [Rn] $5f^{1-14}$, $6d^{0-1}$,$7s^2$

(d) **Ionic Sizes(Actinoid contraction):** The overall decrease in atomic and ionic radii across the series due to poor shielding of 5f electrons is known as **Actinoid contraction**

(e) The actinoid contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

(f) **Oxidation States:** The actinoids show in general +3 oxidation state. The actinoids exhibit a larger number of oxidation states, which is in part attributed to the fact that the 5*f*, 6*d* and 7*s* levels are of comparable energies. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7respectively in Pa, U and Np but decreases in succeeding elements.

(g) The actinoids are highly reactive metals, especially when finely divided.

(h) The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 *f* electrons is roughly parallel to the corresponding results for the lanthanoids

4. POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

(a) **Preparation: -** It takes place in three steps-

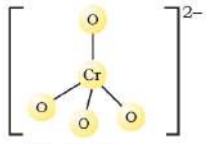
1. $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4$(yellow solution)+ $2Fe_2O_3 + 8CO_2$
2. $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7$(orange sodium) + $2\,Na^+ + H_2O$
3. $Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7$(Orange crystals)+ $2\,NaCl$

(b) The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. $2\,CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$
$Cr_2O_7^{2-} + 2\,OH^- \rightarrow 2CrO_4^{2-} + H_2O$

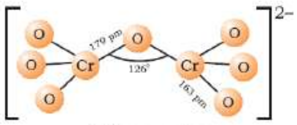
(c) **Potassium dichromate in acidic solution act as oxidizing agent.**

- $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{+3} + 3I_2 + 7H_2O$
- $Cr_2O_7^{2-} + 3H_2S + 8H^+ \rightarrow 2Cr^{+3} + 3S + 7H_2O$
- $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow 2Cr^{+3} + 3Sn^{4+} + 7H_2O$
- $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{+3} + 6Fe^{3+} + 7H_2O$

(d) **Structure of chromates and dichromates**



Chromate ion



Dichromate ion

(e) **Uses:** Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds. Potassium dichromate is used as a primary standard in volumetric analysis.

5. POTASSIUM PERMANGNATE [$KMnO_4$]

a) **Preparation:** -- It takes place in two steps:-

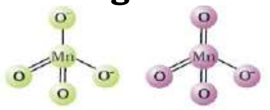
- $2MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4$ (Dark green)+ $2H_2O$
- $3\,MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^-$(Purple)+$MnO_2 + 2H_2O$ [Disproportionation]

b) **Properties of $KMnO_4$**

- Potassium permanganate are isostructural with those of $KClO_4$.
- When heated $KMnO_4$ decomposes at 513 K.
- $2KMnO_4 \xrightarrow{Heat,\Delta} K_2MnO_4 + MnO_2 + O_2$
- $KMnO_4$ act as Oxidising agent in acidic, alkaline & neutral medium.
- $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ (Acidic)
- $2MnO_4^- + 16H^+ + 5C_2O_4^{2} \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$
- $MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$
- $2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$

- $5NO_2^- + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$
- $5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$
- oxidising reactions of $KMnO_4$ In neutral or faintly alkaline solutions.
- $2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$
- $8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 2OH^- + 6SO_4^{2-}$
- $2MnO_4^- + 3Mn^{+2} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$

6. Permanganate titrations in presence of hydrochloric acid are unsatisfactory since hydrochloric acid is oxidised to chlorine.
7. **Uses:** Besides its use in analytical chemistry, potassium permanganate is used as a favourite oxidant in preparative organic chemistry. Its uses for the bleaching of wool, cotton, silk and other textile fibres and for the decolourisation of oils are also dependent on its strong oxidising power.
8. **Structure of Permanganate & Manganate:**



Tetrahedral manganate (green) ion

Tetrahedral permanganate (purple) ion

	MULTIPLE CHOICE QUESTIONS (1 MARKS)
1.	In which of the following pairs, both the ions are coloured in aqueous solutions? [Atomic no of Sc = 21, Ti = 22, Ni = 28, Co = 27, Cu = 29] (a) Sc^{3+}, Ti^{+3} (b) Sc^{3+}, Co^{2+} (c) Ni^{2+}, Cu^+ (d) Ni^{2+}, Ti^{3+}
2.	Which of the following is most stable in aqueous solution? (a) Mn^{3+} (b) Cr^{3+} (c) V^{3+} (d) Ti^{3+}
3.	$KMnO_4$ is not acidified by HCl instead of H_2SO_4 because (a) H_2SO_4 is stronger acid than HCl (b) HCl is oxidised to Cl_2 by $KMnO_4$ (c) H_2SO_4 is dibasic acid (d) rate of reaction is faster in presence of H_2SO_4
4.	Manav poured some potassium chromate solution in test tube for qualitative analysis. The yellow colour of potassium chromate soon turned orange in colour. Manav realised that this happened because the test tube was not clean and contained a few drops of some liquid. Which of the following were the liquid drops most likely to be. (a) Drops of water (b) methyl orange solution (c) NaOH solution (d) HCl solution
5.	Generally, transition elements form coloured salts due to the presence of unpaired electrons. Which of the following compounds will be coloured in solid state? (a) Ag_2SO_4 (b) CuF_2 (c) ZnF_2 (d) Cu_2Cl_2
6.	When $KMnO_4$. solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because (a) CO_2 is formed as the product. (b) Reaction is exothermic. (c) MnO_4^- catalyses the reaction. (d) Mn^{2+} acts as auto catalyst.
7.	Which of the following are d-block elements but not regarded as transition elements? (a) Cu, Ag, Au (b) Zn, Cd, Hg (c) Fe, Co, Ni (d) Ru, Rh, Pd
8.	Transition elements form alloys easily because they have (a) Same atomic number (b) Same electronic configuration (c) Nearly same atomic size (d) None of the above.
9.	Which of the following ion has magnetic moment value of 5.9? (a) Mn^{2+} (b) Fe^{2+} (c) Ni^{2+} (d) Cu^{2+}
10.	Which of the following lanthanoids show +2 oxidation state besides the characteristic oxidation state +3 of lanthanoids? (a) Ce (b) Eu (c) Tb (d) Dy.

ASSERTION REASON TYPE QUESTIONS(1MARKS)

In the Following questions_ a statement of Assertion(A) is followed by a statement of Reason(R). _Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

11. **Assertion(A) :** Magnetic moment values of actinides are lesser than the theoretically predicted values.
Reason(R) : Actinide elements are strongly paramagnetic.

12. **Assertion(A) :** $KMnO_4$ act as an oxidising agent in acidic, basic or neutral medium.
Reason(R) : $KMnO_4$ oxidises ferrous sulphate to ferric sulphate.

13. **Assertion(A) :** Of the $3d^4$species Cr^{2+} is strongly reducing and Mn^{3+} is strongly oxidising**.**
Reason(R) : Cr^{+3} state is stable due to half-filled t_2g set, Mn^{+2} is stable due to half- filled d orbitals

14. **Assertion(A) :**In the series Sc to Zn the enthalpy of atomisation of Zinc is the lowest.
Reason(R): Zinc has greater number of unpaired electrons

15. **Assertion(A) :**Magnetic moment of Mn^{2+} is less than that of Cr^{2+}.
Reason(R): Magnetic moment depends on the number of unpaired electrons.

VERY SHORT ANSWER TYPE QUESTIONS(1 MARK)

16. Which element has highest melting point in 3d series_?
17. Out of Cu_2Cl_2 and $CuCl_2$ which is more stable in aqueous solution.
18. Which element of the first transition series don't exhibit variable oxidation states?
19. Name an oxo anion having oxidation number of metal (3d series) equal to its groupnumber.
20. Name two elements of 3d series which show anomalous electronic configuration.
21. Identify the Transition metal of 3d series that acts as a strong reducing agent in +2 oxidation state in aqueous solution.
22. Name a member of lanthanoid series which is well-known to show +4 oxidation state.
23. Among the elements of 3d series which element is soft?
24. Arrange the following in increasing order of acidic character: CrO_3,CrO, Cr_2O_3
25. Complete the following equation :
$3MnO_4^{2-} + 4H^+ \longrightarrow$

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

26. Name an important alloy which contains some of the lanthanoid metals. Mention its uses.
27. Among Elements of 3d transition series: Write the element
(a) Which is not regarded as transition element.
(b) Which shows maximum number of oxidation states.
(c) Which forms stable divalent(M^{2+}) ion
(d) Which shows only +3 state?
28. What is Lanthanoid contraction? Give its cause. What are its Consequences?
29. When pyrolusite ore MnO_2 is fused of with KOH in presence of air,a green coloured compound (A) is obtained which undergoes disproportionation reaction in acidic medium to give purple coloured compound (B).
(i) Write the formulae of (A) & (B).
(ii) What happens when compound (B) is heated.
30. When chromite ore $FeCr_2O_4$ is fused with NaOH or (Na_2CO_3) in presence of air, a yellow coloured compound (A) obtained which on acidification with dilute

	sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms an orange coloured crystalline compound (C). (a) Write the formulae of (A), (B) & (C). (b) Write one use of compound (C).
	SHORT ANSWER TYPE QUESTIONS (3 MARKS)
31.	Explain giving a suitable reason for each of the following (a) Metal –metal bonding is more frequent for the 4d & 5d series of transition metals than that for the 3d series. (b) Cu^+ salts are colourless while Cu^{2+} salts are Coloured (c) Mn^{2+} exhibits maximum Para magnetism
32.	Account for the following (a) Although Zr belongs to 4d and Hf belongs to 5d transition series but it is quite difficult to separate them. (b) There is in general increase in density of element from titanium to copper. (c) Most of the transition metals and their compounds act as good catalysts.
33.	Explain the following observations. (a) Mn Shows the highest oxidation state of +7 among 3d series elements (b) Mn Shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4. (c)MnO is basic while Mn_2O_7 is acidic in nature.
34.	Account for the following (a) Cu^+ ion is not stable in aqueous solutions. (b) The d^1 configuration is very unstable in ions. (c)E^o value for the Mn^{2+}/Mn much more than expected.
35.	Assign reasons for the following. (a) Scandium is a transition element but Zinc is not. (b) Silver atom has completely filled d orbital ($4d^{10}$) in its ground state, yet it is transition element. (c)In the series Sc(Z = 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is the lowest.
	LONG ANSWER TYPE QUESTIONS (5 MARKS)
36.	Give Reasons for the following (i) Ce^{4+} in aqueous solution is a good oxidising agent. (ii) Actinoids contraction is greater from element to element than lanthanoid contraction. (iii) The actinoids exhibit a larger number of oxidation states than the corresponding lanthanoids. (iv) La^{3+} and Lu^{3+}do not show any colour in solutions. (v) Chemistry of all the lanthanoids are quite similar.
37.	Complete & balance the following reactions: - a) $Cr_2O_7^{2-} + Fe^{2+} + H^+ \rightarrow$ b) $MnO_4^- + H^+ + C_2O_4^{2-} \longrightarrow$ c) $KMnO_4 \xrightarrow{Heat,\Delta}$ d) $MnO_4^- + H_2O + I^- \longrightarrow$ e) $Cr_2O_7^{2-} + OH^- \rightarrow$
	CASE BASED QUESTIONS **The Following questions are case based questions carries 4 (1+1+2) marks. Read the given passage carefully and answer the questions that follow:**
38.	The transition metals react with a number of non-metals like oxygen, nitrogen, Sulphur and halogens to form binary compounds. The first series transition metal oxides are generally formed from the reaction of metals with oxygen at high temperatures. These oxides dissolve in acids and bases to form oxo metallic salts. Potassium dichromate and potassium permanganate are common examples.

	Potassium dichromate is prepared from the chromite ore by fusion with alkali in presence of air and acidifying the extract. Pyrolusite ore (MnO_2) is used for the preparation of potassium permanganate. Both the dichromate and the permanganate ions are strong oxidising agents. (a) What happens when Manganate ions (MnO_4^{2-}) undergoes disproportionation reaction in acidic medium? **(b) Explain why the colour of $KMnO_4$ disappears when oxalic acid is added to its solution in acidic medium.** **(c) When an orange solution containing $Cr_2O_7^{2-}$ ion is treated with an alkali, a yellow solution is formed and when H^+ ions are added to a yellow solution, an orange solution is obtained. Explain why does this happen?** OR **A solution of $KMnO_4$ on reduction yields either colourless solution or a brown precipitate or a green solution depending on the pH of the solution. What different stages of the reduction do these represent and how are they carried out?**
39.	The d-block, which lies between s and p-blocks contains, elements of groups 3-12, in which d- orbitals are progressively filled in each of four long periods of periodic table. These elements are also called transition elements or metals. The elements constituting the f-block are those in which 4 f and 5 f-orbitals are progressively filled. They are place in a separate panel at the bottom of the periodic table. The elements of f-block are also called inner-transition (a) Transition metal are very good catalyst. Why? (1) (b) Transition metals form a large number of interstitial compounds. Give reason(1) (c) Why the paramagnetic characteristic in 3d- transition series increases up to Cr and then decreases? (2) OR Out of $La(OH)_3$ and $Lu(OH)_3$, which is more basic and why?
40.	In the periodic table, the elements are classified into mainly four blocks, i.e. s, p, d and f. The d-block elements are called transition elements. The s-block contains the elements of the group 3-12. They possess properties that are transitional between the s and p-block elements. Zn, Cd, Hg do not exhibit characteristic properties of transition elements. All the elements belong to this section are metals. There are four rows of the transition elements involving filling of 3d, 4d, 5d and 6d orbitals. (a) Why does the transition element scandium not exhibit variable oxidation state? (1) (b) Why chromium is a typical hard metal while mercury is a liquid? (1) (c) Fe^{3+}/Fe^{2+} redox couple has less positive electrode potential than Mn^{3+}/Mn^{2+} couple.Why? (2) OR Copper (I) is diamagnetic, whereas copper (II) is paramagnetic.
41.	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 oxo anions CrO_4^{2-}, MnO_4^-, owing to their willingness to form multiple bonds. 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 neighbour; 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.

(a) Highest fluoride of Mn is MnF_4 where as the highest oxide is Mn_2O_7 (1)

(b) Which is more stable Fe^{2+} or Fe^{3}+? (1)

(c). The higher oxidation states are usually exhibited by the members in the middle of a series of transition elements ? (2)

OR

Electrode potential of copper E^0 Cu^{+2} / Cu is positive, where as E_0 Mn^{+2} / Mn is more negative than expected Why ?

42. Potassium permanganate, ($KMnO_4$) is prepared by fusion of pyrolusite, MnO_2 with KOH in the presence of an oxidising 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 ion. Potassium permanganate is an important oxidising agent in acidic, alkaline as well as neutral medium.

(a) What is the state of hybridisation of Mn in MnO_4^-? (1)

(b) Write an application of potassium permanganate. (1)

(c) How do the oxides of transition elements in lower oxidation states differ from those in higher oxidation state in the nature of metal-oxygen bonding and why? (2)

OR

Draw the structure of permanganate ion. Is it paramagnetic or diamagnetic?

ANSWERS

ANSWERS MULTIPLE CHOICE QUESTIONS:

1.	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**	**9.**	**10.**
d	**b**	**b**	**d**	**b**	**d**	**b**	**c**	**a**	**b**
11.	**12.**	**13.**	**14.**	**15.**					
b	**b**	**a**	**c**	**d**					

16. Cr

17. $CuCl_2$, due to greater hydration enthalpy of Cu^{2+}

18. Sc

19. MnO_4^- or CrO_4^{2-}

20. Cr, Cu

21. Cr

22. Ce

23. Zn

24. $CrO < Cr_2O_3 < CrO_3$

25. $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O$

26. Mischmetal which consists of 95% of lanthanoid metals, 5% iron and traces of S,C,Ca and Al. uses. Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint

27. a)Zn(b)Mn (c)Mn (d)Sc

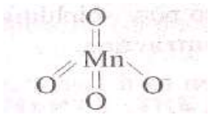
28. Lanthanoid contraction: The regular decrease in the atomic and ionic radii of lanthanoids with increasing atomic number is known as Lanthanoid contraction. Cause for lanthanoid contraction: poor shielding of 4f electrons. Consequences of Lanthanoid contraction:

(i) Difficult to separate the lanthanoids because the change in ionic radii is very small, their chemical properties are similar. Hence, separation of lanthanoids are difficult. (ii) Similarity in size of elements belonging to same group of second and third transition series due to lanthanoid contraction the size of Zr (160 pm) is same as that of Hf (159 pm).

29. (i) A= K_2MnO_4 B= $KMnO_4$

(ii) $2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$

30.	(a) A = Na_2CrO_4 B= $Na_2Cr_2O_7$ C= $K_2Cr_2O_7$ (b) Potassium dichromate is used as a primary standard in volumetric analysis
31.	(a) 4d and 5d transition elements (2nd and 3rd series) are Larger in size than the corresponding 3d elements. Hence the valence electrons are less tightly held and form M-M bond more frequently (b) Due to the absence of unpaired electrons in d-orbitals, Cu^+ salts are colourless while due to presence of unpaired electrons in d-orbitals, Cu^{2+} salts are Coloured (c) Because Mn^{2+} contain 5 unpaired electrons in their 3d sub shells
32.	(a) because of lanthanoid contraction both Zr &Hf have similar radii and similar properties (b) The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density. (c) The catalytic activity of transition metal ions is due to following two reasons: Variable oxidation states & Large surface area.
33.	(a) Total 7 electrons are present in 3d and 4s in Mn and hence it can exhibit maximum oxidation state of +7 (b) Because of ability of oxygen to form multiple bonds using 2p orbitals of oxygen and 3d orbitals of Mn. (c) Mn in Mn_2O_7 is in +7 oxidation state and Mn maximum oxidation state is +7. Hence it is Acidic. If an element in a compound is in lower oxidation state then it will show basic character. Mn is in+2 oxidation state in MnO hence basic.
34.	(a) It disproportionate to give Cu^{2+} and Cu. Or Due to greater hydration enthalpy of Cu^{2+} b) The ions in d^1 configuration tend to lose one more electron to get into stable d^0 configuration. c) due to greater stability of half-filled d-subshell (d^5) in Mn^{+2}
35.	(a) Scandium is a transition element because it has incompletely filled *d* orbitals but Zinc has completely filled *d* orbitals i.e $3d^{10}$ configuration (b) Silver (Z = 47) can exhibit +2 oxidation state wherein it will have incompletely filled *d*-orbitals (4*d*), hence a transition element. (c) because in the formation of metallic bonds, no electrons from 3*d*-orbitals are involved in case of zinc, while in all other metals of the 3*d* series, electrons from the *d*-orbitals are always involved in the formation of metallic bonds
36.	(i) because it can readily change to the most stable +3 oxidation state by gaining one electron (ii) due to greater poor shielding by 5f-electrons in actinoids than that by 4f-electrons in the lanthanoids (iii) because of the very small energy gap between 5f, 6d and 7s subshells. (iv) due to absence of unpaired electron in f orbital (v) The change in the size of the lanthanoids due to lanthanoid contraction is very small
37.	(a) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{+3} + 6Fe^{3+} + 7H_2O$ (b) $2MnO_4^- + 16H^+ + 5C_2O_4^2 \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2$ (c) $KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$ (d) $2\ MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$ (e) $Cr_2O_7^{2-} + 2\ OH^- \rightarrow 2CrO_4^{2-} + H_2O$
38.	(a) MnO_4^{2-} ions disproportionate in acidic medium to give Permanganate ions and Manganese(IV) oxide. $3MnO_4^{2-} + 4\ H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ (b) This is a redox titration. The deep purple colour of $KMnO_4$ disappears due to the formation of $MnSO_4$ (c) When **$Cr_2O_7^{2-}$ ion is treated with an alkali :** $Cr_2O_7^{2-}$ (orange) + 2 $OH^- \rightarrow 2CrO_4^{2-}$(yellow) + H_2O

	When the yellow solution is treated with an acid, we get back the orange solution: 2 CrO_4^{2-} (yellow)+ $2H^+ \rightarrow Cr_2O_7^{2-}$(orange) + H_2O **OR** In acidic medium, permanganate changes to manganous ion which is colourless. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+}$ (colourless) + $4H_2O$ In alkaline medium, permanganate changes to manganate, which is a green solution $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ (green) In a neutral medium, permanganate changes to manganese dioxide which is a brown precipitate, $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2$ (brown) + $4OH^-$
39.	(a) due to variable oxidation state and provides suitable surface area for the reactant molecule to adsorb on it. (b) because small sized atom such C.H, N,O etc. occupy the interstitial site. (c) because up to Cr the number of unpaired electron increases and there after due to pairing in d orbital the number of unpaired electron decreases. So magnetic character decreases. OR $La(OH)_3$ is more basic, $Lu(OH)_3$ is less basic. Size of Lanthanoids ion decreases from La^{3+} to Lu^{3+}, tendency to give hydroxyl ion decreases so basic character decreases.
40.	(a) outer electronic configuration of Sc[Ar]$3d^1$ $4s^2$. Hence, it shows +3 as the only oxidation state, by losing the three electrons it acquires a noble gas configuration. (b) Cr have $3d^5$ $4s^1$configuration. Hence, metallic bond is very strong. In Hg, all d orbitals are fully filled, hence the metallic bond is very weak. (c)In Mn^{2+}, d^5 configuration leads to extra stability of half-filled configuration. So $Mn^{3+}/(d^4)$tends to get converted to stable d^5,onfiguration of Mn^{2+} by accepting an electron so Mn^{3+}/Mn^{2+} redox couple has more positive electrode potential than Fe^{3+}/Fe^{2+} OR Cu^+ = [Ar] $3d^{10}$ have no unpaired electron, so diamagnetic but Cu^{2+} = [Ar] $3d^9$ configuration so have one unpaired electron, hence paramagnetic.
41.	a) As oxygen stabilises highest oxidation state more than Florine by forming multiple bonds. (b) Fe^{3+} (c) It is due to greater number of unpaired electrons in (n-1)d and ns orbitals at the middle of the series. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share. OR Ans due to less hydration enthalpy of Cu^{+2} .The high energy to form From Cu (s) to Cu^{+2} (aq) is not balanced by its hydration enthalpy. due to low sublimation enthalpy of Mn and stable half filled d^5 configuration of Mn^{2+}
42.	(a) Sp^3 (b) It is used as an oxidising agent (c) In the lower oxidation state the transition metal oxides are basic and they are acidic if the metal is in higher oxidation state. The oxides are amphoteric when the metal ion is in intermediate oxidation state.. OR  Tetrahedral, diamagnetic.

MIND MAP : LEARNING MADE SIMPLE

The d– And F– Block Elements

d– Block transition elements groups 3–12

- Position : Between s–and p–blocks
- Electronic configuration : $(n-1)d^{1-10}ns^{1-2}$
- Physical properties : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to imperfect shielding of one e^- by another in same set of orbitals.
- Ionisation enthalpies : Increases from left to right
- Oxidation states : Variable ;higher ON stable
- Trends in M^{2+}/M E° : E° for Mn, Ni and Zn are more negative than expected.
- Trends in M^{3+}/M^{2+} E° : variable
- Chemical reactivity and E° values : Variable; Ti^{2+}, V^{2+} and Cr^{2+} are strong reducing agents.
- Magnetic properties : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- Formation of coloured ions : Form coloured compounds due to d – d transitions
- Formation of complex compounds : Form a large number of complex compounds
- Catalytic properties : Due to variable oxidation states and ability to form complexes.
- Forms interstitial compounds : Non - stoichiometric and are neither ionic nor covalent.
- Alloy formation : Due to similar atomic sizes.

Uses

- Helps in production of iron and steels.
- TiO in pigment industry
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkynes and other organic compounds such as benzene.
- Ag Br in photographic industry.

Oxides and oxoanions of metals

- Potassium dichromate $K_2Cr_2O_7$

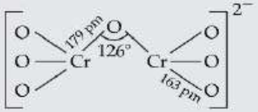
  Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$

  $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$

  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

  Properties : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

  Oxidises iodides to iodine, H_2S to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$

  Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2KMnO_4 + 2H_2O$

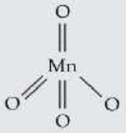
  $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O^+$

  $2Mn^{2+} + 5S_2O_3 \quad + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$

  Properties : Intense colour, weak temperature dependent paramagnetism

  $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

  Oxidizes I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^-



Lanthanoid contraction is progressive decrease in atomic/ionic radii from La^{3+} to Lu^{3+}

f– Block Transition Elements

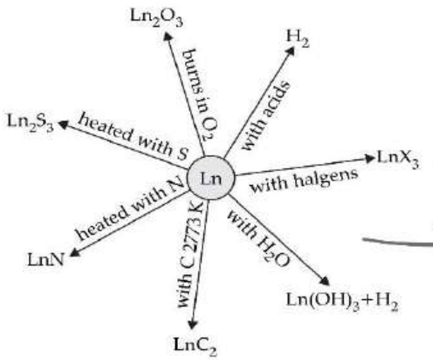
Actinoids

- Electronic : configuration $[Rn]5f^{1-14}6d^{0-2}7s^2$
- Ionic sizes : Gradual decrease along the series
- Oxidation states : Most common is +3. They show ON of +4, +5, +6 and +7.
- **General characteristics :**
  - –Silvery in appearance
  - –Display variety of structures
  - –Highly reactive metals
  - –Irregularities in metallic radii, greater than in Lanthanoids.
  - –Magnetic properties more complex than lanthanoids.

Lanthanoids

- Electronic configuration
  $4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Atomic and ionic sizes
  Decreases from La to Lu
- Oxidation states
  Most common is +3. Some elements exhibit +2 and +4.
- General characteristics
  - •Silvery while soft metals and tarnish rapidly in air.
  - •Hardness increases with increasing atomic number.
  - •Metallic structure and good conductors of heat and electricity.
  - •Variable density
  - •Trivalent Lanthanoid ions are coloured.
- Ionisation Enthalpies : Low third ionisation enthalpies
- Good reducing agents

Chemical Properties



5. COORDINATION COMPOUNDS

Quick Revision Points

Werner's theory

In coordination compounds, metals show two types of linkages (valences)-primary and secondary.

Primary valences	Secondary valences
are ionisable and satisfied by negative ions.	are non-ionisable and satisfied by neutral molecules or negative ions It is equal to the coordination number

Difference between a double salt and a complex salt

Double salts	Complex salts
Dissociate into simple ions completely when dissolved in water.	Do not dissociate into simple ions in water
e.g. Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$	e.g. $K_4[Fe(CN)_6]$.Complex ion $[Fe(CN)_6]^{4-}$ does not dissociate into Fe^{2+} and CN^- ions.

Important Terms

(a)Coordination entity - A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules.

e.g., $[CoCl_3(NH_3)_3]$ is a coordination entity.

(b)Central atom/ion - In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement around it, is called the central atom or ion.

(c) Ligands -Ions or molecules bound to the central atom/ion in the coordination entity are called ligands.

Unidentate ligand	Is bound to a metal ion through a single donor atom. e.g.,Cl^-,H_2O or NH_3
Didentate ligand	Is bound to a metal ion through two donor atoms. e.g.,$H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine) $C_2O_4^{2-}$ (oxalate ion)
Polydentate ligand	It is linked to a metal ion through several donor atoms. e.g., Ethylenediaminetetraacetate ion (EDTA) is a hexadentate ligand.
Chelate ligand	When a di or polydentate ligand uses its two or more donor atoms to bind to a single metal ion, it is said to be a chelate ligand.
Ambidentate ligand.	Can bind to the central metal atom through any of the two donor atoms present in it. e.g., NO_2^-, SCN^-,CN^-

(d) Coordination number – It is the number of ligand donor atoms to which the metal is directly bonded.

$[Ni(NH_3)_4]^{2+}$ - the coordination number of Ni is 4

$[Fe(C_2O_4)_3]^{3-}$ - the coordination number of Fe is 6

(e) Homoleptic and heteroleptic complexes

Homoleptic complexes	**Heteroleptic complexes**
Metal is bound to only one kind of donor groups e.g.,$[Co(NH_3)_6]^{3+}$	Metal is bound to more than one kind of donor groups. e.g.,$[Co(NH_3)_4Cl_2]^{+}$

IUPAC names of some coordination compounds

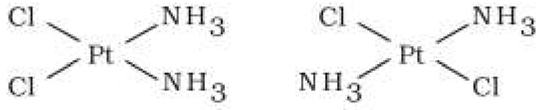
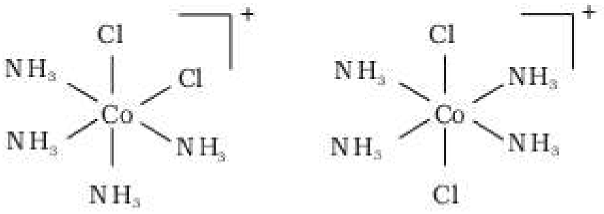
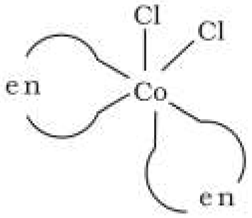
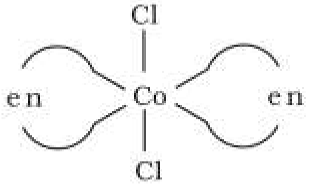
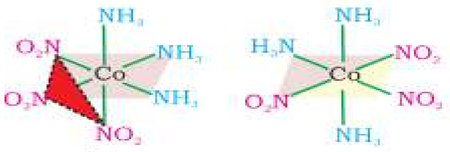
1	$K_2[Zn(OH)_4]$	Potassium tetrahydroxozincate(II)
2	$K_3[Al(C_2O_4)_3]$	Potassium trioxalatoaluminate(III)
3	$[Pt(NH_3)BrCl(NO_2)]^-$	Amminebromidochloridonitrito-N-platinate(II) ion
4	$[CoCl_2(en)_2]Cl$	Dichloridobis(ethane-1,2-diamine)cobalt(III) chloride
5	$[Ni(CO)_4]$	Tetracarbonylnickel(0)

Isomerism in Coordination Compounds

Stereoisomerism

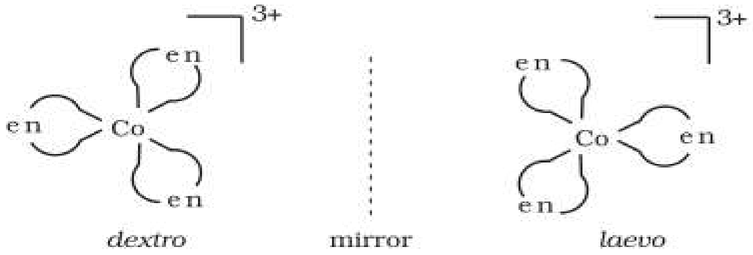
Stereoisomers have the same chemical formula and chemical bonds but they have different spatial arrangements.

(i) Geometrical isomerism (ii) Optical isomerism

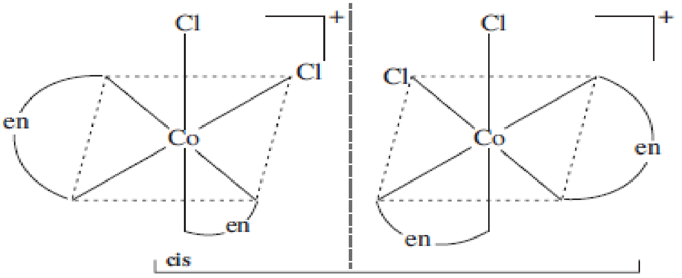
Geometrical Isomerism -This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands		
COORDINATION NO-4 (Square planar complexes)	$[Ma_2b_2]$ $[Pt(NH_3)_2Cl_2]$	 *cis* *trans*
Tetrahedral complexes do not show geometrical isomerism. Reason: The relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other		
COORDINATION NO 6 (Octahedral complexes)	$[Ma_2b_4]$ $[Co(NH_3)_4Cl_2]^+$	 *cis* *trans*
	$[Ma\text{-}a_2b_2]$ $[CoCl_2(en)_2]^+$	 
	$[Ma_3b_3]$ $[Co(NH_3)_3(NO_2)_3]$	 *fac–* *mer–*

Optical Isomerism: Optical isomers are mirror images that cannot be superimposed on one another and are called as enantiomers.

Optical isomers of $[Co(en)_3]^{+3}$



Optical isomers of [$CoCl_2(en)_2]^+$



Trans isomer of $[CoCl_2(en)_2]^+$ does not show optical activity as it has a plane of symmetry.

Structural isomerism

Structural Isomerism: These are isomers which differ in the structural arrangement of ligands around the central atom.

Ionisation Isomerism	Arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
Linkage Isomerism	Seen in a coordination compound containing ambidentate ligand $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$
Coordination Isomerism	Arises from the interchange of ligands between cationic and anionic entities $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
Solvate Isomerism	Arises due to the presence of solvent molecules as a ligand or as free solvent molecules in the crystal lattice. $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Bonding in Coordination Compounds

Valence Bond Theory

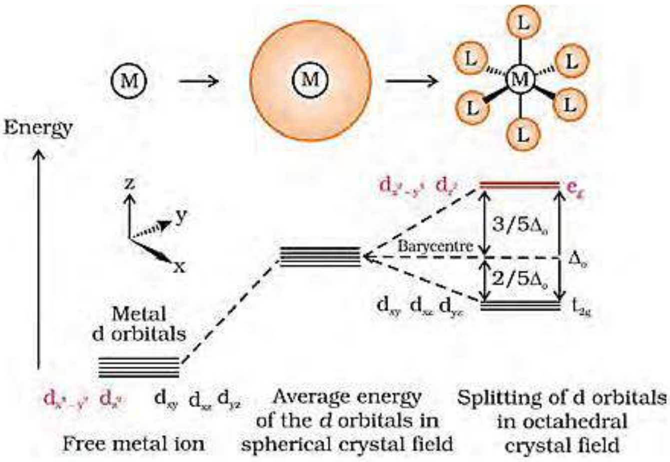
According to this theory, the metal atom or ion under the influence of ligands can use its (n-1)d, ns, np or ns, np, nd orbitals for hybridisation to yield a set of equivalent orbitals of definite geometry.

Complex/ion	Configuration of the metal ion/atom	Hybridisation of the metal ion/atom	Geometry	No of unpaired electrons	Magnetic behaviour
$[NiCl_4]^{2-}$	Ni^{2+} - $3d^84s^0$	sp^3	Tetrahedral	2	Paramagnetic
$[Ni(CO)_4]$	Ni -$3d^84s^2$	sp^3	Tetrahedral	0	Diamagnetic
$[Ni(CN)_4]^{2-}$	Ni^{2+} - $3d^84s^0$	dsp^2	Square planar	0	Diamagnetic

$[Co(NH_3)_6]^{+3}$	Co^{+3} - $3d^64s^0$	d^2sp^3	Octahedral (Inner orbital complex - 3d used)	0	Diamagnetic
$[CoF_6]^{3-}$	Co^{+3} - $3d^64s^0$	sp^3d^2	Octahedral (Outer orbital complex - 4d used)	4	Paramagnetic

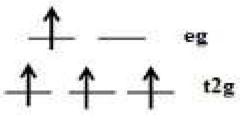
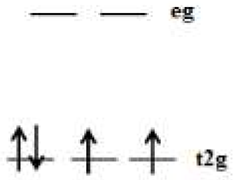
Crystal Field Theory

(a)Crystal field splitting in octahedral coordination entities

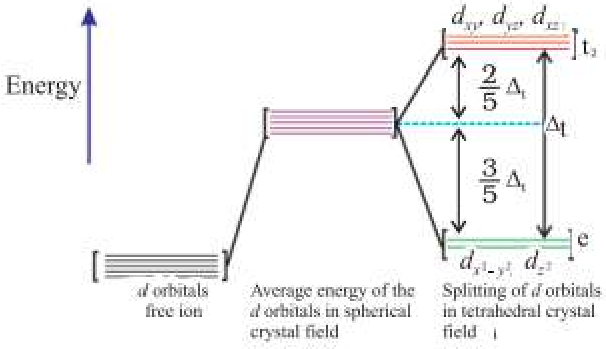


The splitting of degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting**

Ligands arranged in a series in the order of increasing field strength is termed as **Spectrochemical series**

Weak field ligands	Strong field ligands
$\Delta o < P$	$\Delta o > P$
Form high spin complexes	Form low spin complexes
d^4 Configuration	
 $t_2g^3eg^1$	 $t_2g^4eg^0$

(b) Crystal field splitting in tetrahedral coordination entities



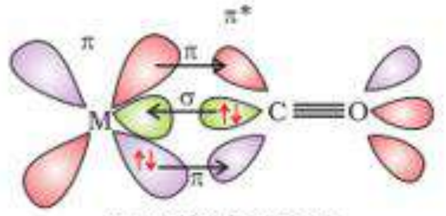
Colour of coordination compounds

The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

In the absence of a ligand, crystal field splitting does not occur and hence the substance is colourless. For example, the removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless.

Bonding in Metal Carbonyls

In metal carbonyls, the M–C σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C π bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant antibonding π* orbital of carbon monoxide. The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

Multiple Choice Questions

1	**Write the no. of ions produced from the complex $K_4[Fe(CN)_6]$ in solution** (A) 2 (B) 5 (C) 4 (D) 1
2	**The denticity of $EDTA^{4-}$ ligand is** (A) 6 (B) 3 (C) 4 (D) 2
3	**Of the following complexes, which one will show linkage isomerism?** (A) $[Cr(NH_3)_6][Co(en)_3]$ (B) $[Cr(NH_3)_6]Cl_3$ (C) $[Cr(en)_3]Cl_3$ (D) $[Cr(NH_3)_5NO_2]Cl_2$
4	**The crystal field splitting energy for octahedral and tetrahedral complexes is related as** (A) $\Delta_t = 2/9\ \Delta_o$ (B) $\Delta_o = 2/9\ \Delta_t$ (C) $\Delta_t = 4/9\ \Delta_o$ (D) $\Delta_o = 4/9\ \Delta_t$
5	**The type of isomerism shown by the complex $[CoCl_2(en)_2]$ is** (A) Geometrical isomerism (B) Ionization isomerism (C) Coordination isomerism (D) Linkage isomerism
6	**The coordination number and oxidation state of Cr in $K_3[Cr(C_2O_4)_3]$ are respectively** (A) 3 and +3 (B) 3 and 0 (C) 6 and +3 (D) 4 and +2
7	**The geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ are** (A) Square planar and paramagnetic (B) Tetrahedral and diamagnetc (C) Square planar and diamagnetic (D) Tetrahedral and paramagnetic

8	**Which of the following complex has minimum magnitude of crystal field splitting?** (A) $[Co(NH_3)_6]^{3+}$ (B) $[Cr(H_2O)_6]^{3+}$ (C) $[Cr(CN)_6]^{3-}$ (D) $[CoCl_6]^{3-}$
9	**The core atom of which of the following biologically significant coordination molecules is cobalt?** (A) Vitamin B12 (B) Haemoglobin (C) Chlorophyll (D) Carboxypeptidase-A
10	**How many isomers are possible for the complex $[Co(NH_3)_4Cl_2]Cl$?** (A) 4 (B) 2 (C) 1 (D) 3

Assertion and Reason Based Questions

Given below are two statements labelled as Assertion (A) and Reason (R)
Select the most appropriate answer from the options given below:
(A) Both A and R are true and R is the correct explanation of A
(B) Both A and R are true but R is not the correct explanation of A.
(C) A is true but R is false.
(D) A is false but R is true

11	**Assertion**: $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio gives the test of Cu^{2+} ion. **Reason**: Cu^{2+} ion forms a complex with ammonia.
12	**Assertion**: Linkage isomerism arises in coordination compounds containing ambidentate ligand. **Reason**: Ambidentate ligand has two donor atoms.
13	**Assertion**: The spin-only magnetic moment of $[MnBr_4]^{2-}$ is 5.9 BM **Reason**: The shape of the complex is square planar.
14	**Assertion**: Low spin tetrahedral complexes are not formed. **Reason:** Orbital splitting energies for tetrahedral complexes are sufficiently large for forcing pairing.
15	**Assertion**: The complex $[Ti(H_2O)_6]^{3+}$ is colourless. **Reason:** Crystal field splitting occurs in presence of ligands.

Very Short Answer Questions (1 Mark)

16	Write the IUPAC name of $[Cr(H_2O)_2(C_2O_4)_2]^-$.
17	Which of the following is more stable complex and why? $[Co(NH_3)_6]^{3+}$ and $[Co(en)_3]^{3+}$
18	Write down the formula of : Tetraammineaquachloridocobalt(III) chloride.
19	When a coordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write the structural formula of the complex.
20	Define denticity of a ligand.
21	Indicate the types of isomerism exhibited by the following complex: $[Co(en)_3]Cl_3$ (en = ethylene diamine)
22	What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$?
23	Out of the following two coordination entities which is chiral (optically active)? (a) cis-$[CrCl_2(ox)_2]^{3-}$ (b) trans-$[CrCl_2(ox)_2]^{3-}$
24	Find the primary and secondary valences of cobalt in $[Co(NH_3)_6]Cl_3$.

25	Give two examples of ligands which form coordination compounds useful in analytical chemistry.

Short Answer Questions TYPE-1 (2 Marks)

26	Draw the structures of optical isomers of each of the following complex ions: $[Cr(C_2O_4)_3]^{3-}$, $[PtCl_2(en)_2]^{2+}$
27	Give a chemical test to distinguish the following pair. $[Co(NH_3)_5Cl]SO_4$ and $[Co(NH_3)_5(SO_4)]Cl$.
28	$[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.(At. no. Fe = 26)
29	What is meant by the chelate effect? Give an example.
30	$CuSO_4.5H_2O$ is blue in colour while $CuSO_4$ is colourless. Why?

Short Answer Questions TYPE-2 (3Marks)

31	(i)Draw the geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$. (ii) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?
32	Discuss briefly giving an example in each case the role of coordination compounds in : (i) biological systems, (ii) medicinal chemistry (iii) extraction/metallurgy of metals.
33	For the complex $[Fe(en)_2Cl_2]Cl$,(en = ethylene diamine), identify (i) the oxidation number of iron, (ii) the hybrid orbitals and the shape of the complex, (iii) the magnetic behaviour of the complex, (iv) the number of geometrical isomers, (v) whether there is an optical isomer also, and (vi) name of the complex. (At. no. of Fe = 26)
34	Write the state of hybridization, the shape and the magnetic behaviour of the following complex entities : (i) $[Cr(NH_3)_4Cl_2]Cl$ (ii) $[Co(en)_3]Cl_3$ (iii) $K_2[Ni(CN)_4]$
35	Explain why $[Fe(H_2O)_6]^{3+}$ has magnetic moment value of 5.92 BM whereas $[Fe(CN)_6]^{3-}$ has a value of only 1.74 BM.

Long Answer Questions (5 Marks)

36	(i) Define the following. (a) Heteroleptic complexes (b) Spectrochemical series (c) Coordination polyhedron (ii)Give reason. (a)The pi complexes are known for transition elements only. (*b*) CO is a stronger ligand than NH_3 for many metals.

37

(i)Using crystal field theory, write electronic configuration of the central metal atom/ion and determine the magnetic moment value in the following.

(a)$[CoF_6]^{3-}$

(b)$[Fe(CN)_6]^{4-}$

(c)$[Fe(H_2O)_6]^{2+}$

(ii) A solution of $[Ni(H_20)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$is colourless. Explain.

Case-Based Questions

Read the passage carefully and answer the questions that follow.

38 Alfred Werner, a Swiss chemist was the first to formulate his idea about the structure of coordination compounds. He proposed the concept of primary and secondary valences for a metal ion. The primary valences are normally ionisable and satisfied by negative ions. The secondary valences are non-ionisable and it is equal to coordination number and is fixed for a metal. The groups bound by the secondary linkages to metal have spatial arrangements corresponding to different coordination numbers. Octahedral, tetrahedral and square planar geometrical shapes are more common in coordination compounds of transition metals.

Double salts and coordination complexes are formed by the combination of two or more stable compounds in stoichiometric ratio. Double salts are dissociated into simple ions completely when dissolved in water whereas complexes do not dissociate completely into its ions. Werner was the first to discover optical activity in certain coordination compounds.

(i)What is the oxidation number of cobalt in coordination entity $[Co(H_2O)(CN)(en)_2]^{2+}$?

(ii) What is the coordination number of chromium in $K[Cr(H_2O)_2(C_2O_4)_2]$?

(iii) Arrange the following complexes in increasing order of conductivity of their solution. Give reason.

$[Co(NH_3)_3Cl_3]$, $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$

OR

(iii)a) How many ions are produced from the complex $[Co(NH_3)_6]Cl_3$ in solution?

b) When 1 mol $CrCl_3.6H_2O$ is treated with excess of $AgNO_3$, 3mol of AgCl are obtained. Write the formula of the complex.

39 Valence bond theory considers the bonding between metal ion and ligands as purely covalent. On the other hand, crystal field theory considers the metal-ligand bond to be ionic arising from electrostatic interaction between the metal ion and the ligands. In coordination compounds, the interaction between the ligand and the metal ion causes the five d-orbitals to split-up. This is called crystal field splitting and the energy difference between the two sets of energy levels is called crystal field splitting energy. The crystal field splitting (Δ_o) depends upon the nature of the ligand and the charge of the metal ion.The electronic configuration of the metal ion in the complexes depends on the relative values of Δ_o and P (pairing energy)

If $\Delta o < P$, then complex will be high spin.

If $\Delta o > P$, then complex will be low spin.

(i)Calculate the magnetic moment of the metal ion in the complex $K_4[(Fe(CN)_6]$.

(ii)On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when $\Delta_O > P$.

(iii)Explain the violet colour of $[Ti\ (H_2O)_6]^{3+}$ complex on the basis of the crystal field theory. (Atomic number of Ti = 22)

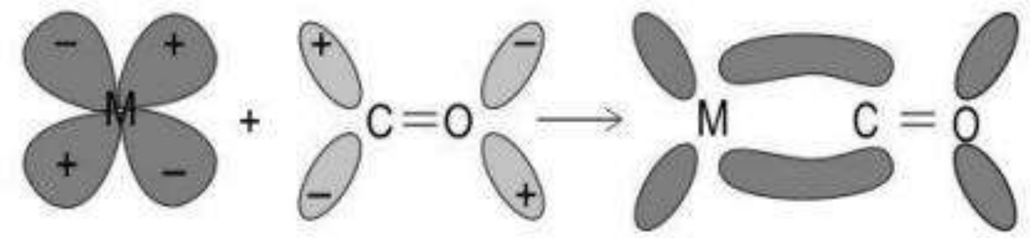
OR

(iii)State the magnetic property of each of the following complexes.

a) Hexaaminechromium (III) ion (At no of Chromium = 24)

b) Tetraamminezinc(II) ion (At number of Zinc =30)

40 In metal carbonyls, there is synergic bonding interaction between metal and carbon monoxide. This leads to increase in strength of metal ligand bond and decrease in bond order of CO in carbonyl complex. Donation of electrons from a filled d-orbital of metal into the vacant antibonding π* bonding orbital of CO decreases the bond order three to two and half or slightly more thus increasing the bond length between C– O.



(i)What type of bond is exists in metal carbonyls?

(ii)How is Δ_0 value affected by the interaction of CO ligands and metal ion in metal carbonyl?

(iii)Describe the bonding between metal and CO ligand in creating a synergic effect.

OR

(iii)Give an example of a homoleptic metal carbonyl complex and also mention the oxidation state of the metal in it.

41 The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry; metallurgy, biological system, industry and medicine. Formation of coordination compound is largely used in analytical chemistry for the qualitative detection and quantitative estimation of metal ions.
(i)Which ligand's complex is used for determination of hardness of water?
(ii)Which complex is used in the treatment of cancer?
(iii)a) Haemoglobin present in Blood is a complex of which metal?
b) Name the complex of magnesium metal which is present in green plants.

OR

(iii)Describe how gold is extracted using complex formation.

42 Compounds that have the same chemical formula but different structural arrangements are called isomers.
Ionization Isomerism-This type of isomerism is due to the exchange of groups between the complex ion and the ions outside it.
Coordination isomerism - This isomerism occurs in compounds containing complex anionic and cationic parts and can be thought of as occurring by interchange of some ligands from the cationic part to the anionic part.
Linkage isomerism -This isomerism occurs with ambidentate ligands that are capable of coordinating in more than one way.
Hydrate isomerism - This isomerism results from the replacement of a coordinated group by a solvent molecule (Solvate Isomerism).
(i)What type of isomerism is exhibited by
$[Co(ONO)(NH_3)_5]Cl$ and $[Co(NO_2)(NH_3)_5]Cl$?
(ii)What type of isomerism is exhibited by $[CrCl_2(H_2O)_4]Cl.2H_2O$, $[CrCl(H_2O)_5]Cl_2.H_2O$,$[Cr(H_2O)_6]Cl_3$?
(iii)What is coordination isomerism? Give one example.

OR

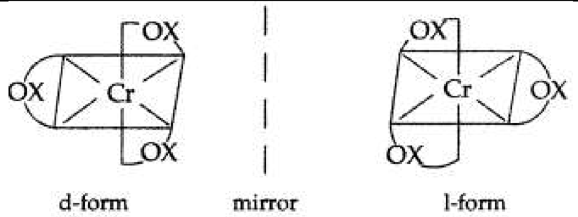
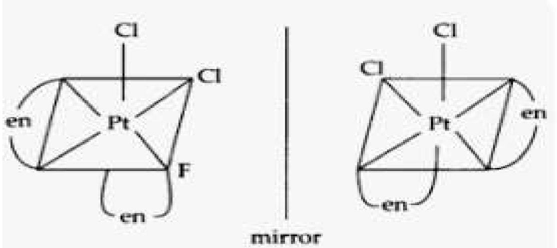
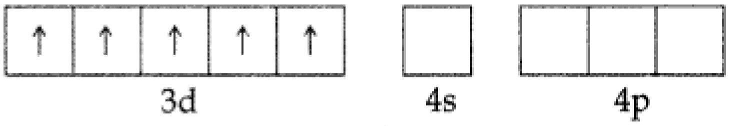
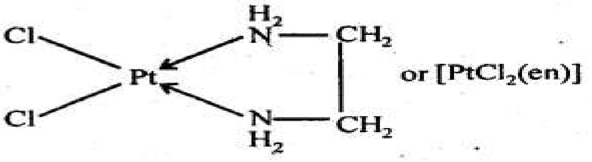
What is an ambidentate ligand? Explain with an example.

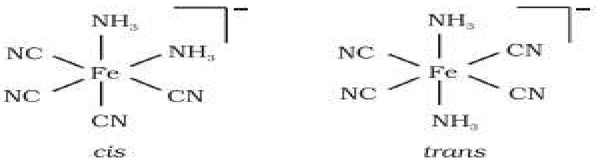
Answers

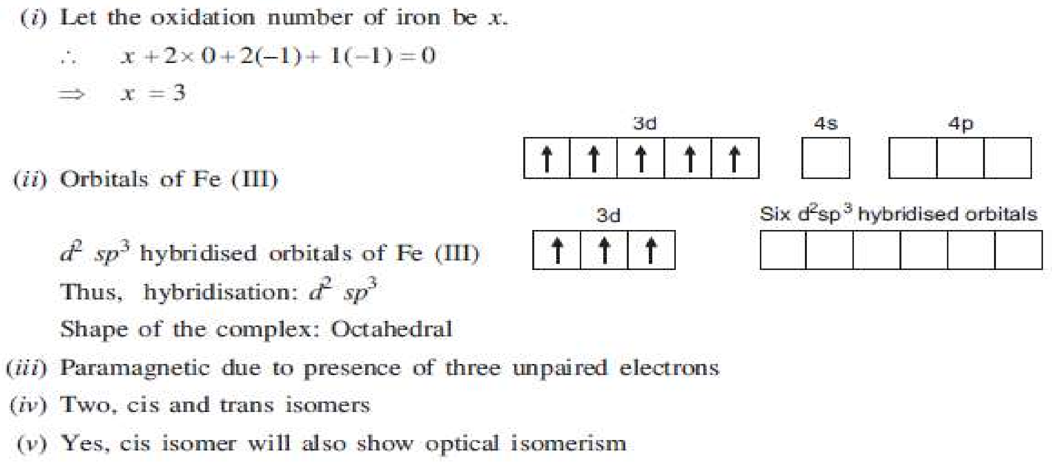
1	2	3	4	5	6	7	8	9	10
B	A	D	C	A	C	B	D	A	B
11	12	13	14	15					
D	A	C	A	D					

16	Diaquadioxalatochromate(III) ion
17	$[Co(en)_3]^{3+}$ is more stable complex than $[Co(NH_3)_6]^{3+}$ because of chelate effect.
18	$[Co(NH_3)_4(H_2O)Cl]Cl_2$
19	$[Cr(H_2O)_5Cl]Cl_2.H_2O$
20	The number of donor atoms in a ligand which forms a coordinate bond with the central metal atom is called denticity of a ligand.
21	Optical isomerism
22	Solvate or Hydrate isomerism
23	cis-$[CrCl_2(ox)_2]^{-3}$
24	Primary valency -3 Secondary valency - 6
25	EDTA and Dimethyl glyoxime (DMG)

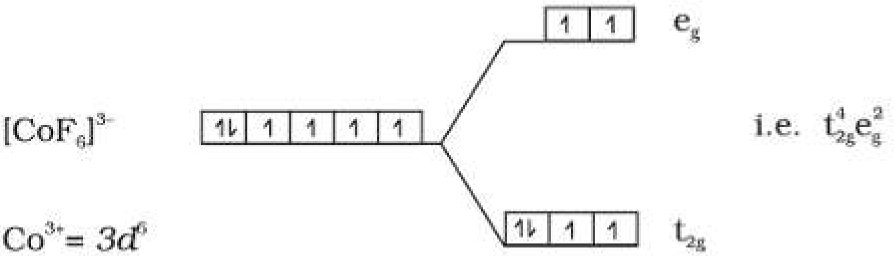
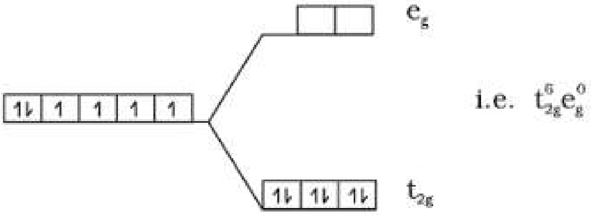
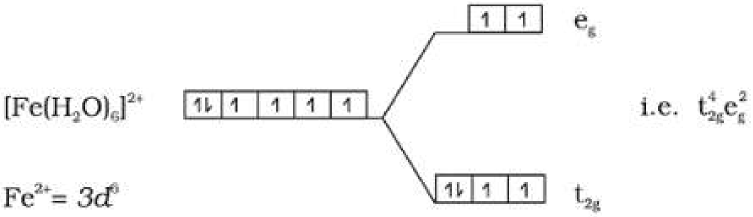
26	Optical isomers of $[Cr(C_2O_4)_3]^{3-}$:

	 Optical isomers of $[PtCl_2(en)_2]^{2+}$ 
27	$[Co(NH_3)_5Cl]SO_4$ with $BaCl_2$ gives white ppt of $BaSO_4$ $[Co(NH_3)_5(SO_4)]Cl$ with $AgNO_3$ gives white ppt of AgCl
28	In both the cases, Fe is in oxidation state +3. Outer electronic configuration of Fe+3 is :  In the presence of CN^-, the 3d electrons pair up leaving only one unpaired electron. The hybridisation involved is d^2sp^3 forming inner orbital complex which is weakly paramagnetic. In the presence of H_2O (a weak ligand), 3d electrons do not pair up. The hybridisation involved is sp^3d^2 forming an outer orbital complex. As it contains five unpaired electrons so it is strongly paramagnetic..
29	Chelate effect is the stabilization of coordination compounds due to formation of metal chelates in which a didentate or a polydentate ligand coordinate with the central metal ion forming a five or a six-membered ring. Example 
30	In $CuSO_4.5H_2O$, water acts as ligand as a result, it causes crystal field splitting. Hence d—d transition is possible in $CuSO_4.5H_2O$ and shows colour. In the anhydrous $CuSO_4$ due to the absence of water (ligand), crystal field splitting is not possible and hence no colour.

31	(i)Geometrical isomers of $[Fe(NH_3)_2(CN)_4]^-$  (ii) Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.
32	

	(i) The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment 1 of blood which acts as oxygen carrier is a coordination compound of iron. (ii) EDTA is used in the treatment of lead poisoning. Cis -platin effectively inhibits the growth of tumours (iii) Used in extraction of metals like silver and gold. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc
33	 (*i*) Let the oxidation number of iron be x. $\therefore \quad x + 2\times 0 + 2(-1) + 1(-1) = 0$ $\Rightarrow \quad x = 3$ (*ii*) Orbitals of Fe (III) d^2sp^3 hybridised orbitals of Fe (III) Thus, hybridisation: d^2sp^3 Shape of the complex: Octahedral (*iii*) Paramagnetic due to presence of three unpaired electrons (*iv*) Two, cis and trans isomers (*v*) Yes, cis isomer will also show optical isomerism (vi) Dichloridobis (ethane-1, 2- diamine) Iron (III) chloride.
34	(i) $[Cr(NH_3)_4Cl_2]Cl$:, Hybridization : d^2sp^3,Shape : Octahedral,Magnetic behaviour: Paramagnetic (ii) $[Co(en)_3]$ Cl_3 :Hybridization : d^2sp^3,Shape : Octahedral, Magnetic behaviour : Diamagnetic (iii) $K_3[Ni(CN)_4]$: Hybridization ; dsp^2,Shape : Square planar,Magnetic behaviour: Diamagnetic
35	$[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridisation with one unpaired electron and $[Fe(H_2O)_6]^{3+}$involves sp^3d^2 hybridisation with five unpaired electrons. This difference is due to the presence of strong ligand CN^- and weak ligand H_2O in these complexes.

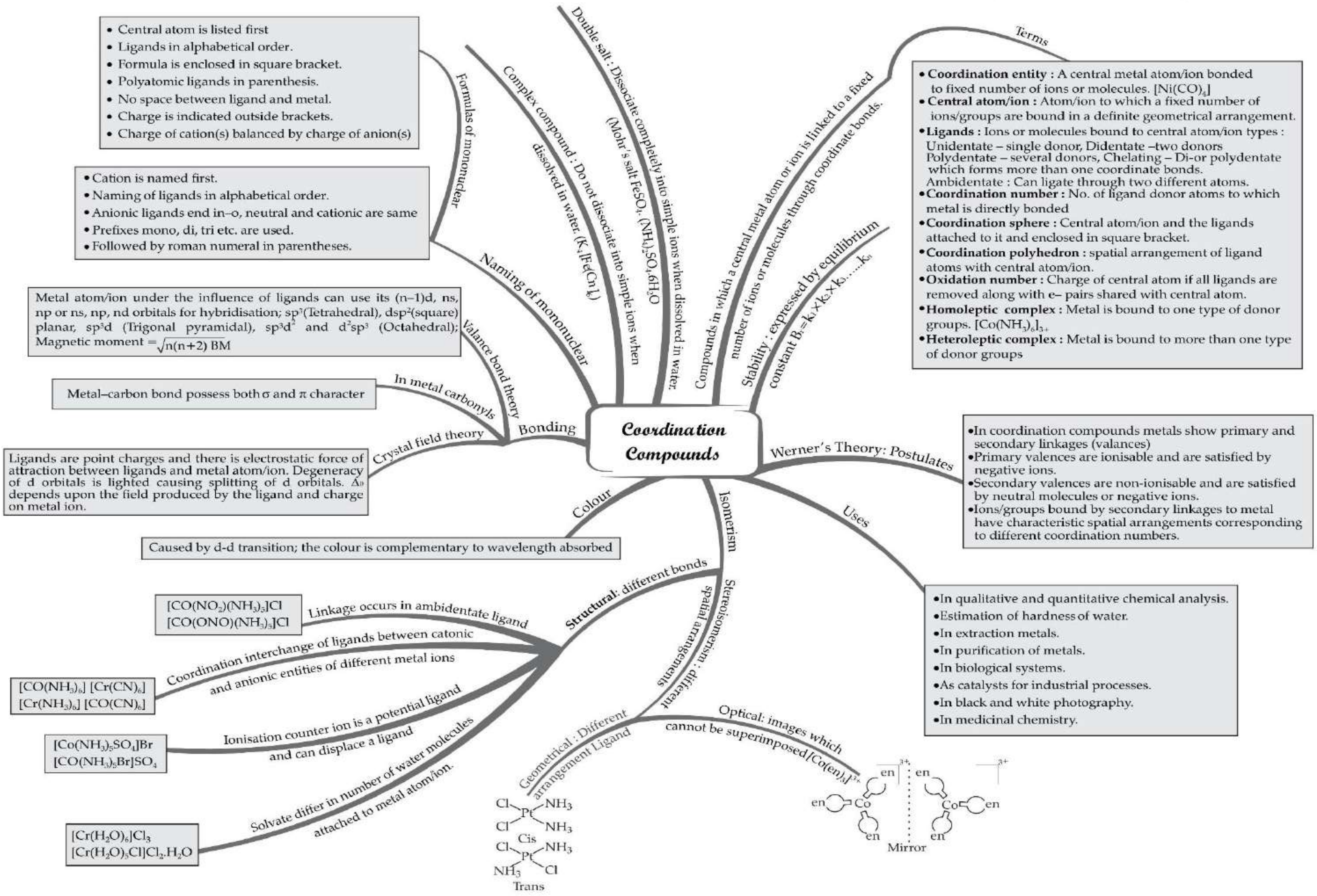
36	(i)(a) **Complexes in which a m**etal is bound to more than one kind of donor groups. (b)Ligands arranged in a series in the order of increasing field strength is termed as Spectrochemical series c) The spatial arrangement of ligand atoms attached to metal ion is termed as coordination polyhedron.
	(ii) (a)Transition metals have vacant d orbitals in their atoms or ions into which the electron pairs can be donated by ligands containing π electrons, e.g., C_6H_6, $CH_2 = CH_2$, etc. Thus dπ-pπ bonding is possible. (b) Because in case of CO back bonding takes place in which the central metal uses its filled d orbital with empty anti bonding π * molecular orbital of CO

37(i)	 (a) $\sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM $[Fe(CN)_6]^{4-}$ $Fe^{2+} = 3d^6$ Since CN^- is strong field ligand all the electrons get paired.  (b) No unpaired electron.Magnetic moment =0  (c) $\sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9$ BM (ii) In $[Ni(H_2O)_6]^{2+}$, Ni is in + 2 oxidation state and having $3d^8$ electronic configuration, in which there are two unpaired electrons which do not pair in the presence of the weak H_2O ligand. Hence, it is coloured. The d-d transition absorbs red light and the complementary light emitted is green. In $[Ni(CN)_4]^{2-}$ Ni is also in + 2 oxidation state and having $3d^8$ electronic configuration. But in presence of strong ligand CN^- the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

38	(i) $x + 0 + (-1) + (0) \times 2 = +2 \rightarrow x = +3$. Therefore O.N. of Co is +3 (ii)Coordination number = 6 (iii)Increasing order $[Co(NH_3)_3Cl_3] < [Co(NH_3)_4Cl_2]Cl < [Co(NH_3)_5Cl]Cl_2 <$, $[Co(NH_3)_6]Cl_3$ As no. of ions in solution increases their conductivity also increases. **OR** (iii) a)4 b)$[Cr(H_2O)_6]Cl_3$
39	(i)Magnetic moment= $\sqrt{\boxed{n\times(n+2)}}$ **n=4, so μ=$\sqrt{4\boxed{\times(4+2)}}$** **μ=$\sqrt{\boxed{24\ BM}}$** (ii)$t_{2g}^4\ e_g^0$

	(iii)$[Ti(H_2O)_6]^{3+}$is an octahedral complex. The oxidation state of Ti is +3 with the coordination number 6. Its outer electronic configuration is $3d^1$, which means that it has one unpaired electron. This unpaired electron is excited from t_{2g} level to eg level by absorbing yellow light and hence appears violet coloured/(d-d Transition) **OR** (iii) a) Paramagnetic. b) Diamagnetic
40	(i)Synergic bonding (ii)Δ_0 value increases in metal carbonyls. (iii) In metal carbonyl the CO to Metal bond C → M is a sigma (σ) bond. There is also an overlapping of electrons from filled metal d orbitals into empty antibonding orbital of CO. This results in the formation of a π bond and is and called back bonding. The M → C bond strengthens the bond between CO and the metal and this type of bonding creates a synergic effect. **OR** (iii)$[Ni(CO)_4]$ Oxidation Number of Ni = zero
41	(i)EDTA (ii)cisplatin (iii)a)Fe b) Chlorophyll **OR** (iii)Gold combines with cyanide in the presence of oxygen and water to form complex $[Au(CN)_2]^-$in aqueous solution. Gold is separated by the addition of zinc.
42	(i)Linkage isomerism (ii)Solvate/ Hydrate Isomerism **(iii)**Arises from the interchange of ligands between cationic and anionic entities $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ OR Ambidentate ligand – It is a ligand that can bind to the central metal atom through any of the two donor atoms present in it. Ex: NO_2^-, SCN^-

MIND MAP : LEARNING MADE SIMPLE



Coordination Compounds

Formulas of mononuclear

- Central atom is listed first
- Ligands in alphabetical order.
- Formula is enclosed in square bracket.
- Polyatomic ligands in parenthesis.
- No space between ligand and metal.
- Charge is indicated outside brackets.
- Charge of cation(s) balanced by charge of anion(s)

Naming of mononuclear

- Cation is named first.
- Naming of ligands in alphabetical order.
- Anionic ligands end in–o, neutral and cationic are same
- Prefixes mono, di, tri etc. are used.
- Followed by roman numeral in parentheses.

Complex compound : Do not dissociate into simple ions when dissolved in water. ($K_4[Fe(Cn)_6]$)

Double salt : Dissociate completely into simple ions when dissolved in water. (Mohr's salt $FeSO_4.(NH_4)_2SO_4.6H_2O$

Compounds in which a central metal atom or ion is linked to a fixed number of ions or molecules through coordinate bonds.

Stability : expressed by equilibrium constant $B_1=k_1 \times k_2 \times k_3 \ldots\ldots k_n$

Terms

- **Coordination entity :** A central metal atom/ion bonded to fixed number of ions or molecules. $[Ni(CO)_4]$
- **Central atom/ion :** Atom/ion to which a fixed number of ions/groups are bound in a definite geometrical arrangement.
- **Ligands :** Ions or molecules bound to central atom/ion types : Unidentate – single donor, Didentate –two donors Polydentate – several donors, Chelating – Di-or polydentate which forms more than one coordinate bonds. Ambidentate : Can ligate through two different atoms.
- **Coordination number :** No. of ligand donor atoms to which metal is directly bonded
- **Coordination sphere :** Central atom/ion and the ligands attached to it and enclosed in square bracket.
- **Coordination polyhedron :** spatial arrangement of ligand atoms with central atom/ion.
- **Oxidation number :** Charge of central atom if all ligands are removed along with e– pairs shared with central atom.
- **Homoleptic complex :** Metal is bound to one type of donor groups. $[Co(NH_3)_6]_{3+}$
- **Heteroleptic complex :** Metal is bound to more than one type of donor groups

Werner's Theory: Postulates

- In coordination compounds metals show primary and secondary linkages (valances)
- Primary valences are ionisable and are satisfied by negative ions.
- Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions.
- Ions/groups bound by secondary linkages to metal have characteristic spatial arrangements corresponding to different coordination numbers.

Uses

- In qualitative and quantitative chemical analysis.
- Estimation of hardness of water.
- In extraction metals.
- In purification of metals.
- In biological systems.
- As catalysts for industrial processes.
- In black and white photography.
- In medicinal chemistry.

Bonding

Valance bond theory: Metal atom/ion under the influence of ligands can use its (n–1)d, ns, np or ns, np, nd orbitals for hybridisation; sp^3(Tetrahedral), dsp^2(square) planar, sp^3d (Trigonal pyramidal), sp^3d^2 and d^2sp^3 (Octahedral); Magnetic moment $=\sqrt{n(n+2)}$ BM

In metal carbonyls: Metal–carbon bond possess both σ and π character

Crystal field theory: Ligands are point charges and there is electrostatic force of attraction between ligands and metal atom/ion. Degeneracy of d orbitals is lighted causing splitting of d orbitals. Δ_0 depends upon the field produced by the ligand and charge on metal ion.

Colour: Caused by d-d transition; the colour is complementary to wavelength absorbed

Isomerism

Structural: different bonds

- Linkage occurs in ambidentate ligand: $[CO(NO_2)(NH_3)_5]Cl$ $[CO(ONO)(NH_3)_5]Cl$
- Coordination interchange of ligands between catonic and anionic entities of different metal ions: $[CO(NH_3)_6][Cr(CN)_6]$ $[Cr(NH_3)_6][CO(CN)_6]$
- Ionisation counter ion is a potential ligand and can displace a ligand: $[Co(NH_3)_5SO_4]Br$ $[CO(NH_3)_5Br]SO_4$
- Solvate differ in number of water molecules attached to metal atom/ion.: $[Cr(H_2O)_6]Cl_3$ $[Cr(H_2O)_5Cl]Cl_2.H_2O$

Stereoisomerism : different spatial arrangements

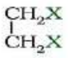
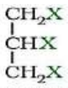
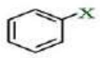
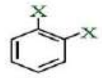
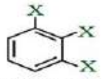
- Geometrical : Different arrangement Ligand
- Optical: images which cannot be superimposed $[Co(en)_3]^{3+}$

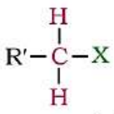
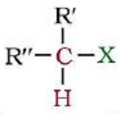
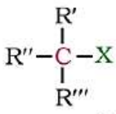
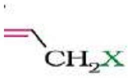
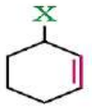
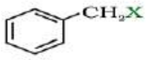
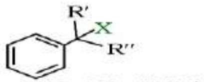
6. HALOALKANES AND HALOARENES

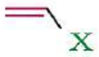
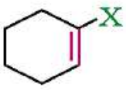
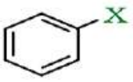
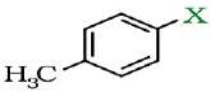
QUICK REVISION POINTS

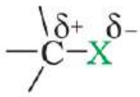
The replacement of hydrogen atom(s) in a hydrocarbon, aliphatic or aromatic, by a halogen atom(s) result in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Classification: Haloalkanes and haloarenes may be classified as follows-

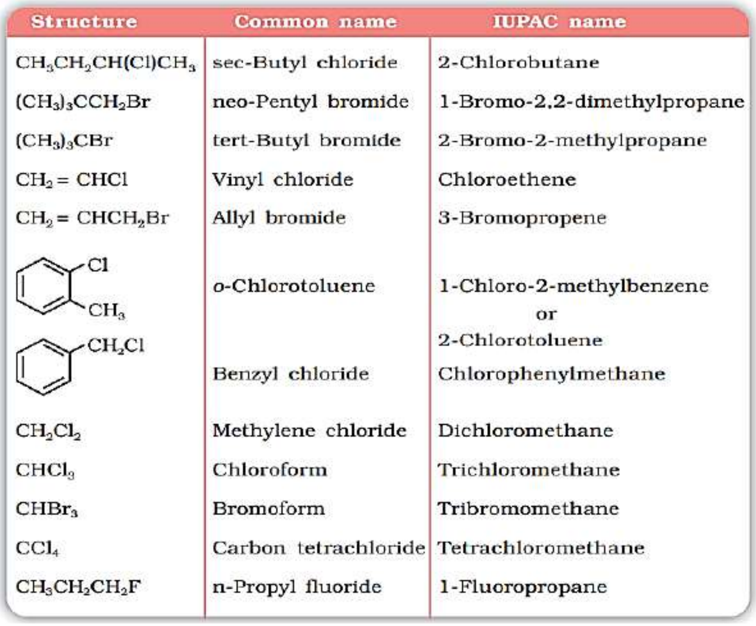
On the Basis of Number of Halogen Atoms	These may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two, or more halogen atoms in their structures.	C_2H_5X Monohaloalkane  Dihaloalkane  Trihaloalkane  Monohaloarene  Dihaloarene  Trihaloarene

Compounds Containing sp³ C—X Bond	(a) Alkyl halides or haloalkanes (R—X)	 Primary (1°)  Secondary (2°)  Tertiary (3°)
	(b) Allylic halides	 
	(c) Benzylic halides	 (1°)  R′ = CH₃, R″ = H (2°) R′ = R″ = CH₃ (3°)

Compounds Containing sp² C—X Bond	(a) Vinylic halides	 
	(b) Aryl halides	 

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.	

Nomenclature:



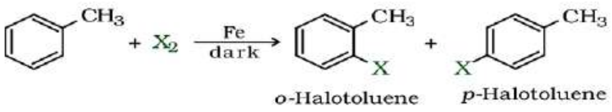
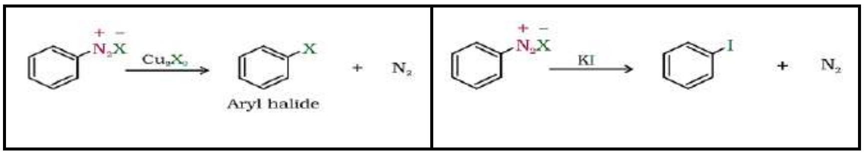
Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	sec-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	tert-Butyl bromide	2-Bromo-2-methylpropane
$CH_2 = CHCl$	Vinyl chloride	Chloroethene
$CH_2 = CHCH_2Br$	Allyl bromide	3-Bromopropene
	o-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$	Chloroform	Trichloromethane
$CHBr_3$	Bromoform	Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	n-Propyl fluoride	1-Fluoropropane

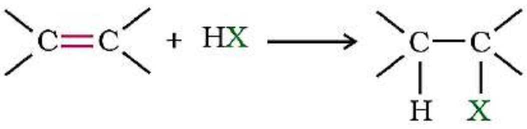
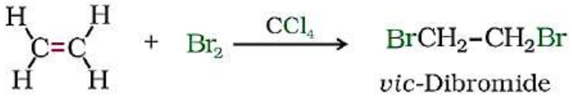
Common Name	Alkyl halide
IUPAC Name	Halo alkane

Methods of Preparation: 1. From Alcohols

$R\text{–}OH + HX \xrightarrow{ZnCl_2} R\text{–}X + H_2O$ $R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$ $3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$ $R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$ $R\text{–}OH \xrightarrow[X_2=Br_2, I_2]{red\ P/X_2} R\text{–}X$ $R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$	Thionyl chloride is preferred because the other two products are escapable gases. Hence the reaction gives pure alkyl halides. The reactions of 1° and 2° alcohols with HX require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. The order of reactivity of alcohols with a given haloacid is 3°>2°>1°.

2. From Hydrocarbons

(a) By free radical halogenation	$CH_3CH_2CH_2CH_3 \xrightarrow[or\ heat]{Cl_2/UV\ light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
(b) By electrophilic substitution	
(c) Sandmeyer's reaction	

(d) From alkenes (i) Addition of hydrogen halides (ii) Addition of halogens	 

3. Halogen Exchange:

Finkelstein reaction	$R{-}X + NaI \longrightarrow R{-}I + NaX$
Swarts reaction	$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$

Physical Properties:

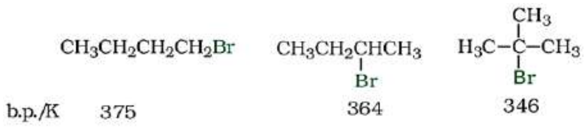
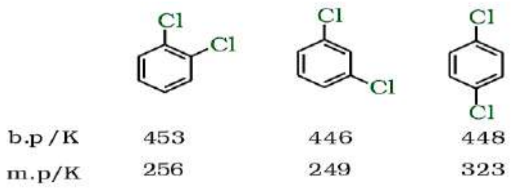
a) Alkyl halides are colourless when pure. However, bromides and iodides develop colour when exposed to light. Many volatile halogen compounds have a sweet smell

b) **Physical State**: Lower members of alkyl halides (CH_3F, CH_3Cl, CH_3Br and C_2H_5Cl) are colourless gases at room temperature. The higher members up C_{18} are colourless liquids whereas other members are colourless solids.

c) **Solubility:** Despite of polar nature of alkyl halides, they are **insoluble in water due to the inability to form hydrogen bonds**. Still, they are soluble in non-polar solvents.

d) **Melting and Boiling Point:**

- Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are more robust in the halogen derivatives. That is why the boiling points of chlorides, bromides, and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.
- The boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because the magnitude of van der Waal forces increases with the increase in size and mass of halogen atom.

The boiling points of isomeric haloalkanes decrease with an increase in branching.	
Boiling points of isomeric dihalobenzenes are nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to the symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.	

e) **Density:** The density increases with an increase in the number of carbon atoms, halogen atoms, and atomic mass of the halogen atoms.

Chemical Reactions: The reactions of haloalkanes may be divided into the following categories-

1. Nucleophilic substitution 2. Elimination reactions 3. Reaction with metals

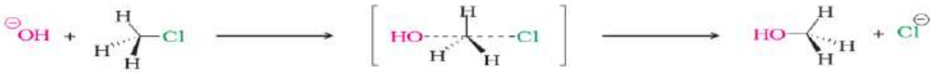
1. Nucleophilic substitution reactions

a. CH_3CH_2Cl + K**OH** (aq) ⟶ CH_3CH_2OH (Alcohol) + KCl
b. CH_3CH_2Br + Na**OH**(aq) ⟶ CH_3CH_2OH (Alcohol) +NaBr
c. CH_3CH_2I + Na**OR** ⟶ CH_3CH_2OR (Alkoxy alkane) +NaI
d. CH_3CH_2I + AgCN ⟶ CH_3CH_2NC (Alkyl Isocyanide) +Ag I
e. CH_3CH_2I + K**CN** ⟶ CH_3CH_2CN (Alkyl cyanide) +KI
f. CH_3CH_2Cl + Ag**NO**$_2$ ⟶ $CH_3CH_2\ NO_2$ (Nitroalkane) +AgCl
g. CH_3CH_2Cl + KNO_2 ⟶ CH_3CH_2ONO(Alkylnitrite) +KI
h. CH_3CH_2Br +NH_3 ⟶ $CH_3CH_2NH_2$ (Primary Amines) +HBr
i. CH_3CH_2Br +RNH_2 ⟶ CH_3CH_2NHR +HBr
j. $CH_3CH_2Br \xrightarrow{LIAlH_4} CH_3CH_2\text{–}H$

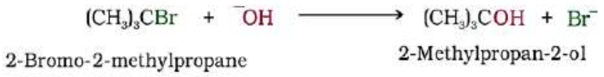
- ★ **Ambident nucleophiles**: Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Cyanide group, linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly, nitrite ion linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.
- ★ Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the main product. Since KCN is predominantly ionic and provides cyanide ions in solution. However, AgCN is mainly covalent in nature and Nitrogen is free to donate electron pairs forming isocyanide as the main product.

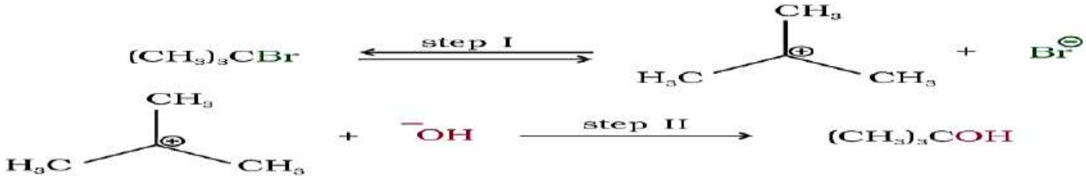
Mechanism: This reaction has been found to proceed by two different mechanisms-

(a) Substitution nucleophilic bimolecular (S_N2): The reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion follows second order kinetics, i.e., the rate depends upon the concentration of both the reactants. This process is called an inversion of configuration (Walden inversion).

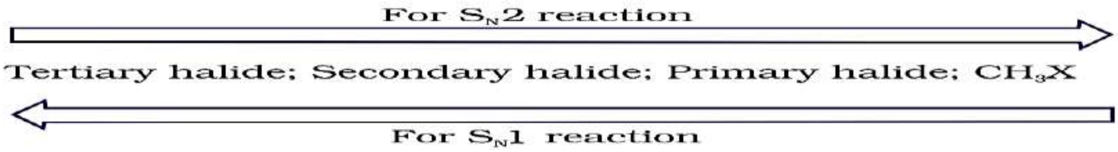


(b) Substitution nucleophilic unimolecular (S_N1):

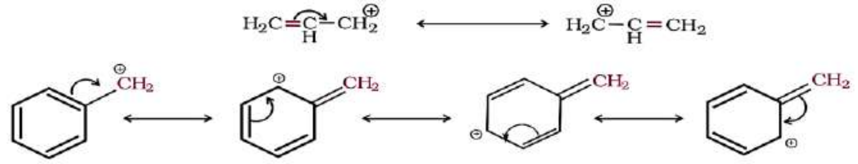
These reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between tert-butyl bromide and hydroxide ion yields tert-butyl alcohol and follows the first order kinetics, i.e., the rate of reaction depends upon the concentration of only one reactant, which is tert- butyl bromide.	 $(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^-$ 2-Bromo-2-methylpropane 2-Methylpropan-2-ol



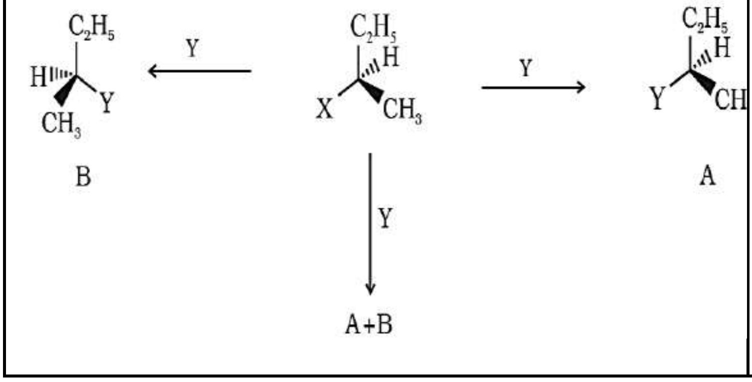
- We can sum up the order of reactivity of alkyl halides towards S_N1 and S_N2 reactions as follows:



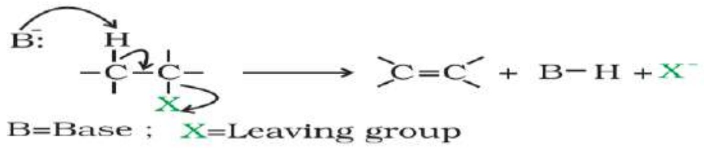
- For the same reasons, allylic and benzylic halides show high reactivity towards the $S_N{}^1$ reaction. The carbocation thus formed gets stabilized through resonance.



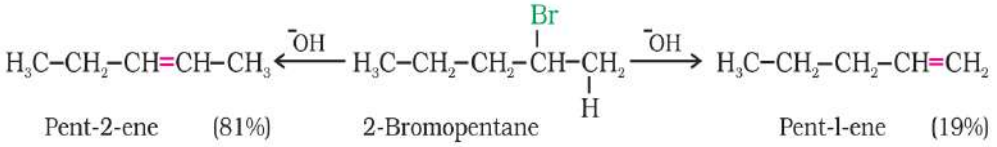
- For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F.
- A $S_N{}^2$ reaction proceeds with complete stereochemical inversion while a S_N1 reaction proceeds with racemization.
- The stereoisomers related to each other as non-superimposable mirror images are called enantiomers. Enantiomers possess identical physical properties namely, melting point, boiling point, solubility, refractive index, etc. They only differ with respect to the rotation of plane polarised light. If one of the enantiomers is dextro rotatory, the other will be laevorotatory.
- A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as a racemic mixture or racemic modification and the process is known as racemization. A racemic mixture is represented by prefixing dl or (±) before the name.
- Retention of configuration is the preservation of the integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction or transformation.
- **Inversion, retention, and racemization:** There are three outcomes for a reaction at an asymmetric carbon atom. Consider the replacement of a group X by Y in the following reaction;

 	-If (A) is the only compound obtained, the process is called retention of configuration. -If (B) is the only compound obtained, the process is called inversion of configuration. -If a 50:50 mixture of the above two is obtained then the process is called racemization.

2. Elimination reactions When a haloalkane with a β-hydrogen atom is heated with an alcoholic solution of potassium hydroxide, there is the elimination of hydrogen atom from β-carbon and a halogen atom from the α-carbon atom. As a result, an alkene is formed as a product. Since the β-hydrogen atom is involved in elimination, it is often called β-elimination.



If there is the possibility of the formation of more than one alkene due to the availability of more than one α-hydrogen atom, as per Saytzeff rule, “the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.” Thus, 2-bromopentane gives pent-2-ene as the major product.



$$\underset{\text{Pent-2-ene (81\%)}}{H_3C-CH_2-CH=CH-CH_3} \xleftarrow{^-OH} \underset{\text{2-Bromopentane}}{H_3C-CH_2-CH_2-\overset{Br}{\underset{H}{CH}}-CH_2} \xrightarrow{^-OH} \underset{\text{Pent-1-ene (19\%)}}{H_3C-CH_2-CH_2-CH=CH_2}$$

Elimination versus substitution: A chemical reaction is the result of competition; it is a race that is won by the fastest runner. A collection of molecules tend to do, by and large, what is easiest for them. An alkyl halide with α-hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution (S_N1 and S_N2) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile, and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstract a proton rather than approach a tetravalent carbon atom (steric reasons) and vice versa. Similarly, a primary alkyl halide will prefer a S_N2 reaction, a secondary halide- S_N2 or elimination depending upon the strength of base/nucleophile and a tertiary halide- S_N1 or elimination depending upon the stability of carbocation or the more substituted alkene.

3. Reaction with metals:

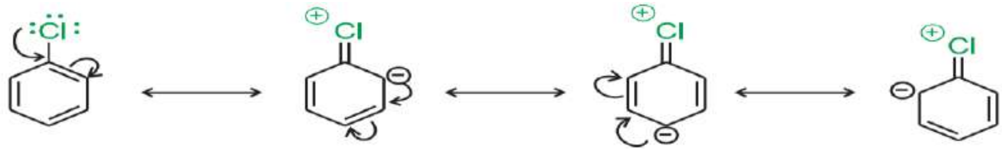
$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

Wurtz reaction	$2RX + Na \longrightarrow RR + NaX$

Reactions of Haloarenes:

1. Nucleophilic substitution Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is more difficult than in haloalkane, and therefore, they are less reactive toward nucleophilic substitution reaction.

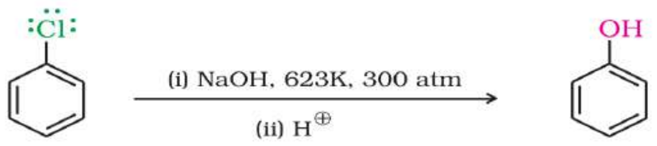


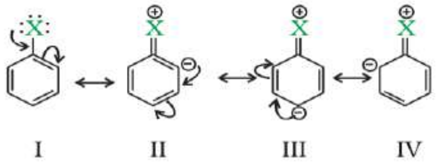
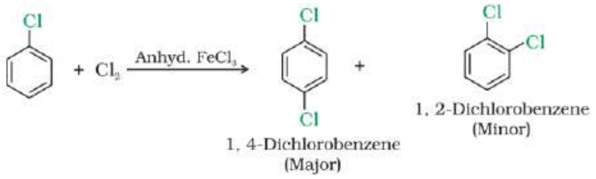
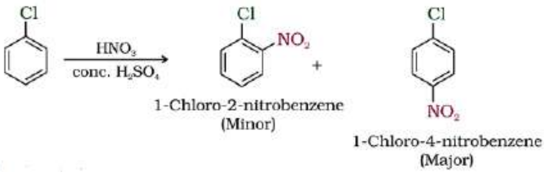
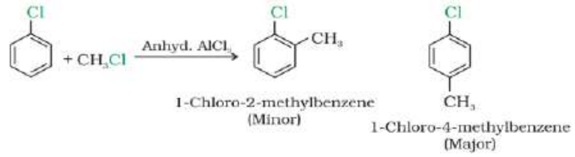
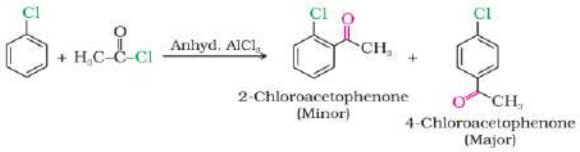
(ii) In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in the case of haloarene, the carbon atom attached to halogen is sp^2-hybridised.

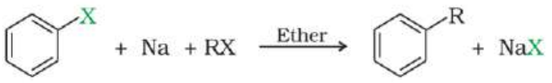
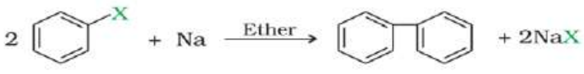
(iii) In the case of haloarenes, the phenyl cation formed as a result of self-ionization will not be stabilized by resonance and therefore, S_N1 mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich arenes.

Replacement by hydroxyl group

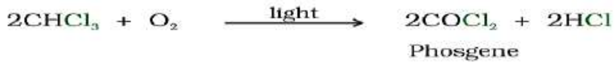
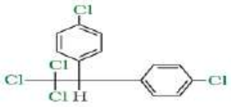
	The presence of an electron-withdrawing group (-NO_2) at ortho- and para-positions increases the reactivity of haloarenes.

2. Electrophilic substitution reactions	
I. Halogenation	 1, 4-Dichlorobenzene (Major) 1, 2-Dichlorobenzene (Minor)
II. Nitration	 1-Chloro-2-nitrobenzene (Minor) 1-Chloro-4-nitrobenzene (Major)
III. Sulphonation	 2-Chlorobenzene sulfonic acid (Minor) 4-Chlorobenzene sulfonic acid (Major)
IV. Friedel-Crafts reaction	 1-Chloro-2-methylbenzene (Minor) 1-Chloro-4-methylbenzene (Major)  2-Chloroacetophenone (Minor) 4-Chloroacetophenone (Major)

3. Reaction with metals	**Wurtz-Fitting reaction**	
	Fitting reaction	

Polyhalogen Compounds

Dichloromethane (Methylene chloride)	Used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs.

Trichloromethane (Chloroform)	The major use of chloroform today is in the production of the freon refrigerant R-22. Chloroform is slowly oxidized 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.  $2CHCl_3 + O_2 \xrightarrow{light} \underset{Phosgene}{2COCl_2} + 2HCl$
Triiodomethane (Iodoform)	It was used as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.
Tetrachloromethane (Carbon tetrachloride)	Is used in the manufacture of refrigerants and propellants for aerosol cans. When carbon tetrachloride is released into the air, it rises into the atmosphere and depletes the ozone layer.
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. In the stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.
p,p'-dichlorobiphenyl trichloroethane (DDT)	The DDT is effective against the mosquito that spreads malaria and lice that carry typhus. 

MULTIPLE CHOICE QUESTIONS (1 MARK)

1. 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

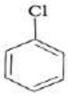
(c) Free radical addition reaction (d) Nucleophilic substitution reaction

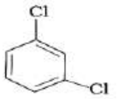
2. Which reagent will you use for the following reaction?

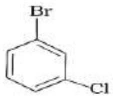
$CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

(a) Cl_2/UV light (b) NaCl + H_2SO_4 (c) Cl_2 gas in dark (d) Cl_2 gas in the presence of iron

3. Arrange the following compounds in the increasing order of their densities.

(a)  (b) 

(c) 

(d) 

(a) (a) < (b) < (c) < (d) (b) (a) < (c) < (d) < (b)

(c) (d) < (c) < (b) < (a) (d) (b) < (d) < (c) < (a)

4. Which of the following is an example of vicinal dihalide?

(a) Dichloromethane (b) 1,2-dichloroethane (c) Ethylidene chloride (d) Allyl chloride

5. Based on the position of –Br in the compound in $CH_3CH=CHC(Br)(CH_3)_2$ can be classified as ___________ halide.
(a) Allyl (b) Aryl (c) Vinyl (d) Secondary

6. Chlorobenzene is formed by the reaction of chlorine with benzene in the presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction?
(a) Cl^- (b) Cl^+ (c) $AlCl_3$ (d) $[AlCl_4]^-$

7. Ethylidene chloride is a/an _____________.
(a) vicinal dihalide (b) geminal dihalide (c) allylic halide (d) vinylic halide

8. A primary alkyl halide would prefer to undergo ____________.
(a) S_N1 reaction (b) S_N2 reaction (c) α–Elimination (d) Racemisation

9. Which of the following alkyl halides will undergo S_N1 reaction most readily?
(a) $(CH_3)_3C—F$ (b) $(CH_3)_3C—Cl$ (c) $(CH_3)_3C—Br$ (d) $(CH_3)_3C—I$

10. What should be the correct IUPAC name for Diethyl bromomethane?
(a) 1-Bromo-1,1-diethylmethane (b) 3-Bromopentane
(c) 1-Bromo-1-ethylpropane (d) 1-Bromopentane

ASSERTION REASON TYPE QUESTIONS(1MARK)

For following questions select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

11. **Assertion:** Hydrogen halides (HX) are preferred over thionyl chloride for the preparation of alkyl halides from alcohols.
Reason: Gaseous side products are formed in the case of thionyl chloride.
12. **Assertion:** Tertiary alkyl halides are least reactive towards S_N1 reaction.
Reason: In S_N1 reaction, the rate of reaction depends only on the concentration of alkyl halide.
13. **Assertion:** Haloalkanes are sparingly soluble in water.
Reason: Haloalkanes do not form hydrogen bonds with water.
14. **Assertion:** Propene reacts with HBr to form 2-bromo propene.
Reason: As intermediate formed carbocation is secondary which is more stable than primary.
15. **Assertion:** S_N2 mechanism leads to the inversion of configuration.
Reason: As in this mechanism optical activity is lost.

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

16. What happens when an excess of bromine attacks on $CH_2=CH—CH_2—C≡CH$?

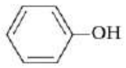
17. Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does the preparation of aryl iodides require the presence of an oxidizing agent?

18. Out of o-and p-dibromo benzene which one has a higher melting point and why?

19. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and H_2SO_4. Explain why?

(a) $CH_3CH_2CH_2OH$

(b)



20. Which of the products will be the major product in the reaction given below? Explain.

$$CH_3CH=CH_2 + HI \longrightarrow \underset{(A)}{CH_3CH_2CH_2I} + \underset{(B)}{CH_3CHICH_3}$$

21. Draw resonance structures of haloarene and find out whether the functional group present in the molecule is ortho, para directing, or meta directing.

22. Write the structures and names of the compounds formed when compound 'A' with the molecular formula, C_7H_8 is treated with Cl_2 in the presence of $FeCl_3$.

23. Identify the products A and B formed in the following reaction:

$$CH_3—CH_2—CH=CH—CH_3 + HCl \longrightarrow A + B$$

24. Write down the structure and IUPAC name for neo-pentyl bromide.

25. 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

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

26. Compound 'A' with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. In KOH solution, the rate of reaction was found to be dependent on the concentration of the compound and KOH both.
(i) Write down the structural formula of both compounds 'A' and 'B'.
(ii) Out of these two compounds, which one will be converted to the product with an inverted configuration?

27. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of $ZnCl_2$?

28. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?

29. Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:

30. Cyanide ion acts as an ambient nucleophile. From which end it acts as a stronger nucleophile in the aqueous medium? Give a reason for your answer.

LONG ANSWER TYPE QUESTIONS (5 MARKS)

31. Some alkyl halides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples that are responsible for this difference.

32. 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

33. Case-based question (4 Marks)

Case 1

The substitution reaction of alkyl halides occurs in S_N1 and S_N2 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 S_N1 reactions is governed by the stability of carbocation whereas for S_N2 reactions steric factor is a 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.

1. Among 1-bromopropane and 2-methyl-2-bromo propane, which will follow S_N1 mechanism? 1
2. Among following in which inversion of configuration will occur on reaction with aq alkali
1-bromo propane, and 2-methyl-2-bromo butane
1
3. What is the role of polar protic solvent in S_N1 reaction? (2)

OR

How will a protic solvent system affect the S_N2 reaction? (2)

Case 2

Chlorofluorocarbons (CFCs) described as 'miracle chemicals' have no natural resources. They were first manufactured in the 1930s and industries soon found variety of applications for them due to their chemical non-reactivity and heat absorbing properties. CFCs have been used as refrigerants in air conditioners and refrigerators, in aerosol spray cans, in manufacturing foams and as cleansing agents in the manufacture of electronics. These chemicals have been given the tradename 'Freons' and the term since became a household name.
1.What is 'Freon – 12'? (1)
2. Draw its molecular structure (1)
3. State any two harmful effects of CFCs on the environment. (2)

OR

3. State any two ways to reduce the harmful effect of CFCs. (2)

Case 3

Alkyl Halides can be readily prepared from Alkenes by addition reactions with Hydrogen Halides. When the alkene is symmetrical about the double bond, only one product is obtained. But if the alkene is unsymmetrical the addition of Hydrogen Bromide results in formation of two products. The addition of HBr to an unsymmetrical alkene in presence of an organic peroxide also results in the formation of two products. The only difference is in the quantities of isomeric bromides obtained in each case since the mechanism is different.

1.What is the major product obtained when Propene reacts with HBr? What rule governs the formation of this product? (1)

2. What mechanism is adopted in presence of Benzoyl Peroxide. (1)

3. Why does only HBr show these anomalies unlike HI or HCl. (2)

OR

3. Write the mechanism of the addition reaction of Propene with HBr in presence or in absence of organic peroxides. (2)

Case 4

Alkyl Halides have higher melting and boiling points than Alkanes of comparable molecular mass. The other trends observed are as follows;

i.For a given Alkyl Halide the melting point and boiling point increases with increase in molecular mass. So, the order is RCl<RBr<RI.

ii. For a given halogen the boiling point rises with increasing Carbon number.

iii. The boiling point also varies as per the nature of the Carbon i.e primary> secondary> tertiary.

1.Arrange CH_3I, CH_3F, CH_3Br and CH_3Cl in decreasing order of melting points. (1)

2. Which has a lower boiling point – Chloropropane or 2-Chloropropane. Why? (2)

OR

2. Arrange the following in increasing order of boiling points. (2)

$(CH_3)_3CBr$, $CH_3CH(Br)CH_2CH_3$, $CH_3(CH_2)_3Br$, $(CH_3)_3CCl$

3. Among the isomeric Chlorotoluene, which isomer has the highest melting point?

Case 5:

Chloroform is a colourless, volatile liquid with sweetish sickly odour and burning taste. It is denser than water. It is soluble in organic solvents but insoluble in water. It itself acts as a good solvent. Chloroform causes temporary unconsciousness when its vapours are inhaled. For this reason, it was used as an anaesthetic until recently. It is also used as a preservative for anatomical specimen and as a laboratory reagent.

1.What is the IUPAC name of Chloroform? (1)

2. How is Chloroform commercially prepared? (1)

3. Why should Chloroform be stored in dark bottles which are completely filled? Give chemical equation in support of your answer. (2)

OR

3. Write a short note on any two-name reactions where Chloroform is used as a reagent. (2)

ANSWERS

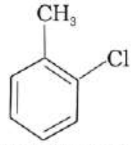
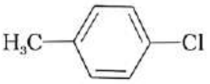
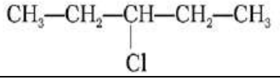
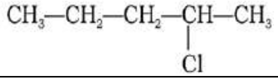
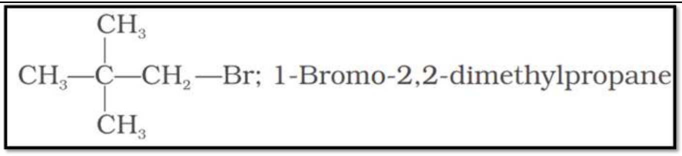
Multiple choice questions

1	2	3	4	5	6	7	8	9	10
b	a	a	b	a	b	b	b	d	b

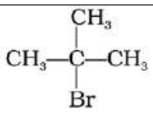
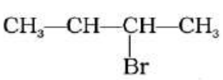
Assertion & Reasoning

11	12	13	14	15
d	b	a	a	c

Very Short Answers

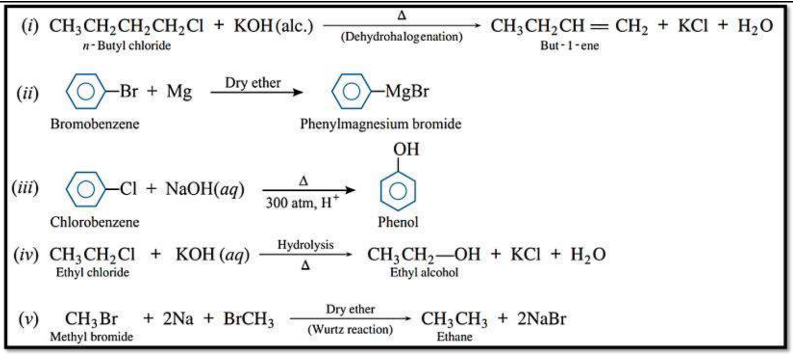
16	1,1,2,2,4,4-hexabromopentance formed
17	Iodination reactions are reversible in nature. To carry out the reaction in the forward direction, HI formed during iodination is removed by oxidation. HIO4 is used as an oxidizing agent.
18	p-Dibromo benzene has a higher melting point than its o-isomer. It is due to the symmetry of the p-isomer which fits in the crystal lattice better than the o-isomer.
19	(b), C—O bond is more stable in (b) because of resonance.
20	'B' is the major product of the reaction as per Markonikov's rule.
21	Ortho-para directing due to increase in the electron density at ortho and para positions.
22	(i)  *o*-Chlorotoluene (ii)  *p*-Chlorotoluene
23	(A)  $CH_3-CH_2-\underset{\underset{Cl}{\mid}}{CH}-CH_2-CH_3$ (B)  $CH_3-CH_2-CH_2-\underset{\underset{Cl}{\mid}}{CH}-CH_3$
24	 $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}-CH_2-Br$; 1-Bromo-2,2-dimethylpropane
25	iii); The tertiary carbocation formed in the reaction is stable

Short Answer Type

26	(i) Compound A :  $CH_3-\overset{\overset{CH_3}{\mid}}{\underset{\underset{Br}{\mid}}{C}}-CH_3$ Compound B :  $CH_3-CH-\underset{\underset{Br}{\mid}}{CH}-CH_3$ (ii) Compound 'B'.
27	C—O bond in phenols is more stable due to resonance effect and it has double bond character, hence breaking of this bond is difficult.
28	Grignard reagents are highly reactive and react with water to give corresponding hydrocarbons. $\boxed{RMgX + H_2O \longrightarrow RH + Mg(OH)X}$
29	III > II > I
30	It acts as a stronger nucleophile from the carbon end because it will lead to the formation of C–C bond which is more stable than the C–N bond.

Long Answer Type

31	Primary alkyl halides prefer to undergo substitution reaction by S_N2 mechanism whereas tertiary halides undergo elimination reaction due to the formation of a stable carbocation.

32	

33. **Case Study Based**

Case I

1: 2-methyl-2-bromo propane

2. 1-bromo propane

3. Polar protic solvents help to stabilize both the carbocation and the anion and that solvation of both cations and anions helps the S_N1 mechanism proceed. So that's why polar protic solvent will favor an S_N1 mechanism.

OR

For S_N2 reactions involving anions as the nucleophile, protic solvents act to decrease the nucleophilicity of that anion by solvation through hydrogen bonding. The anion acquires a “coating” of solvent molecules thus inhibiting the ability of the anion to approach the substrate.

Case II

1.	Dichlorodifluoromethane, CF_2Cl_2
2.	Tetrahedral Structure Diagram
3.	i. Depletion of Ozone layer in the Stratosphere. ii. Green- House Effect and global warming OR i. Buy air-conditioning and refrigeration equipment that does not use CFCs ii. Buy aerosol products that do not use CFCs as propellants iii. Conduct regular inspection and maintenance of AC and refrigeration appliance to prevent leakage.

Case III

1.	2-Bromopropane; Markovnikov’s Rule
2.	Free Radical Electrophilic addition.
3.	The bond dissociation enthalpy of H-Cl is large. In case of HI, the I^- oxidises to I_2 OR Refer Class XI TB for answer

Case IV

1.	$CH_3I > CH_3Br > CH_3Cl > CH_3F$
2.	2- Chloropropane, since branching decreases surface area of contact and hence Vander Waals Forces. OR $(CH_3)_3CCl < (CH_3)_3CBr < CH_3CH(Br)CH_2CH_3 < CH_3(CH_2)_3Br$
3.	The para-isomer because it is symmetrical and fits better in the crystal lattice.

Case V

1.	Trichloromethane
2.	By direct halogenation of Methane in presence of sunlight.
3.	In presence of air and sunlight, Chloroform produces poisonous gas Phosgene; $CHCl_3 + O_2 \rightarrow COCl_2 + HCl$ OR The Reimer-Tiemann reaction is a classic organic reaction that involves the conversion of phenols to salicylaldehyde (ortho-hydroxybenzaldehyde) in the presence of chloroform ($CHCl_3$) and a strong base, typically aqueous sodium hydroxide (NaOH) or potassium hydroxide (KOH). The Carbylamine Reaction, also known as the Isocyanide Test, involves the reaction of primary amines with chloroform and alcoholic potassium hydroxide to form foul-smelling isocyanides (carbylamine), which can be detected by their characteristic odour.

MIND MAP : LEARNING MADE SIMPLE

Haloalkanes and Haloarenes

Polyhalogen compounds

Chloroform
- Solvent for fats, alkaloids, I etc.
- Production of Freon

Iodoform
- Antiseptic

Carbon tetrachloride
- Manufacture of refrigerants and propellants.
- Cleaning fluid

Freons
- For aerosol propellants, refrigeration and air conditioning purposes

D.DT.
- As insecticide

Dichloromethane
- Paint remover
- Propellant in aerosols
- Metal cleaning and finishing solvent.

Racemisation S_N1

- Chiral : Objects which are non-superimposable
- Achiral : objects which are superimposable

S_N2 Stereochemical inversion

- (a) Dextro (+/d)
- (b) laevo (–/l)

Haloalkanes

- Preparation
  - From alcohol :

$R–OH + HCl \xrightarrow{ZnCl_2} R–Cl + H_2O$

$3R–OH + PX_3 \longrightarrow 3R–X + H_3PO_3$

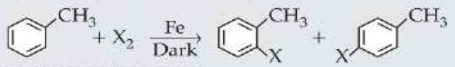
$ROH + PCl_5 \longrightarrow R–Cl + POCl_3 + HCl$

  - From hydrocarbons :

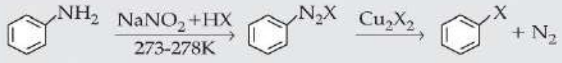
(a) By free radical halogenations

$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/UV} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$

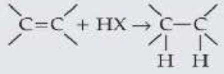
(b) By electrophilic substitution



(c) Sand meyer's reaction



(d) From alkenes



$H_2C=CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2–CH_2Br$

  - Halogen exchange :

$R–X + NaI \rightarrow R – I + NaX$

- Properties
  - Physical : Colourless, volatile, sweet smell.

Lower members are gases at room temperature while higher are solids.

B.P : RI > R Br > RCl > RF.

M.P : Para isomers have high m.p. than ortho and meta – isomers.

Density : Increases with increase in number of C/X atoms and atomic masses of the X atoms.

Solubility : Very slightly soluble in water.

  - Chemical :

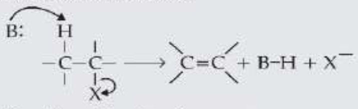
(a) Nucleophilic substitution

$\xrightarrow{\text{For } S_N2 \text{ reaction}}$

Tertiary, Secondary, Primary

$\xleftarrow[\text{For } S_N1 \text{ reaction}]{}$

(b) Elimination reaction



B = Base; X = Leaving group

(c) Reaction with metals

$CH_2CH_2Br + M \longrightarrow CH_3CH_2MgBr$

Wurtz reaction :

$2RX + 2Na \xrightarrow{\text{Dry ether}} RR + 2NaX$

Classification

- No. of halogen atoms

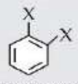
C_2H_5X

Monohaloalkane

$CH_2X–CH_2X$

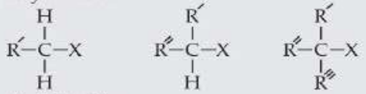
Dihaloalkane


Monohaloarene

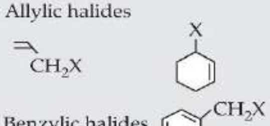

Dihaloarene


Trihaloarene

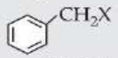
- Compounds containing sp^3 C–X bond
  - (a) Alkyl halides



  - (b) Allylic halides

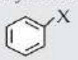


  - (c) Benzylic halides



- Compounds containing sp^2 C–X bond
  - (a) Vinylic halides

  - (b) Aryl halides



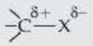
- Nomenclature

Common name : alkyl group followed by halides. Dihalogen derivatives, prefixes o–, m–, p– are used.

IUPAC name : numerals are used

- Nature of C –X bond

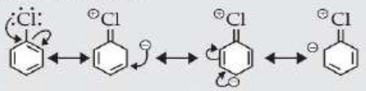
: Carbon –halogen bond is polarized



Haloarenes

- Reactions :
  - (a) Nucleophilic substitution

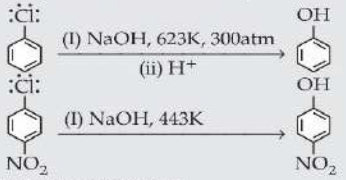
(i) Resonance effect



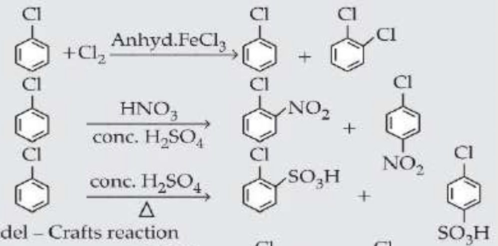
(ii) Hybridization of C – X bond in :

Haloalkane –sp^3; Haloarence –sp^2

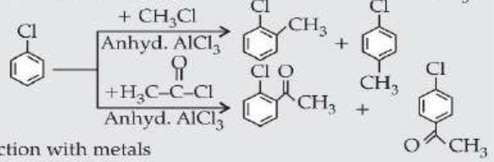
(iii) Phenyl cation unstabilised by resonance



  - (b) Electrophilic substitution



Friedel – Crafts reaction



  - (c) Reaction with metals

Wurtz – Fitting reaction

Fittig reaction

7. Alcohols, Phenols and Ethers

Quick Revision Points: -

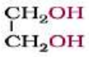
Alcohols	Phenols	Ethers
$RH \xrightarrow[+OH]{-H} ROH$	$ArH \xrightarrow[+OH]{-H} ArOH$	$RH \xrightarrow[+O\text{-}R]{-H} RO\text{-}R$ $RH \xrightarrow[+O\text{-}Ar]{-H} RO\text{-}Ar$

Classification of Alcohols and Phenols

- Alcohols and phenols may be classified as mono–, di–, tri- or polyhydric compounds depending on whether they contain one, two, three or many hydroxyl groups respectively

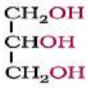
C_2H_5OH

Monohydric



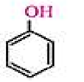
CH_2OH-CH_2OH

Dihydric

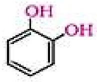


$CH_2OH-CHOH-CH_2OH$

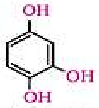
Trihydric



Monohydric



Dihydric

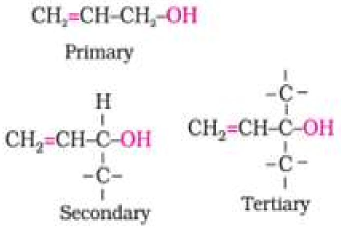
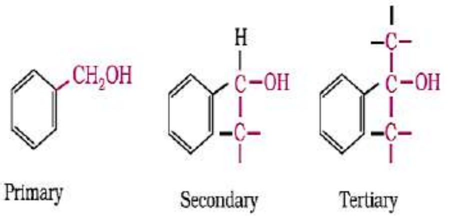


Trihydric

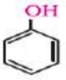
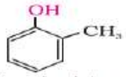
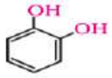
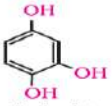
Classification of Monohydric alcohols

according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

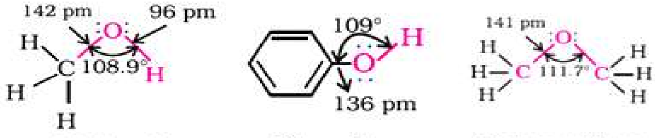
(i)Compounds containing $C_{sp^3}-OH$ bond:

(a) Alkyl alcohols	**(b) Allylic alcohols**	**(c) Benzylic alcohols**
–OH group is attached to an *sp³* hybridised carbon atom of an alkyl group.	—OH group is attached to a sp³ hybridised carbon adjacent to the carbon-carbon double bond, that is to an allylic carbon	—OH group is attached to a sp³—hybridised carbon atom next to an aromatic ring.
 Primary (1°) Secondary (2°) Tertiary (3°)	 Primary Secondary Tertiary	 Primary Secondary Tertiary

(ii) Compounds containing $C_{sp^2}-OH$ bond:

(a)Vinylic alcohol	**(b) Aryl alcohols or Phenols**
—OH group bonded to a carbon-carbon double bond, i.e., to a vinylic carbon	—OH group bonded to the sp²-hybridised carbon atom of an aromatic ring
$CH_2=CH-OH$	 Monohydric  Monohydric  Dihydric  Trihydric

Classification of Ethers

(a) simple or symmetrical ether- if the alkyl or aryl groups attached to the oxygen atom are the same. Diethyl ether, $C_2H_5OC_2H_5$	**Structures of Functional Groups**  Methanol Phenol Methoxymethane
(b)mixed or unsymmetrical ether- if the two groups are different. $C_2H_5OCH_3$ and $C_2H_5OC_6H_5$	

Isomerism in Alcohols: Alcohols exhibit four types of isomerism: (i)Chain isomerism: $C_4H_{10}O$ Butan-1-ol, 2-methylpropan-1-ol (ii)Position isomerism: C_3H_8O Propan-1-ol, propan-2-ol (iii)Functional isomerism: C_2H_6O Ethanol, methoxy methane (iv)Optical isomerism: Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism. E.g. Butan-2-ol, Pentan-2-ol

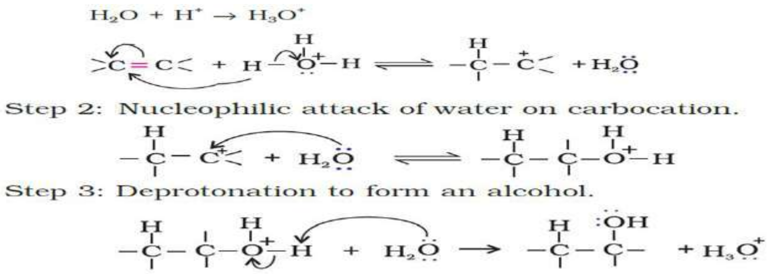
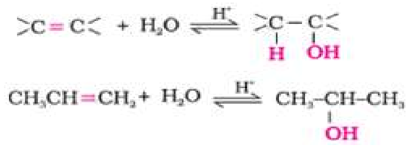
Nomenclature of Alcohols : According to IUPAC system, 'e' of the parent alkane is replaced with the suffix 'ol'. For naming polyhydric alcohols, the 'e' of alkane is retained and the ending 'ol' is added.

Nomenclature of Phenols: - The simplest hydroxy derivative of benzene is phenol. It is its common name and IUPAC name. For disubstituted compounds the terms *ortho* (1,2-disubstituted), *meta* (1,3 disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

Nomenclature of Ethers:- The larger (R) group is chosen as the parent hydrocarbon and smaller group is written as alkoxy or phenoxy

Preparation of Alcohols

(1) From alkenes

(i)*By acid catalysed hydration:* Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule	**Mechanism** Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ or H^+.  Step 2: Nucleophilic attack of water on carbocation. Step 3: Deprotonation to form an alcohol.
 $>C=C< + H_2O \overset{H^+}{\rightleftharpoons} >C(H)-C(OH)<$ $CH_3CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} CH_3-CH(OH)-CH_3$	

(ii) *By hydroboration–oxidation*:

Diborane $(BH_3)_2$ reacts with alkenes to give trialkyl boranes as addition product.

This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide

$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow (CH_3-CH_2-CH_2)_3B \xrightarrow{3H_2O_2,\ \bar{O}H} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propan-1-ol

(2). From carbonyl compounds

By reduction of aldehydes and ketones:

Reducing agents : H_2 with catalyst, sodium borohydride ($NaBH_4$) or $LiAlH_4$.

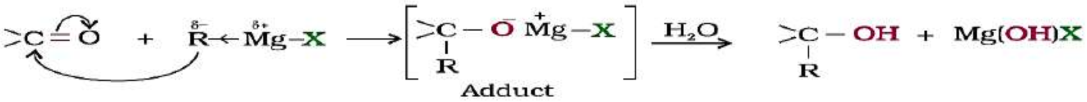
Aldehydes yield primary alcohols whereas ketones give secondary alcohols.

$$RCHO + H_2 \xrightarrow{Pd} RCH_2OH \qquad RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R'$$

(3) By reduction of carboxylic acids and esters:

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH \qquad RCOOR' \xrightarrow[Catalyst]{H_2} RCH_2OH + R'OH$$

(4) From Grignard reagents:

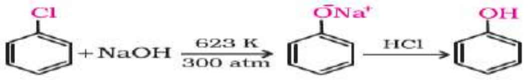
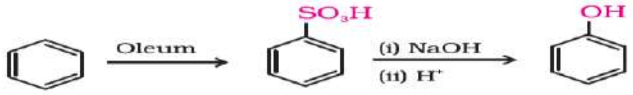
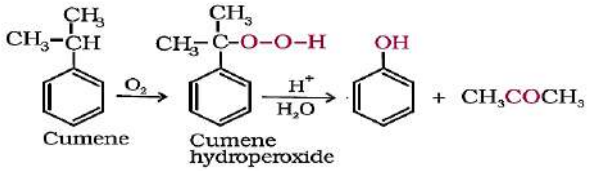


$$>C=O + \overset{\delta-}{R}\leftarrow\overset{\delta+}{Mg}-X \longrightarrow \left[>C(R)-\bar{O}\overset{+}{Mg}-X\right] \xrightarrow{H_2O} >C(R)-OH + Mg(OH)X$$

Adduct

Methanal→ primary alcohol, Other aldehyde → secondary alcohol, Ketones → tertiary alcohol

Preparation of Phenols

(1)From haloarenes  *(2)From diazonium salts* 	(3). From benzenesulphonic acid  *4. From cumene* 

Physical Properties of Alcohols and Phenols

Boiling Points

- Increase with increase in the number of carbon atoms (increase in van der Waal's forces).
- In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waal's forces with decrease in surface area).
- Due to the presence of intermolecular hydrogen bonding, boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses.

Solubility

- Soluble in water due to their ability to form hydrogen bonds with water molecules.
- The solubility decreases with increase in size of alkyl/aryl (hydrophobic) groups.
- Several of the lower molecular mass alcohols are miscible with water in all proportions.

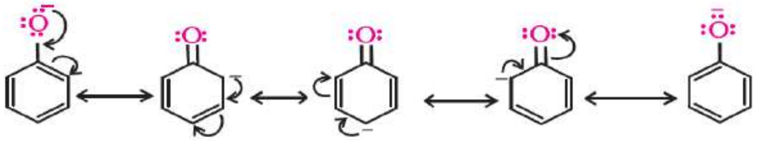
Chemical Reactions of Alcohols and Phenols

(i) **Reactions involving cleavage of O – H Bond**

(a) Acidity of alcohols and phenols:

$R - OH + 2Na \rightarrow 2R - ONa + H_2$ $C_6H_5 - OH + 2Na \rightarrow 2C_6H_5 - ONa + H_2$

Alcohols are weaker acids than water due to (+I effect) group present in alcohols, which decreases the polarity of -O-H bond. Acid strength of alcohols: 1° > 2° > 3° Electron releasing group increases electron density on oxygen to decrease the polarity of – OH bond. Order of acidity is: $RCOOH > H_2CO_3 > C_6H_5OH > H_2O > ROH$. Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance.



Presence of electron withdrawing groups ($-NO_2$, -CN, -X) increases the acidity of phenol by stabilizing phenoxide ion while presence of electron releasing groups (-R, -NH_2, -OR) decreases the acidity of phenol by destabilizing phenoxide ion. Thus, increasing acidic strength is o-cresol < p-cresol < m-cresol < phenol < o-nitrophenol < 2, 4, 6 Trinitrophenol (picric acid) Higher K_a and lower pK_a value correspond to the stronger acid.

(b) Esterification

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters.

$$Ar/ROH + R'-COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

The introduction of acetyl (CH_3CO-) group in phenols is known as acetylation.

(ii)Reactions involving cleavage of carbon – oxygen (C–O) bond in Alcohols

1. **Reaction with hydrogen halides:**

- Alcohols react with hydrogen halides to form alkyl halides.

$$ROH + HX \rightarrow R\text{–}X + H_2O$$

- Reactivity of Alcohols: Tertiary > Secondary > Primary
- Lucas Test: - Used to distinguish primary, secondary and tertiary alcohols
  - Lucas reagent (conc. HCl and $ZnCl_2$)
  - Alcohols are soluble in Lucas reagent while Alkyl halides (RX) are immiscible and produce turbidity in solution.
  - tertiary alcohols- Immediate turbidity
  - Secondary alcohols- Turbidity appears After 5 minutes
  - Primary alcohols- No turbidity at room temperature.

2. **Reaction with phosphorus trihalides:**

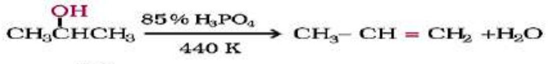
$$3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br) \qquad R\text{–}OH \xrightarrow[X_2=Br_2, I_2]{red\ P/X_2} R\text{–}X$$

3. **Dehydration:**

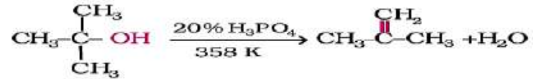
$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \xrightarrow[Heat]{H^+} >C=C< + H_2O$$

$$C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2 = CH_2 + H_2O$$

Secondary and tertiary alcohols are dehydrated under milder conditions. For example



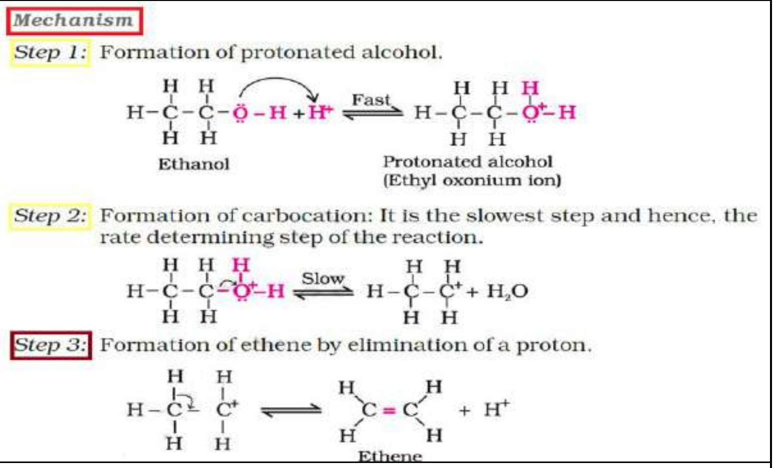
$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[440\ K]{85\%\ H_3PO_4} CH_3-CH=CH_2 + H_2O$$



$$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH \xrightarrow[358\ K]{20\%\ H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

the relative ease of dehydration of alcohols

Tertiary > Secondary > Primary



Mechanism

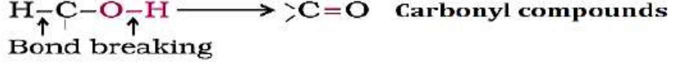
Step 1: Formation of protonated alcohol.

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.

Step 3: Formation of ethene by elimination of a proton.

4. **Oxidation:**

- Oxidation of alcohols involves the formation of a carbon oxygen double bond with cleavage of an O-H and C-H bonds.



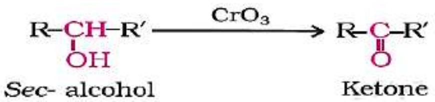
- also known as catalytic dehydrogenation reactions as it involves loss of dihydrogen from an alcohol molecule
- Primary alcohol → Aldehyde → Carboxylic acid
- Primary alcohol → Carboxylic acid (strong oxidizing agent, acidified $KMnO_4$)
- Secondary alcohol → Ketone
- CrO_3 (Chromic anhydride)in anhydrous medium is used as the oxidising agent for the isolation of aldehydes.

$$RCH_2OH \xrightarrow{CrO_3} RCHO$$

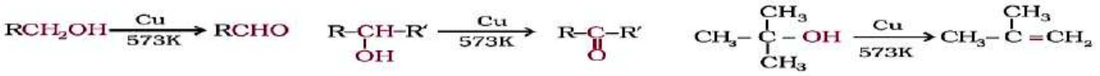
- A better Oxidizing agent: pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl. (PCC retains C=C bond, if present)

$$CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$$

- Secondary alcohols are oxidised to ketones by chromic anhydride (CrO_3).

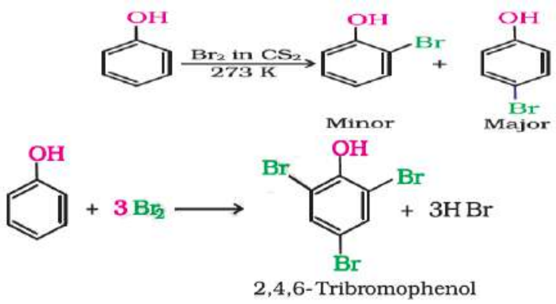

$R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} R-\underset{O}{C}-R'$

- Tertiary alcohols do not undergo oxidation reaction.
- When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place and an aldehyde or a ketone is formed while tertiary alcohols undergo dehydration.

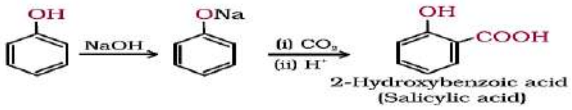

$RCH_2OH \xrightarrow[573K]{Cu} RCHO \quad R-\underset{OH}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{O}{C}-R' \quad CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{C}=CH_2$

Chemical Reactions of Phenols

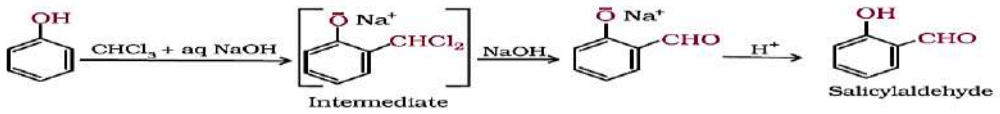
1. Electrophilic aromatic substitution on aromatic ring of Phenol
   -OH group is activating and ortho and para directing.
   Due to resonance electron density is more at o- and p- position

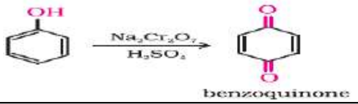
Nitration	Halogenation (Bromination)
	

2. Kolbe's reaction

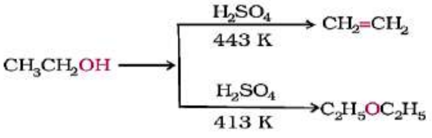
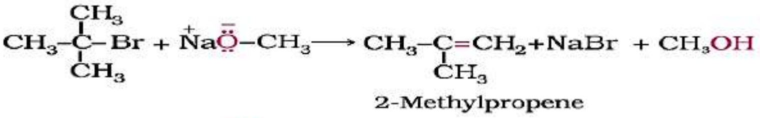
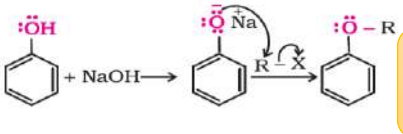


3. Reimer-Tiemann reaction



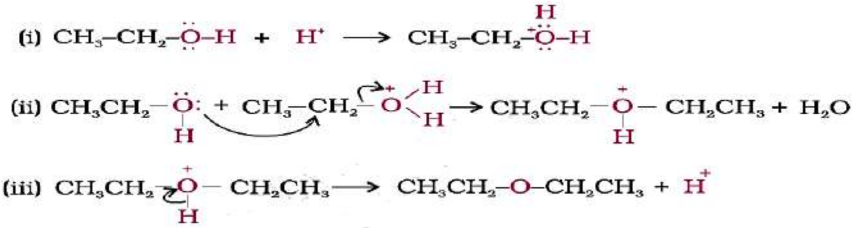
4. Reaction of phenol with zinc dust	5. Oxidation
	

Preparation of Ethers

1. By dehydration of alcohols	2. Williamson synthesis
	- an alkyl halide is reacted with sodium alkoxide. $R-X + R'-\overset{-}{\ddot{O}}\overset{+}{Na} \longrightarrow R-\ddot{O}-R' + NaX$ - Better results are obtained if the alkyl halide is primary (as tert. halide under goes elimination reaction)  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}\overset{-}{\ddot{O}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + CH_3OH$  Aryl halide + sodium alkoxide→?

Mechanism of Dehydration of Alcohol to Ether

The formation of ether is a nucleophilic bimolecular reaction (S_N2) involving the attack of alcohol molecule on a protonated alcohol



It is not appropriate for the preparation of mixed ether like ethyl methyl ether.

Chemical Reactions of Ethers

1. Reactions involving Cleavage of C–O bond in ethers

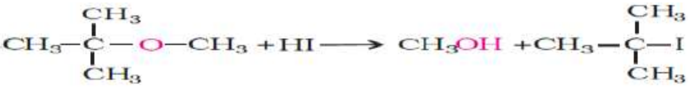
$$R{-}O{-}R + HX \longrightarrow RX + R{-}OH$$
$$R{-}OH + HX \longrightarrow R{-}X + H_2O$$

Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to the more stable aryl-oxygen bond. The reaction yields phenol and alkyl halide

When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (S_N2 reaction).

$$CH_3-\ddot{O}-CH_2CH_3 + H{-}I \longrightarrow CH_3{-}I + CH_3CH_2{-}OH$$

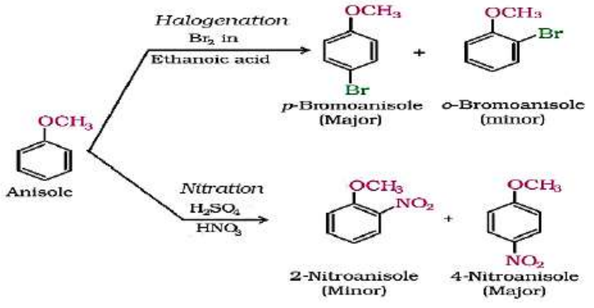
- when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide (S_N1 reaction).

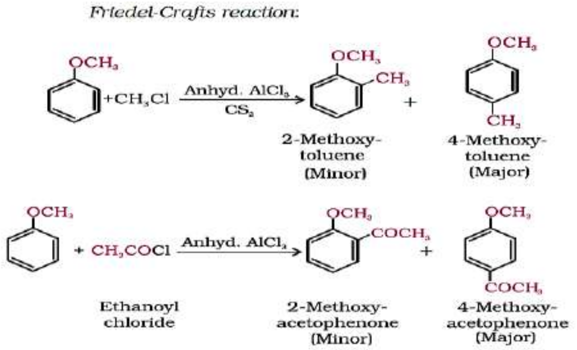


$$(CH_3)_3C{-}O{-}CH_3 + HI \longrightarrow CH_3OH + (CH_3)_3C{-}I$$

2. **Electrophilic substitution**

The alkoxy group (-OR) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution





<u>**MULTIPLE CHOICE QUESTIONS (1 MARKS)**</u>

1. What is the correct order of reactivity of alcohols in the following reaction?

$$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$$

a) 1° > 2° > 3°   b) 1° < 2° > 3°   c) 3° > 2° > 1°   d) 3° > 1° > 2°

2. CH_3CH_2OH can be converted into CH_3CHO by _______________.

a) catalytic hydrogenation   c) treatment with $LiAlH_4$

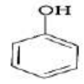
b) treatment with pyridinium chlorochromate   d) treatment with $KMnO_4$

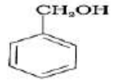
3. The process of converting alkyl halides into alcohols involves

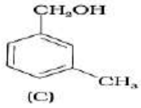
a) addition reaction   c) substitution reaction

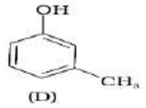
b) dehydrohalogenation reaction   d) rearrangement reaction

4. Which of the following compounds is/are Benzylic alcohols?


[A]

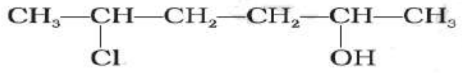

[B]


(C)


(D)

a) A, B, C, D b) A,D c) B, C d) A

5. Give IUPAC name of the compound

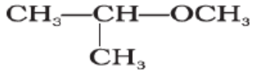


$$CH_3-\underset{Cl}{CH}-CH_2-CH_2-\underset{OH}{CH}-CH_3$$

a) 2-Chloro-5-hydroxyhexane c) 5-Chlorohexan-2-ol

b) 2-Hydroxy-5-chlorohexane d) 2-Chlorohexan-5-ol

6. IUPAC name of the following compound



$$CH_3-\underset{CH_3}{CH}-OCH_3$$

a) 1-methoxy-1-methylethane c) 2-methoxypropane

b) 2-methoxy-2-methylethane d) isopropylmethyl ether

7. Phenol is less acidic than

a) Ethanol b) o-nitrophenol c) o-methylphenol d) o-methoxyphenol

8. Arrange the following compounds in increasing order of boiling point.
Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol

b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

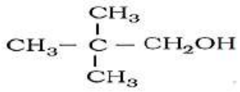
9. Which of the following reagents can be used to oxidise primary alcohols to aldehydes?

(i) CrO_3 in anhydrous medium. (iii) Pyridinium chlorochromate

(ii) $KMnO_4$ in acidic medium (iv) Heat in the presence of Cu at 573K.

a) (i), (ii) b) (i), (iii), (iv) c) (ii), (iii), (iv) d) (iii), (iv)

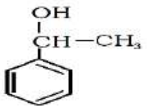
10. Which one is secondary alcohol

(i) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2OH$$

(ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$

(iv) 

b) (i) b) (ii) c) (iii) d) (iv)

ANSWERS MULTIPLE CHOICE QUESTIONS:

Q.No	1	2	3	4	5	6	7	8	9	10
Answer	c)	b)	c)	c)	c)	c)	b)	a)	b)	d)

ASSERTION REASON TYPE QUESTIONS(1MARKS)

The following questions are 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 statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

1. Assertion: p-nitrophenol is more acidic than phenol.
Reason: Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

2. Assertion: Ethanol is a weaker acid than phenol.
Reason: Ethanol reacts with Na and phenol reacts with Na and NaOH

3. Assertion: o-Nitrophenol is more soluble in water than the m-and p-isomers.
Reason: m- and p- Nitrophenols exist as associated molecules because of inter molecular hydrogen bonding.

4. Assertion: Phenols give o- and p-nitrophenol on nitration with conc. HNO_3 and Sulphuric acid mixture.
Reason: —OH group in phenol is o–, p– directing.

5. Assertion: Bromination of phenol does not require the presence of Lewis acid.
Reason: -OH group attached to benzene ring has highly activating effect

ANSWERS ASSERTION REASON BASED QUESTIONS:

Q.No	1	2	3	4	5
Answer	a)	b)	d)	d)	a)

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

1. Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain
Answer: - o-nitrophenol, due to intramolecular hydrogen bonding, is more volatile in nature. In para-nitrophenol, there is intermolecular hydrogen bonding.

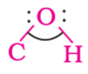
2. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?
Answer: -Phenol will be easily nitrated since the —OH group attached to the benzene ring activates it towards electrophilic substitution due to +R effect.

3. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?
Answer: -Phenoxide ion is more activating than phenol towards electrophilic substitution reaction. Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile.

4. Arrange the following sets of compounds in order of their increasing boiling points:
(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.
(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.
Answer: - (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.
(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol.

5. The carbon– oxygen bond length (136 pm) in phenol is slightly less than that in methanol (142 pm). Explain.
Answer: - This is due to
(i) partial double bond character of C-O bond because of resonance in phenol and
(ii) sp^2 hybridised state of carbon of phenol to which oxygen is attached.

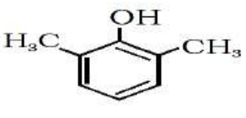
6. Give reasons: -

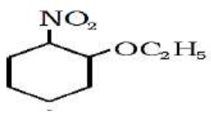
a.The bond angle  in alcohols is slightly less than the tetrahedral angle (109°-28').

b. In methoxymethane  bond angle is slightly greater than the tetrahedral angle

Answer: -a) It is due to the repulsion between the unshared electron pairs of oxygen.
b) It is due to more repulsive interaction between the two bulky methyl groups.

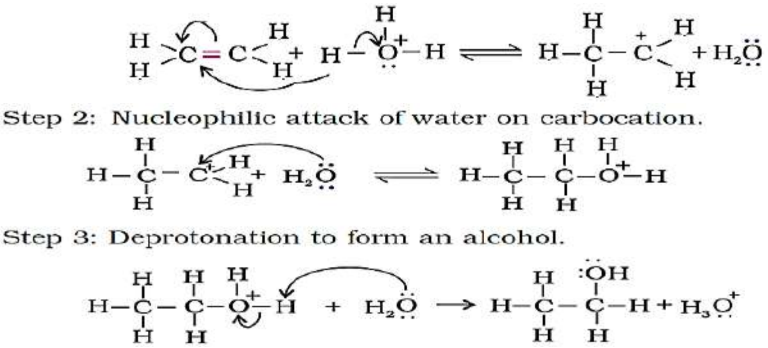
7. Give the IUPAC names of the following compounds:-

(i) 

(ii) 

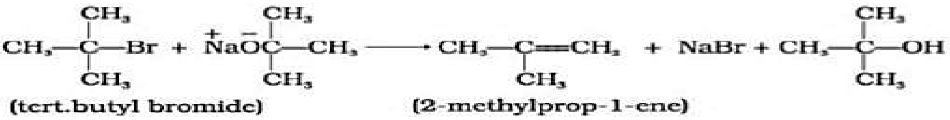
Answer: -(i) 2,6-Dimethylphenol (ii) 1-Ethoxy-2-nitrocyclohexane

8. Explain the mechanism of the acid catalysed hydration of ethene.
Answer: -Step 1: Protonation of ethene to form carbocation by electrophilic attack of H_3O^+ or H^+.



9. Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-tert-butyl ether can’t be prepared by this method. Explain.

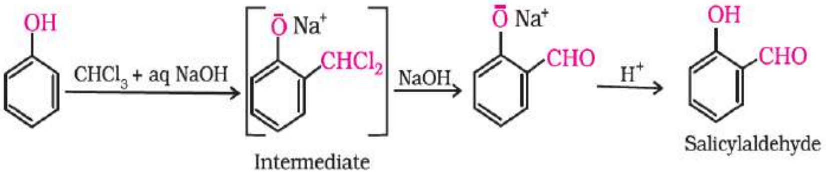
Answer: -In tert-butyl halides, elimination is favoured over substitution, so alkene is the major product formed and ether is not formed.



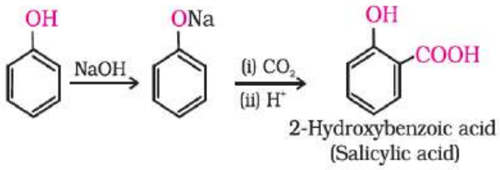
10. Write the equations involved in the following reactions:

a) Reimer - Tiemann reaction b) Kolbe‘s reaction

Answer:-a)



Answer:-b)



SHORT ANSWER TYPE QUESTIONS (3 MARKS)

1. Give reasons for the following:

a) Phenol is more acidic than ethanol.

b) Boiling point of ethanol is higher in comparison to methoxymethane.

c) $(CH_3)_3C-O-CH_3$ on reaction with HI gives $CH_3OH$and $(CH_3)_3C-I$ as the main products and not $(CH_3)_3C-OH$ and CH_3I.

Answer: -

a) It is because after the removal of H^+ion the phenoxide ion formed is more stable than ethoxide ion.

b) It is because ethanol molecules are more associated due to presence of intermolecular H-bonding, whereas methoxymethane does not have intermolecular H – bonding in it.

c) This reaction follows S_N1 mechanism and the $(CH_3)_3C^+$(Tert. carbocation) formed is more stable which reacts with Iodide to form tert. butyl iodide.

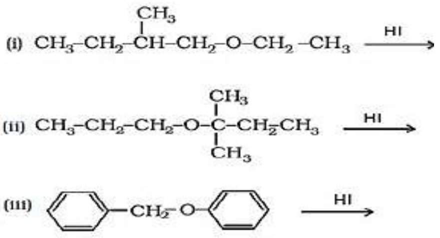
2. Give one chemical test each to distinguish between the following pairs of compounds: (i) Phenol and Benzoic acid (ii) Propan-1-ol and Propan-2-ol (iii) Methanol and ethanol.

Answer: -(i) Add $NaHCO_3$to each. Phenol will not react, whereas benzoic acid will give brisk effervescence due to CO_2.

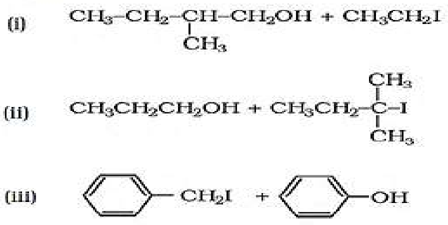
(ii) Add I_2 and NaOH to each one. Propan-2-ol will give yellow ppt. of iodoform (iodoform test), whereas propan-1-ol will not give yellow ppt.

(iii) Add I_2 and NaOH to each one. Ethanol will give yellow ppt. of iodoform (iodoform test), whereas methanol will not give yellow ppt.

3. Give the major products that are formed by heating each of the following ethers with HI.



Answer:-



4. Give the structures and IUPAC names of the products expected from the following reactions:

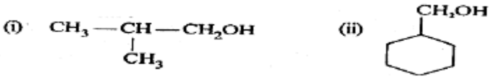
(a) Catalytic reduction of butanal.

(b) Hydration of propene in the presence of dilute sulphuric acid.

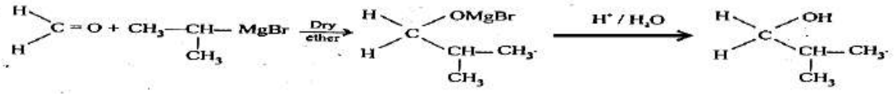
(c) Reaction of propanone with methyl magnesium bromide followed by hydrolysis.

Answer: -

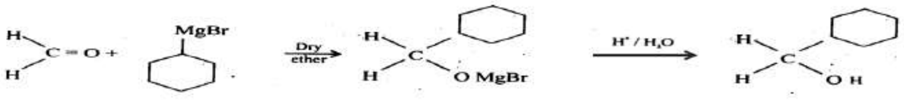
5. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?



Answer: -(i)



(ii)



LONG ANSWER TYPE QUESTIONS (5 MARKS)

(1) Give reasons for the following: -

(a) Alcohols are more soluble in water than the hydrocarbon of comparable molecular masses.

(b) Lower alcohols are soluble in water higher alcohols are not.

(c) Ortho nitro phenol is more acidic than Ortho-methoxyphenol.

(d) 2,4,6-trinitrophenol gives sodium bicarbonate test.

(e) Alcohol reacts with sodium metal whereas ether do not.

Answer: -(a)Alcohols have hydrogen bonding whereas hydrocarbons have weak van der Waal's force of attraction.

(b) Due to steric hindrance higher alcohols are incapable of forming hydrogen bonding with water and so are insoluble in water.

(c) Ortho nitrophenol is more acidic due to electron withdrawing effect of nitro group which facilitates release of proton

(d) 2,4,6-trinitrophenol is stronger acid due to presence of three nitro group showing electron withdrawing effect.

(e) Alcohol reacts with sodium metal due to presence of active hydrogen in it.

(2) Account for the following: -

(a) Phenol doesn’t react with $NaHCO_3$ whereas carboxylic acid reacts.

(b) Phenol is more easily nitrated than benzene.

(c) Sodium metal can be used for drying Di ethyl ether but not ethyl alcohol.

(d) Ether acts as Lewis base.

(e) Ortho nitro phenol is more volatile than para nitro phenol

Answer: -(a) Phenol is less acidic than carbonic acid whereas carboxylic acid is more acidic than carbonic acid.

(b) Phenol has activating group -OH which shows +R effect and so increases electron density at ortho and para position. so, phenol gets easily nitrated

(c) Sodium metal does not react with ether whereas it reacts with alcohol.

(d) Ether has two lone pair of electrons on oxygen and also two alkyl groups showing +I effect which helps in donation of electrons.

(e) Ortho nitro phenol has intramolecular hydrogen bonding and so molecules are less associated with each other whereas para nitro phenol has intermolecular hydrogen bonding.

CASE BASED QUESTIONS

Read the passage given below and answer the following questions:

Both alcohols and phenols are acidic in nature, but phenols are more acidic than alcohols. Acidic strength of alcohols mainly depends upon the inductive effect. Acidic strength of phenols depends upon a combination of both inductive effect and resonance effects of the substituent and its position on the benzene ring. Electron withdrawing groups increases the acidic strength of phenols whereas electron donating groups decreases the acidic strength of phenols. Phenol is a weaker acid than carboxylic acid.

1. Arrange the following compounds in increasing order of their acid strength: 1 mark
   Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol

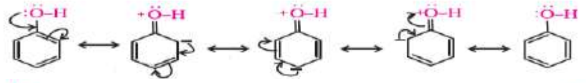
Answer: - Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol

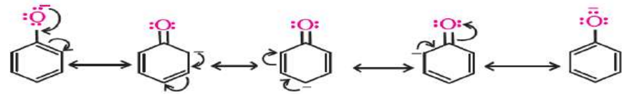
2. Alcohols act as Bronsted bases also. Explain 1 mark

Answer: -It is due to the presence of unshared electron pairs on oxygen, which makes them proton acceptors.

3. Draw the resonating structures of phenol and phenoxide ions 2 mark

Answer:-





OR

Explain why phenoxide ion is more stable than phenol.

Answer: -Resonance structures of phenol have charge separation due to which the phenol molecule is less stable than phenoxide ion which has charge delocalization.

MULTIPLE CHOICE QUESTIONS (ONE CORRECT ANSWER)

1. Phenol reacts with Br_2 in CS_2 at low temperature to give
   (a) o-Bromophenol
   (b) o-and p-bromophenols
   (c) p-Bromophenol
   (d) 2, 4, 6Tribromophenol

2. The correct order of boiling points of alcohol of the same molecular mass :
   (a) 1° > 2° > 3°
   (b) 3° > 2° > 1°
   (c) 2° > 1° > 3°
   (d) 2° > 3° > 1°

3. When Phenol is distilled with zinc dust, it gives
   (a) Benzene
   (b) Toluene
   (c) Benzaldehyde
   (d) Benzoic acid

4. Which of the following cannot be made by using Williamson Synthesis:
   (a) Methoxybenzene
   (b) Benzyl p-nitrophenyl ether
   (c) tert. butyl methyl ether
   (d) Ditert. butyl ether

5. Dehydration of alcohol to ethers is catalysed by
   (a) cone. H_2SO_4 at 413 K
   (b) Hot NaOH
   (c) Hot HBr
   (d) Hot HNO_3

ASSERTION-REASON TYPE QUESTION

Each question consists of two statements, namely, Assertion (A) and Reason (R).For selecting the correct answer, use the following code:

(a) Both Assertion (A) and Reason (R) are the true and Reason (R) is a correct explanation of Assertion (A).
(b) Both Assertion (A) and Reason (R) are the true but Reason (R) is not a correct explanation of Assertion (A).
(c) Assertion (A) is true and Reason (R) is false.
(d) Assertion (A) is false and Reason (R) is true.

1. Assertion (A): Phenol is more acidic than ethanol.
   Reason (R): Phenoxide ion is stabilized by resonance but ethoxide ion is not.
2. Assertion (A): Phenol gives o-and p- nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.
   Reason (R): -OH group in phenol is O- and P-directing.
3. Assertion (A): Alcohols have higher boiling point than ethers.
   Reason (R): They can form intermolecular hydrogen bonding.

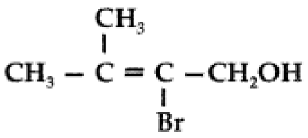
4. Assertion (A): O – nitrophenol is less volatile than P-nitrophenol.
   Reason (R): Intramolecular hydrogen bonding is present in O-nitrophenol while intermolecular hydrogen bonding is present in O-nitrophenol.

5. Assertion (A): Lucas test can be used to distinguish between 1-propanol and 2-propanol.
   Reason (R): Lucas test is based upon the difference in reactivity of primary, secondary and tertiary alcohols with conc. HCl and anhydrous $ZnCl_2$.

NOMENCLATURE TYPE QUESTIONS

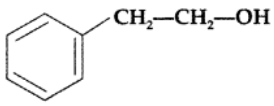
1. Write the IUPAC name of the following compounds.

(a)

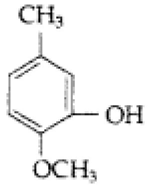


$CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2OH$

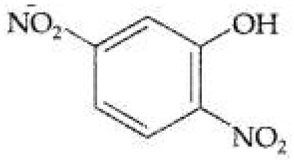
(b)



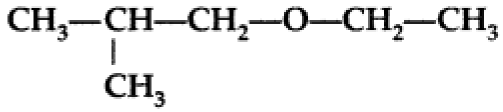
(c)



(d)



(e)



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3$

2. Write the structure of the following compound whose IUPAC name are as follows:
   - (a) 2-methylpropan- 2-ol molecule.
   - (b) Hex-l-en-3-ol
   - (c) Butane-1,3-diol
   - (d) 1-phenylpropan-2-ol
   - (e) 2-Methoxypropane

COMPETENCY BASED QUESTIONS

REASONING TYPE QUESTIONS

1. Ortho nitrophenol has lower boiling point than p-nitrophenol. Why?
2. Ortho-nitrophenol is more acidic than ortho-methoxyphenol. Why?
3. Of the two hydroxy organic compounds ROH and R'OH, the first one is basic and other is acidic in behaviour. How is R different from R'?
4. Which of the following isomers is more volatile : o-nitrophenol or p-nitrophenol?
5. Out of CH_3OH and C_6H_5OH which one is more acidic and why?
6. Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses?
7. The boiling point of ethanol is higher than that of methoxymethane?
8. The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle (190°28′)?
9. $(CH_3)_3C—O—CH_3$ on reaction with HI gives $(CH_3)_3C—I$ and $CH_3—OH$ as the main products and not $(CH_3)_3C—OH$ and $CH_3—I$?
10. $(CH_3)_3C—Br$ on reaction with sodium methoxide (Na+ _OCH$_3$) gives alkene as the main product and not an ether.

CHEMICAL TEST TYPE QUESTIONS

1. Give one chemical test to distinguish between: Propan-1-ol and Propan-2-ol
2. Give one chemical test to distinguish Phenol and Acetic acid.

3. Give one chemical test to distinguish Methanol and ethanol.
4. Give one chemical test each to distinguish between the following pair: (i)Phenol and Propan-1-ol (ii)Ethanol and dimethyl ether (iii) propan-1-ol and 2-methyl propan-2-ol
5. Give one chemical test to distinguish (i) Ethanol and propan-1-ol (ii) Propan-2-ol and pentan-3-ol
6. Give one chemical test to distinguish

(i) β – naphthol and ethanol

(ii) diethyl ether and n-butane

(iii) Diethyl ether and but-1-ene

NAME REACTION TYPE QUESTIONS

1. Write the following name reaction:

a) Kolbe's reaction

b) Reimer-Tiemann reaction

c) Williamson synthesis

d) Hydroboration

e) Esterification

MECHANISM TYPE QUESTIONS

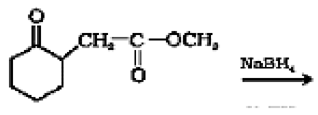
1. Write the mechanism of acid catalysed hydration of alkenes.
2. Write the mechanism of acid catalysed dehydration of ethanol to yield ethene at 443K.
3. Write the mechanism of dehydration of Alcohol to form Ether at 413 K.

CONVERSION TYPE QUESTIONS

1. How are the following conversions carried out? (i) Propane to Propan-2-ol (ii) Phenol to acetophenone (iii) Propene to propan-1-ol
2. How will you bring about the following conversions? (i) Ethyl chloride to Ethanal (ii) Phenol to salicylic acid (ii) Benzyl chloride to Benzyl alcohol
3. Write the chemical reactions for the following conversions. (i) Phenol to anisole (ii) Ethyl magnesium chloride to Propan-1-ol (iii) Cumene to phenol (iv) Phenol to picric acid

COMPLETE THE REACTIONS TYPE QUESTIONS

1. Predict the products of the following reactions :
   a) $CH_3 - CH_2 - CH_2 - CH_2 - OH + SOCl_2 \rightarrow$
   b) $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$
   c) $C_6H_5 - CH_2 - O - C_6H_5 + HI \xrightarrow{heat}$
   d) $CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+}$



ARRANGE IN CORRECT ORDER TYPE QUESTIONS

1. Arrange each set of compounds in the decreasing order of property indicated
   a) Methanol, ethanol, diethyl ether, ethylene glycol. (Boiling point)
   b) Phenol, O- nitrophenol, p- methoxyphenol, p- nitrophenol. (K_a value)
   c) Dimethyl ether, ethanol, phenol. (Solubility in water)
   d) 2-methylpropan-1-ol, n-Butanol, 2-methylpropan-2-ol (acidic nature)
   e) Ethanol, n-butane, water, propane. (Boiling point)
   f) Isobutane, n-butane, n- butanol, n-butyl chloride (boiling point)
   g) Water, ethanol, phenol (acidity character)
   h) Ethanol, isopropanol, tertiary butyl alcohol (reactivity towards Lucas reagent)
   i) Methanol, ethyl alcohol, ethylene glycol, glycerol. (Solubility in water)
   j) Phenol, o- nitrophenol, p-nitrophenol, m-nitrophenol (boiling point order)

WORD PROBLEM TYPE QUESTIONS

1. An organic compound A with molecular formula $C_8H_{16}O_2$ was hydrolysed with sulphuric acid to give a carboxylic acid B and alcohol C. Oxidation of C with chromic acid produced B. C on dehydration gives but-1-ene. Write reactions involved.
2. When an aromatic organic compound with molecular formula C_6H_6O is treated with bromine water, white precipitate of compound Y is obtained. Give the structure and the name of X and Y and write the chemical reaction involved.
3. An organic compound 'A' having molecular formula C_3H_6 on treatment with aq. H_2SO_4 give 'B' which on treatment with Lucas reagent gives 'C'. The compound 'C' on treatment with ethanolic KOH gives back 'A'. Identify A, B, C.
4. An organic compound A (C_6H_6O) gives a characteristic colour with aq.$FeCl_3$ solution. (A) On reacting with CO_2 and NaOH at 400 K under pressure gives (B) which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer. Deduce the structure of A, B, C& D.
5. An organic compound (X) when dissolved in ether and treated with magnesium metal forms a compound Y. The compound, Y, on treatment with acetaldehyde and the product on acid hydrolysis gives isopropyl alcohol. Identify the compound X. What is the general name of the compounds of the type Y.

ANSWERS

MULTIPLE CHOICE QUESTIONS (ONE CORRECT ANSWER)

1. (b)o-and p-bromophenols
2. (a) 1° > 2° > 3°
3. (a) Benzene
4. (d) Ditert. butyl ether
5. (a) conc. H_2SO_4 at 413 K

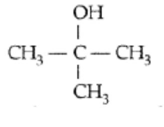
ASSERTION-REASON TYPE QUESTION

1. a 2.d 3. c 4. d 5. a

NOMENCLATURE TYPE QUESTIONS

1. (a) 2-bromo-3-methylbut-2-en-1-ol (b)2. 2-Phenylethanol (c)2-Methoxy-5-methyl phenol
(d)2, 5-dinitrophenol (e)1-Ethoxy-2-methylpropane

2 (a)

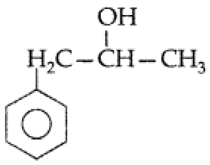


$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3$

(b) $CH_2 = CH - CH(OH) - CH_2 - CH_2 - CH_3$

(c) CH_3-CH (OH)-CH_2-CH_2OH

(d)



(e)CH_3-O-CH $(CH_3)_2$

REASONING TYPE QUESTIONS

1. Intermolecular hydrogen bonding
2. $-NO_2$ is EWG while OCH_3 is EDG so H^+ release is easy from o-nitrophenol.
3. Where R=alkyl, ROH behaves as *Bronsted* base and where R=aryl, R'OH behaves as a Bronsted acid.
4. o-nitrophenol due to intramolecular H-bonding.
5. Phenol, phenoxide ion is resonance stabilized.
6. Alcohols can form H-bonds with water.
7. intermolecular H-bonding.
8. Repulsion between lone pair of electrons of oxygen of alcohols.
9. $(CH_3)_3$ is tert. Carbocation which is more stable for S_N1 reaction.
10. Tert. Alkyl halide undergo elimination in the presence of strong nucleophile and form alkene.

CHEMICAL TEST TYPE QUESTIONS

1. Propan-2-ol (2*) alcohol takes 5 minutes to give turbidity with Lucas reagent ($HCl/ZnCl_2$)
Whereas propan-1-ol(1*) does not give test

$CH_3CH(OH)CH_3 + HCl/ZnCl_2 \rightarrow CH_3CH(Cl)CH_3$ (five minutes)

2. Add $NaHCO_3$ to each. Phenol will not react, whereas acetic acid will give brisk effervescence due to CO_2.(comparison of acidic nature)
$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + H_2O + CO_2$ (brisk effervescence)

3. Add I_2 and NaOH to each one. Ethanol will give yellow ppt. of iodoform (iodoform test), whereas methanol will not give yellow ppt.
CH_3CH_2OH ---- $I_2/NaOH \rightarrow CHI_3$ (YELLOW PPT)

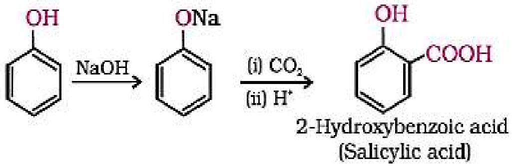
4. (i) Phenol gives violet colouration with neutral $FeCl_3$ where prop-1-ol does not
$6\ C_6H_5OH + FeCl_3 \rightarrow [Fe(O\ C_6H_5)_6]^{-3} + 3H^+ + 3HCl$
(ii) Ethanol gives yellow ppt in Iodoform test where di methyl ether does not
$CH_3CH_2OH + I_2/NaOH \rightarrow CHI_3$ (YELLOW PPT)
(iii)2-methylpropan-2-ol gives turbidity immediately with Lucas reagent while propan-1-ol does not.

5. (i)Both the alcohols are primary alcohols so can be distinguished by Iodoform test
$CH_3CH_2OH + I_2/NaOH \rightarrow CHI_3$ (YELLOW PPT) Prop-1-ol does not perform Iodoform test
(ii) Propan-2-ol gives yellow ppt in Iodoform test where Pentan-3-ol does not
$CH_3CH(OH)CH_3 + I_2/NaOH \rightarrow CHI_3$ (yellow ppt)

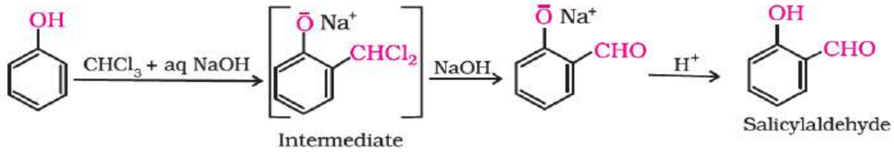
6. (i) β – naphthol gives violet colouration with neutral $FeCl_3$ where Ethenol does not
(ii)Di ethyl ether dissolves in con. H_2SO_4 where n-butane does not
(iii)But-1-ene decolourises potassium permanganate solution where di ethyl ether does not.

NAME REACTION TYPE QUESTIONS

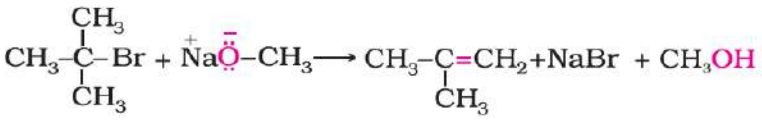
a. Kolbe's reaction



b. Reimer-Tiemann reaction



c. Williamson synthesis


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + \overset{+}{Na}\overset{-}{\ddot{O}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + NaBr + CH_3OH$$

2-Methylpropene

d. Hydroboration

$$CH_3-CH=CH_2 + (H-BH_2)_2 \longrightarrow (CH_3-CH_2-CH_2)_3B \xrightarrow{3H_2O_2,\ \bar{O}H} 3CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propan-1-ol

e. Esterification

$$Ar/ROH + R'-COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$$

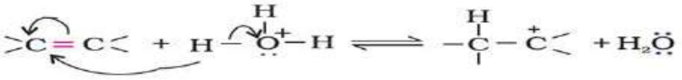
$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

MECHANISM TYPE QUESTIONS

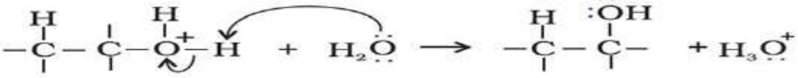
1. Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ or H^+.

$H_2O + H^+ \rightarrow H_3O^+$



Step 2: Nucleophilic attack of water on carbocation.

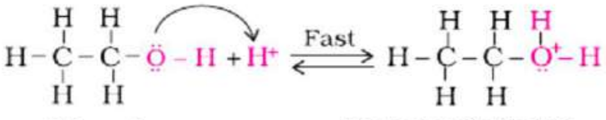
Step 3: Deprotonation to form an alcohol.



2.

Mechanism

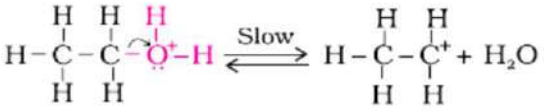
Step 1: Formation of protonated alcohol.



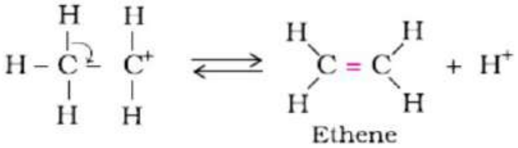
Ethanol

Protonated alcohol
(Ethyl oxonium ion)

Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



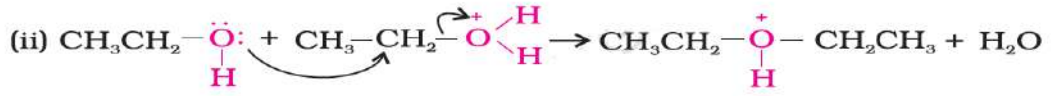
Step 3: Formation of ethene by elimination of a proton.



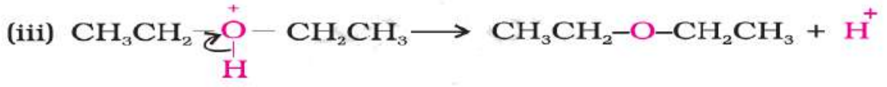
Ethene

3. **Mechanism**

$$\text{(i) } CH_3{-}CH_2{-}\ddot{O}{-}H + H^+ \longrightarrow CH_3{-}CH_2{-}\overset{H}{\overset{+}{O}}{-}H$$



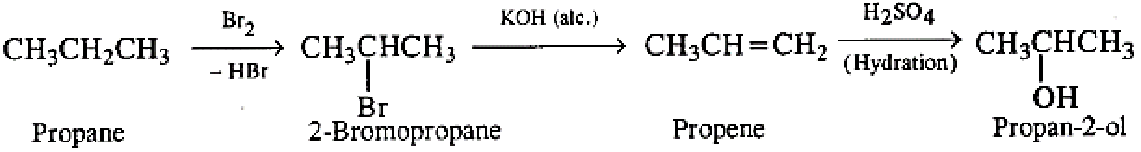
$$\text{(ii) } CH_3CH_2{-}\underset{H}{\ddot{O}}: + CH_3{-}CH_2{-}\overset{+}{O}{<}^{H}_{H} \longrightarrow CH_3CH_2{-}\underset{H}{\overset{+}{O}}{-}CH_2CH_3 + H_2O$$



$$\text{(iii) } CH_3CH_2{-}\underset{H}{\overset{+}{O}}{-}CH_2CH_3 \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + H^+$$

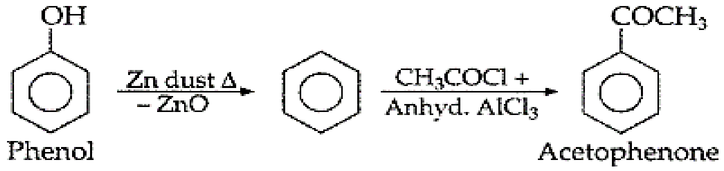
CONVERSION TYPE QUESTIONS

1 (i)



$$CH_3CH_2CH_3 \xrightarrow[-HBr]{Br_2} CH_3\underset{Br}{C}HCH_3 \xrightarrow{KOH\ (alc.)} CH_3CH{=}CH_2 \xrightarrow[(Hydration)]{H_2SO_4} CH_3\underset{OH}{C}HCH_3$$

(ii)



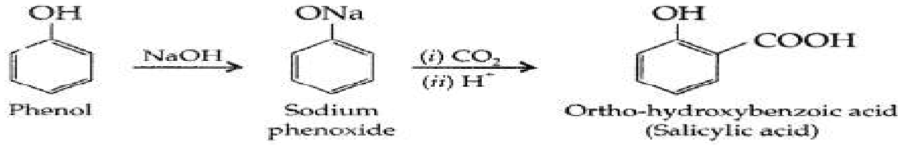
(iii)

$$CH_3CH{=}CH_2 \xrightarrow[(Anti\text{-}Mark\ addn.)]{HBr/Peroxide} CH_3CH_2CH_2Br \xrightarrow[\Delta\ (Hydrolysis)]{Aq.\ KOH} CH_3CH_2CH_2OH$$

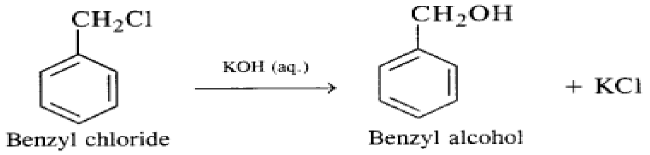
2 (i)

$$CH_3CH_2Cl \xrightarrow{Aq.KOH} CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO$$

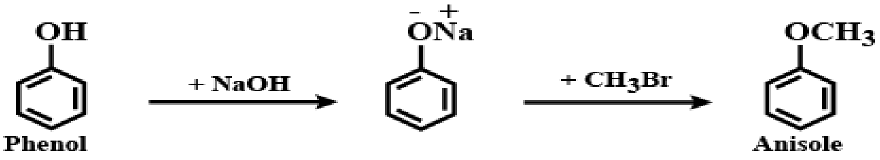
(ii)



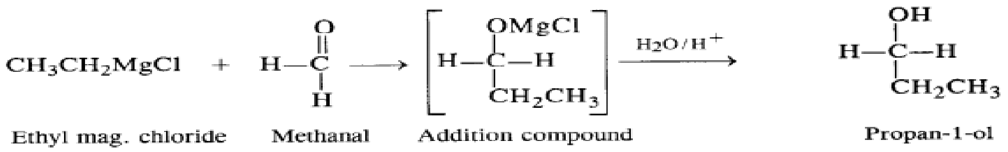
(iii)



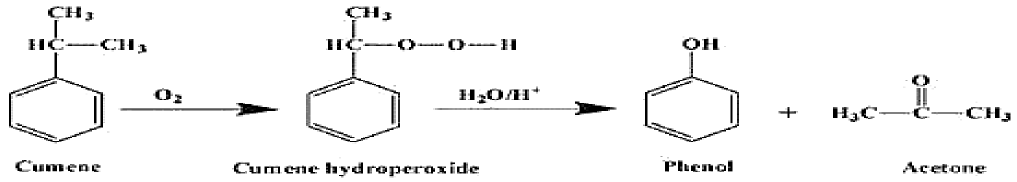
3 (i)



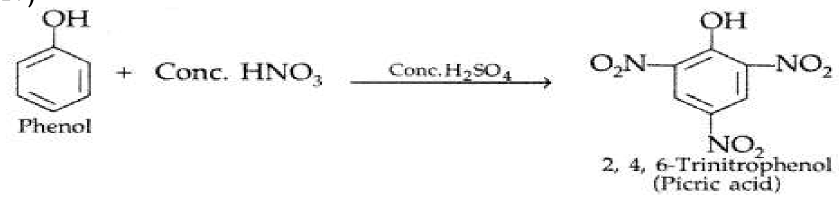
(ii)



(iii)

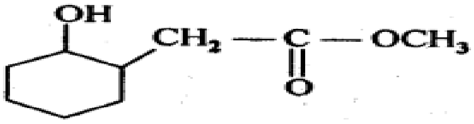


(iv)



COMPLETE THE REACTIONS TYPE QUESTIONS

a) $CH_3 - CH_2 - CH_2 - CH_2 - Cl + SO_2 + HCl$
b) $CH_3 - CH_2 - CH_2 - OH + CH_3\,Br$
c) $C_6H_5 - CH_2$ -I + $C_6H_5 - OH$
d) d.CH_2 - CH (OH) - CH_3
e)

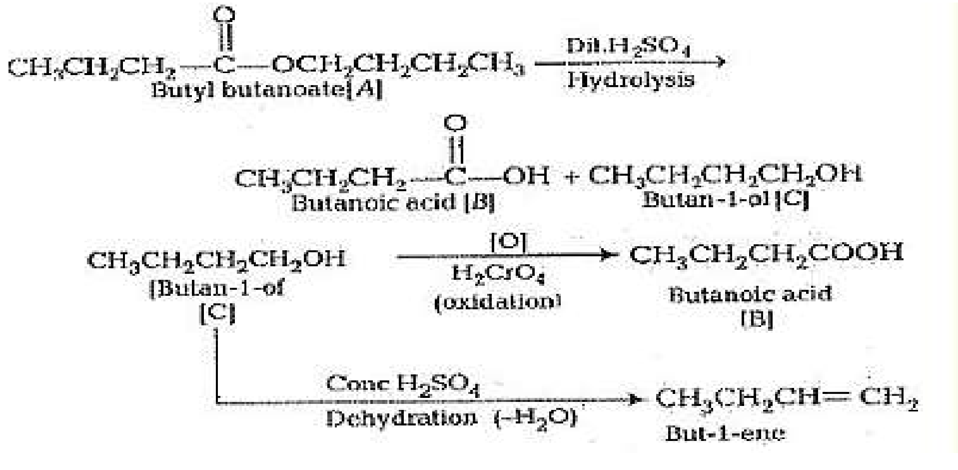


ARRANGE IN CORRECT ORDER TYPE QUESTIONS

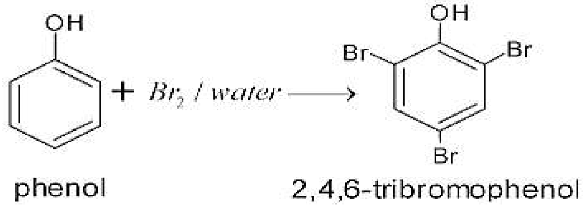
1.
   - a) Ethylene glycol > diethyl ether > ethanol > Methanol.
   - b) O- nitrophenol>, p- nitrophenol> Phenol > p- methoxyphenol.
   - c) Ethanol > phenol > Dimethyl ether.
   - d) n-Butanol> 2-methylpropan-1-ol > 2-methylpropan-2-ol.
   - e) Water > Ethanol > n-butane > propane.
   - f) n- butanol> n-butyl chloride > n-butane >Isobutane.
   - g) phenol> Water > ethanol.
   - h) tertiary butyl alcohol > isopropanol > Ethanol.
   - i) glycerol> ethylene glycol > methanol > ethyl alcohol.
   - j) p-nitrophenol> o- nitrophenol> phenol

WORD PROBLEM TYPE QUESTIONS

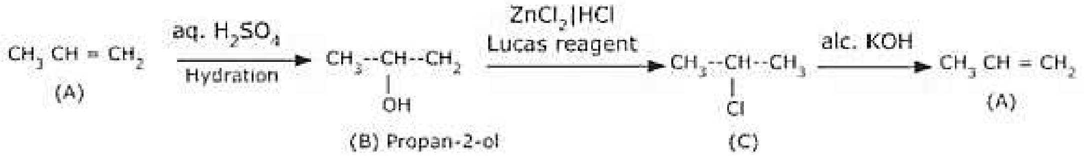
1. A - Butylbutanoate , B - Butanoic acid , C - Butan-1-ol



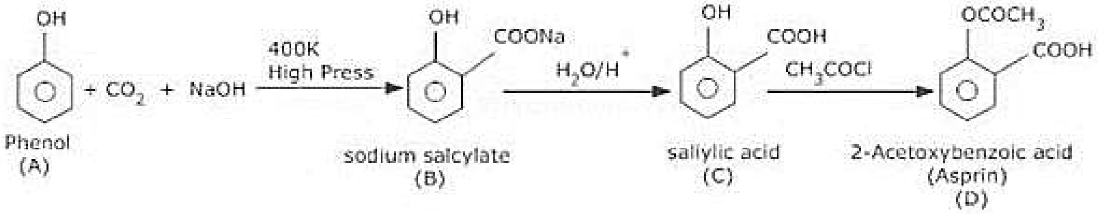
2.X - C_6H_5OH (Phenol)   Y- $C_6H_2Br_3OH$ (2,4,6-tribromophenol)



3. A- Propene   B- Propan-2-ol   C - 2-chloropropane



4. A- Phenol   B - Sodium salicylate   C- Salicylic acid   D- Aspirin



5.The compound X is CH_3Br (bromomethane) and Y is CH_3MgBr (Methyl magnesium bromide) The compounds of the type 'Y' are called Grignard reagent. Y has one C atom and acetaldehyde has 2 C atoms so 3 C containing isopropyl alcohol is produced on acid hydrolysis.

COMPETENCY/ CASE BASED QUESTIONS

1. Read the passage given below and answer the following questions: An organic compound (A) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (A) on treatment with CO_2 and NaOH at 400 K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

1. Name the compound A.
2. How many carbon atoms are there in compound D?
3. Write the equation and name of reaction involved in conversion (A) to (C)

OR

Write the equation for reaction of compound A with neutral $FeCl_3$

2. Read the passage given below and answer the following questions:

Alcohol and phenols are acidic in nature. Electron withdrawing group in phenol increases its acidic strength whereas electron donating groups decreases it. Alcohols undergo nucleophilic substitution reactions with hydrogen halide to give alkyl halide. Oxidation of primary alcohols yields aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of –OH groups in phenols activates the ring towards electrophilic substitution. various important products are obtained from phenol like salicylaldehyde, salicylic acid, picric acid.

1.Give the structure of alcohol which is resistant to oxidation?

2.Name any one group that increases the acidic character of phenol.

3.Consider the following equation:

X←----(i)NaOH,CO_2----------   **C_6H_5OH**   ---------(i)$CHCl_3$+ NaOH-----→ Y

(ii)H^+ (ii) H^+

Identify X and Y

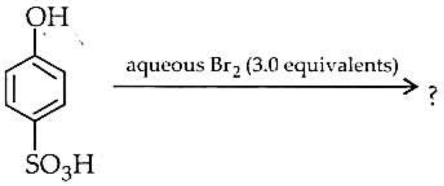
OR

p-nitrophenol is a stronger acid than phenol while p-cresol is a weaker acid. why?

3. Read the passage given below and answer the following questions: Although chlorobenzene is inert towards nucleophilic substitution, however it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. As far as electrophilic substitution in phenol is concerned the - OH group is an activating group, hence, its presence enhances the electrophilic substitution at o- and p-positions.

1. Name the reaction mechanism involved in conversion of chlorobenzene to phenol?
2. Phenol undergoes electrophilic substitution more readily than benzene. why?
3.Phenol on treatment with excess of conc. HNO_3 gives a yellow-coloured explosive compound. Name the compound and give reaction involved?

OR



Give major product of reaction?

ANSWERS

Case based question 1

1. Phenol
2. 9($C_9H_8O_4$)
3. Kolbe reaction

Or

$6\ C_6H_5OH + FeCl_3 \text{--------}\rightarrow [Fe(O\ C_6H_5)_6]^{-3} + 3H^+ + 3HCl$

Case based question 2

1.$(CH_3)_3C\text{-}OH$ (2-Methyl propane -2-ol)

2.Nitro group ($-NO_2$)

3.X= salicylic acid, Y= salicylic aldehyde

Or

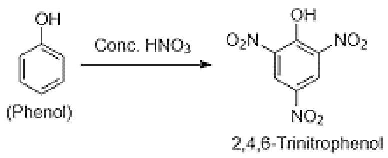
p-nitro phenol is stronger acid than p- cresol because Nitro group is electron withdrawing group which reduces electron density on benzene ring resulting in increase in acidic strength.

Case based question 3

1.Unimolecular nucleophilic substitution (S_N1)

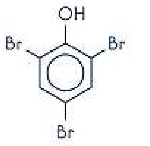
2.Phenol readily undergoes nucleophilic substitution because hydroxy group in phenol is activation group, which increases electron density on benzene ring.

3.Picric acid (2,4,6 tri nitro phenol)



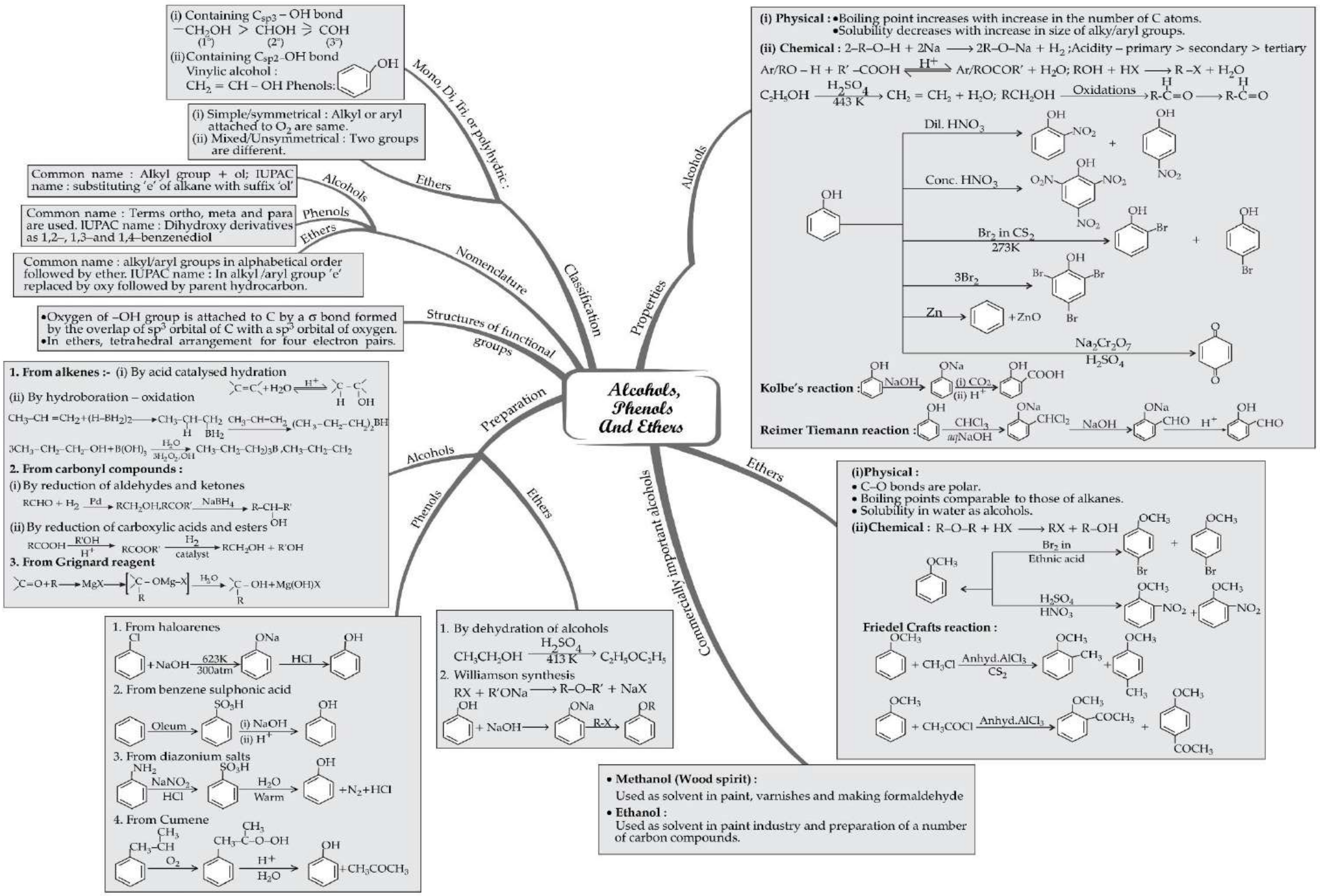
2,4,6-Trinitrophenol
(Picric acid)

Or



2,4,6-Tribromophenol

MIND MAP : LEARNING MADE SIMPLE



(i) Containing C_{sp3} – OH bond
$-CH_2OH > CHOH \geqslant COH$
(1°) (2°) (3°)
(ii) Containing C_{sp2}-OH bond
Vinylic alcohol :
$CH_2 = CH – OH$ Phenols:

(i) Simple/symmetrical : Alkyl or aryl attached to O_2 are same.
(ii) Mixed/Unsymmetrical : Two groups are different.

Common name : Alkyl group + ol; IUPAC name : substituting 'e' of alkane with suffix 'ol'

Common name : Terms ortho, meta and para are used. IUPAC name : Dihydroxy derivatives as 1,2–, 1,3–and 1,4–benzenediol

Common name : alkyl/aryl groups in alphabetical order followed by ether. IUPAC name : In alkyl /aryl group 'e' replaced by oxy followed by parent hydrocarbon.

- Oxygen of –OH group is attached to C by a σ bond formed by the overlap of sp^3 orbital of C with a sp^3 orbital of oxygen.
- In ethers, tetrahedral arrangement for four electron pairs.

1. From alkenes :- (i) By acid catalysed hydration

(ii) By hydroboration – oxidation

$CH_3–CH = CH_2 + (H–BH_2)_2 \longrightarrow CH_3–CH–CH_2 \xrightarrow{CH_3–CH=CH_2} (CH_3–CH_2–CH_2)_2BH$

$3CH_3–CH_2–CH_2–OH + B(OH)_3 \xrightarrow[3H_2O_2, OH]{H_2O} CH_3–CH_2–CH_2)_3B, CH_3–CH_2–CH_2$

2. From carbonyl compounds :

(i) By reduction of aldehydes and ketones

$RCHO + H_2 \xrightarrow{Pd} RCH_2OH, RCOR' \xrightarrow{NaBH_4} R–CH(OH)–R'$

(ii) By reduction of carboxylic acids and esters

$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[catalyst]{H_2} RCH_2OH + R'OH$

3. From Grignard reagent

$>C=O + R–MgX \longrightarrow [>C(R)–OMg–X] \xrightarrow{H_2O} >C(R)–OH + Mg(OH)X$

1. From haloarenes
2. From benzene sulphonic acid
3. From diazonium salts
4. From Cumene

1. By dehydration of alcohols

$CH_3CH_2OH \xrightarrow[413 K]{H_2SO_4} C_2H_5OC_2H_5$

2. Williamson synthesis

$RX + R'ONa \longrightarrow R–O–R' + NaX$

(i) Physical :
- Boiling point increases with increase in the number of C atoms.
- Solubility decreases with increase in size of alky/aryl groups.

(ii) Chemical : $2–R–O–H + 2Na \longrightarrow 2R–O–Na + H_2$;Acidity – primary > secondary > tertiary

$Ar/RO – H + R' –COOH \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + H_2O$; $ROH + HX \longrightarrow R –X + H_2O$

$C_2H_5OH \xrightarrow[443 K]{H_2SO_4} CH_2 = CH_2 + H_2O$; $RCH_2OH \xrightarrow{Oxidations} R\text{-}\overset{H}{C}{=}O \longrightarrow R\text{-}\overset{H}{C}{=}O$

Kolbe's reaction :

Reimer Tiemann reaction :

(i)Physical :
- C–O bonds are polar.
- Boiling points comparable to those of alkanes.
- Solubility in water as alcohols.

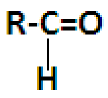
(ii)Chemical : $R–O–R + HX \longrightarrow RX + R–OH$

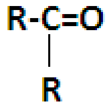
Friedel Crafts reaction :

- **Methanol (Wood spirit) :**
Used as solvent in paint, varnishes and making formaldehyde
- **Ethanol :**
Used as solvent in paint industry and preparation of a number of carbon compounds.

8. Aldehydes, Ketones & Carboxylic Acids

Quick Revision Notes:



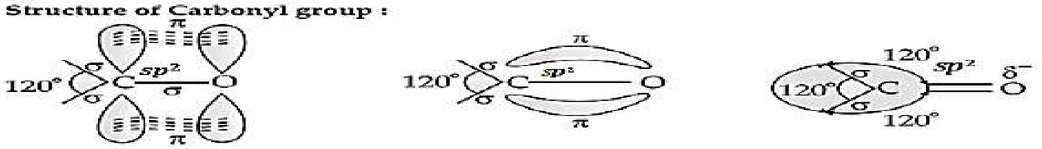


General formula: $C_nH_{2n}O$ having >C=O group.

Aldehydes: where *R* = H, e.g., CH_3CHO, HCHO, C_6H_5CHO, etc.

Ketones: where *R* = alkyl or aryl group. e.g., CH_3COCH_3, $CH_3COC_6H_5$, $C_6H_5COC_6H_5$, etc.

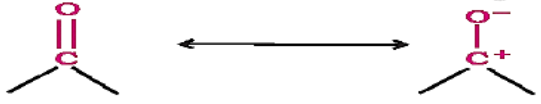
Structure:



1] In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones; it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively.

2] Aldehydes, Ketones are important classes of organic compounds containing carbonyl groups. They are highly polar molecules. They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers. Lower members are soluble in water because they can form H-bond with water. Higher members are insoluble in water due to large size of their hydrophobic group.

3] The carbonyl carbon atom is sp2 -hybridised and forms three sigma (σ) bonds. The π Electron cloud of >C=O is unsymmetrical. On the other hand, due to same electronegativity of the two carbon atoms, the π-electron of the >C=C< bond is symmetrical. The structure of the carbonyl group in aldehydes and Ketones is, not entirely adequately represented by >C=O, nor by the alternative>C+— O-. The real structure or resonance hybrid lies somewhere between the following structure:

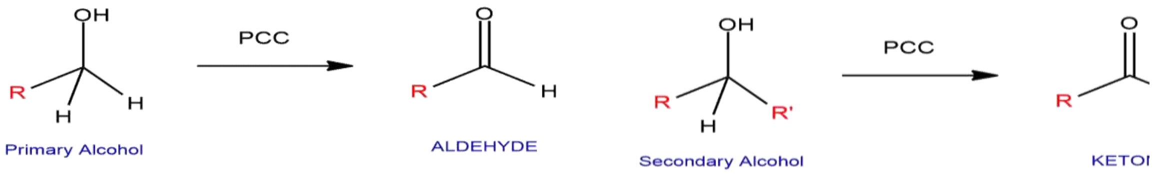


(A) (B)

4] The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –al and –one respectively.

5] **General Methods of Preparation**:

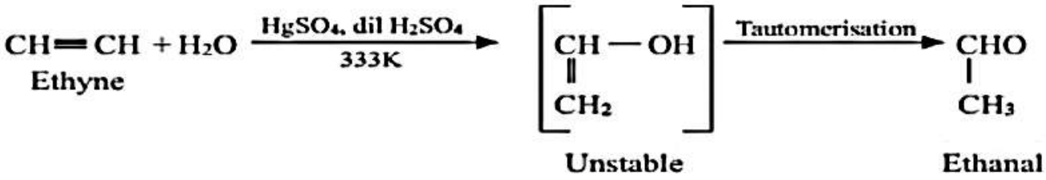
A} By oxidation of alcohols Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.



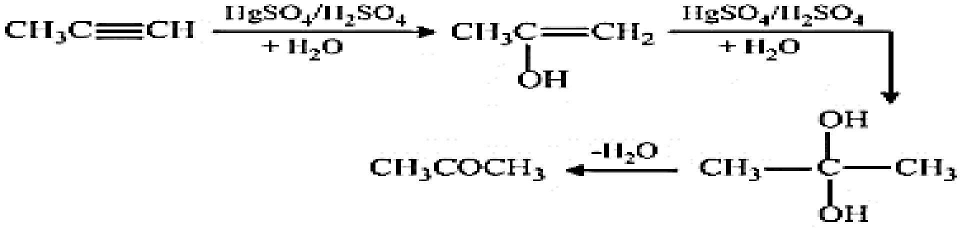
Controlled oxidation of alcohols:

B} By hydration of alkynes:

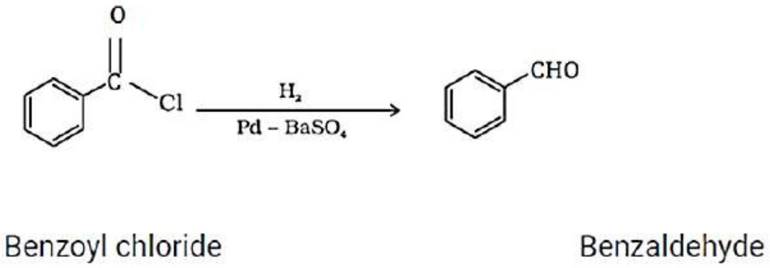
Ethyne on hydration with $HgSO_4$/dil.H_2SO_4 at 333 K forms acetaldehyde.



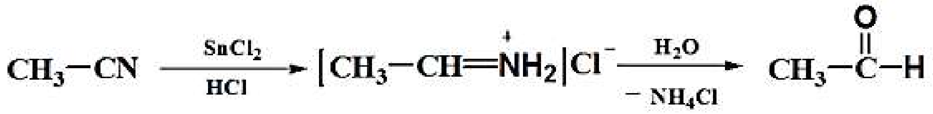
Propyne on hydration gives propanone.



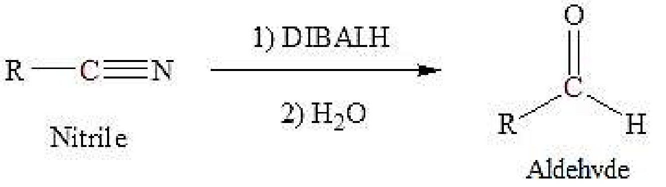
C} By Rosenmund reduction- Hydrogenation of acyl chloride over palladium on barium sulphate gives aldehyde.



D} Stephen Reaction: Reduction of nitriles in presence of stannous chloride in presence of HCl gives imine which on hydrolysis gives corresponding aldehyde.



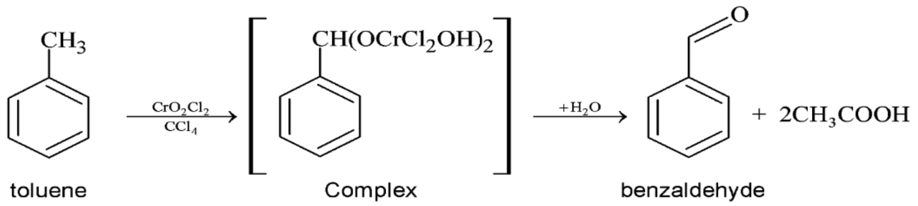
Nitriles are selectively reduced by DIBAL-H (Diisobutylaluminium hydride) to aldehydes.



E} From Hydrocarbons:

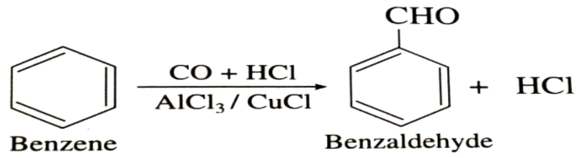
(i) By oxidation of methyl benzene:

Etard Reaction: Chromyl chloride (CrO_2Cl_2) oxidizes methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.



Gattermann-Koch reaction:

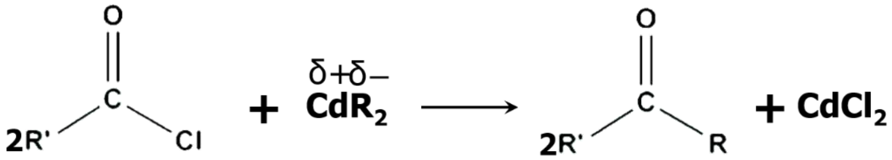
Benzene or its derivatives on treatment with carbon monoxide and HCl in presence of anhydrous aluminium chloride or cuprous chloride (CuCl) gives benzaldehyde or substituted benzaldehydes.



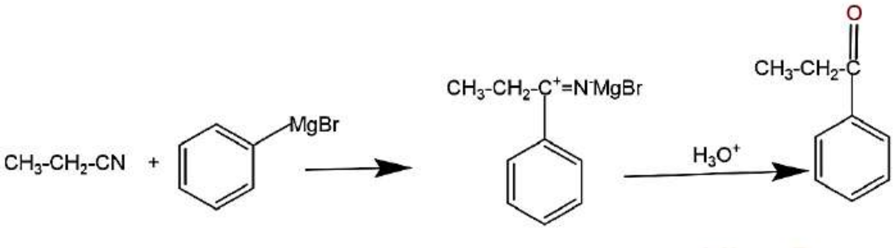
Oxidation of secondary alcohols in presence of oxidizing agent like $K_2Cr_2O_7/H_2SO_4$, $KMnO_4$, CrO_3 gives ketones.

$R_2CH(OH) \rightarrow RCOR$

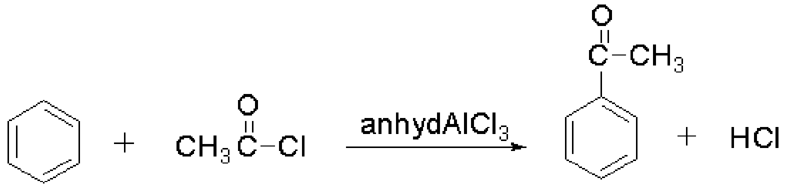
Acyl chloride on treatment with dialkyl cadmium (prepared by reaction of cadmium chloride with Grignard reagent gives ketone.



From nitriles:
Nitriles on treatment with Grignard reagent followed by hydrolysis give ketones.



By Friedel Crafts acylation reaction:
Benzene or substituted benzene on treatment with acid chloride in presence of anhydrous aluminium chloride forms ketone.



PROPERTIES:

*The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions. Also, their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

*The lower members of aldehydes and ketones such as methanal, ethanal and propanone are miscible with water in all proportions, because they form hydrogen bond with water

NUCLEOPHILIC ADDITION REACTIONS

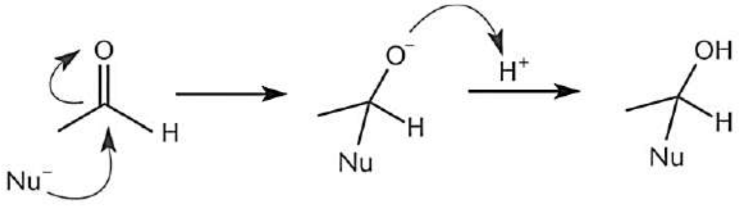
*Since aldehydes and ketones both possess the carbonyl functional group, they undergo similar chemical reactions Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two relatively large substituents in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent. Electronically, aldehydes are more reactive than ketones because two alkyl groups reduce the electrophilicity of the carbonyl carbon more effectively than in former.

Order of reactivity of aldehydes and ketones towards nucleophilic addition is :

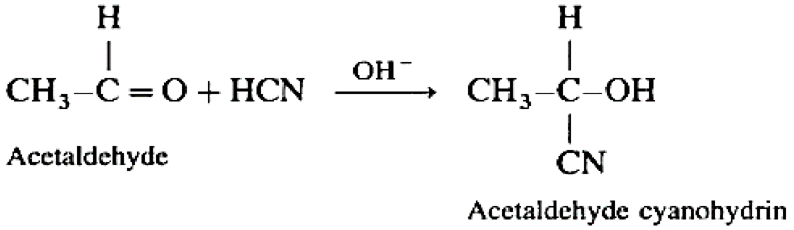
$HCHO > CH_3CHO > CH_3CH_2CHO$.

$HCHO > RCHO > R\ CO\ R$.

$ArCHO > Ar\ COR > Ar\ CO\ Ar$.

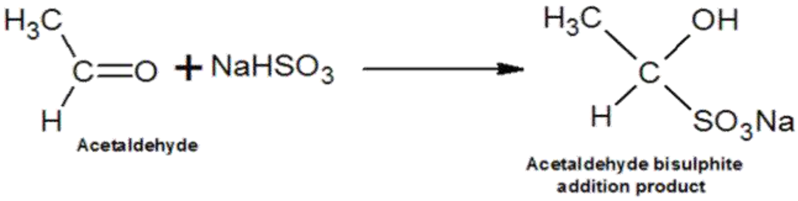


With HCN

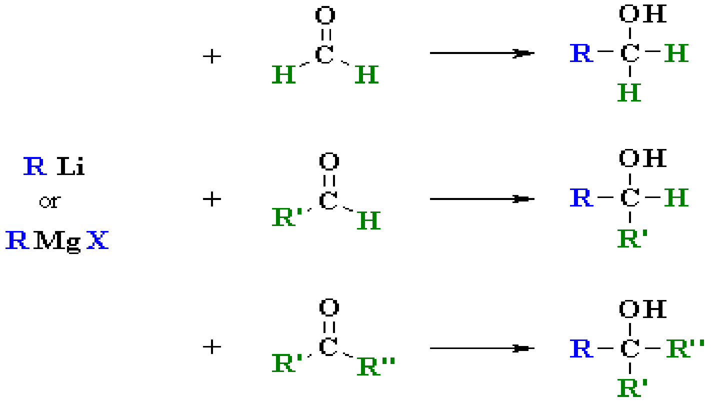


$$CH_3-\overset{\displaystyle H}{\overset{|}{C}}=O + HCN \xrightarrow{OH^-} CH_3-\underset{\displaystyle CN}{\underset{|}{\overset{\displaystyle H}{\overset{|}{C}}}}-OH$$

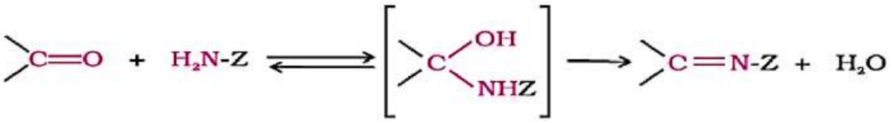
With Sodium bisulphite

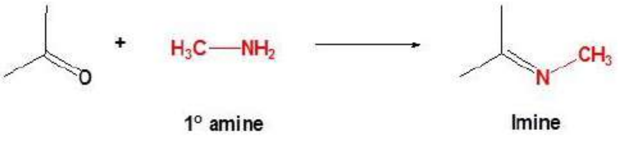


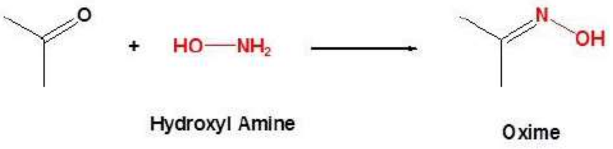
With Grignard reagent to produce alcohols

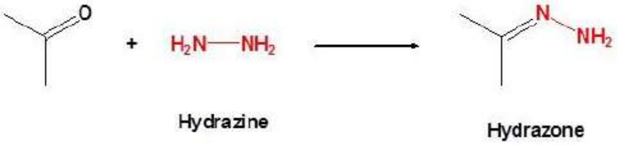


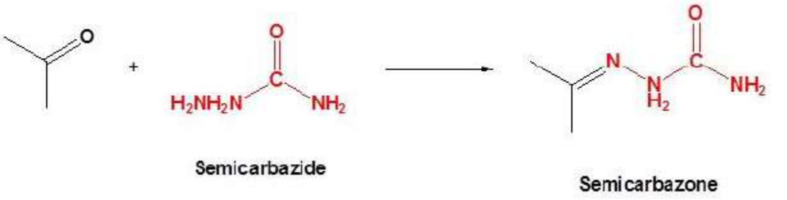
With ammonia derivatives





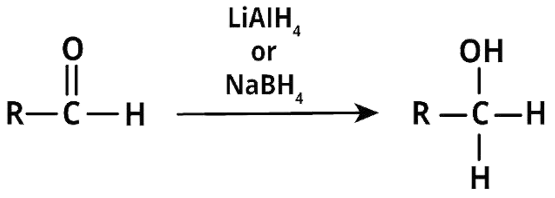


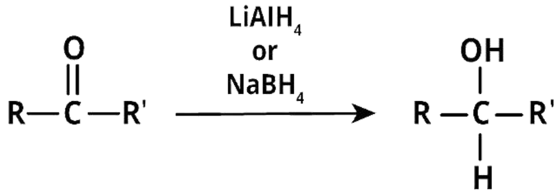




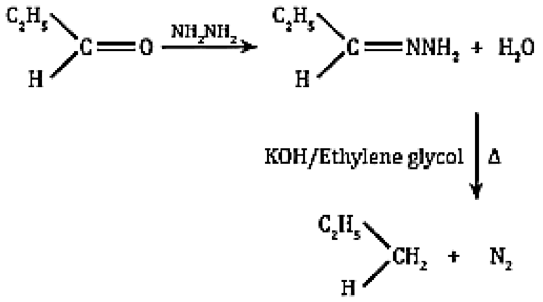
REDUCTION OF ALDEHYDES AND KETONES

Catalytic reduction to obtain alcohols





Wolff -Kishner Reduction- to obtain alkane



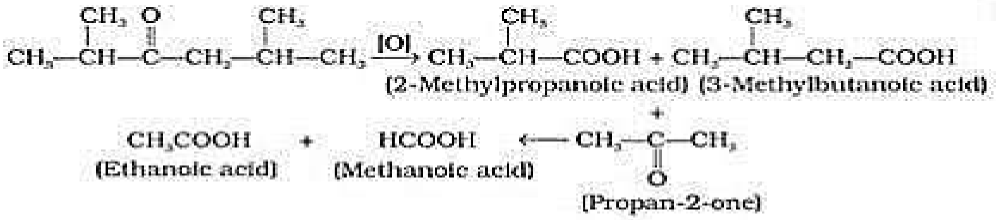
Clemmensen Reduction to obtain alkane

Oxidation of aldehydes and ketones:

(i) Aldehydes are oxidized to acids in presence of oxidising agents HNO_3, $K_2Cr_2O_7$, $KMnO_4$

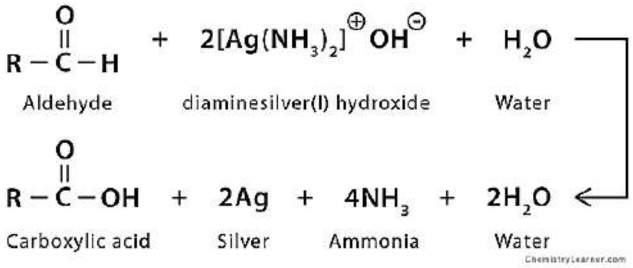
$$R\text{-}CHO \xrightarrow{[O]} R\text{-}COOH$$

ii)Ketones are oxidized under drastic conditions i.e. with powerful oxidising agents like HNO_3, $K_2Cr_2O_7$, $KMnO_4$. at higher temperature.: ketones give mixture of carboxylic acids.



Test to distinguish aldehydes and ketones:

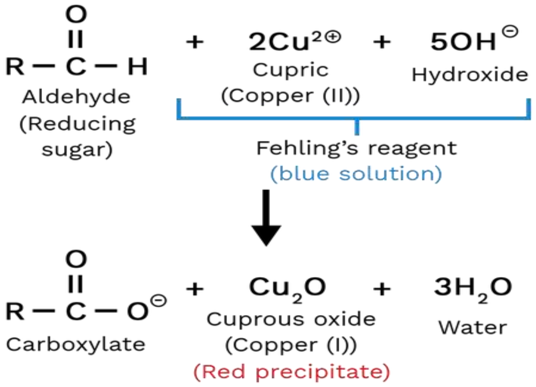
1]Tollen's test: When an aldehyde is heated with Tollen's reagent it forms silver mirror. Tollen's reagent is ammoniacal solution of $AgNO_3$. Ketones do not form silver mirror and hence do not give this test.



$$R-\overset{O}{\overset{\|}{C}}-H + 2[Ag(NH_3)_2]^{\oplus}OH^{\ominus} + H_2O \rightarrow R-\overset{O}{\overset{\|}{C}}-OH + 2Ag + 4NH_3 + 2H_2O$$

2)Fehling's test: When an aliphatic aldehyde is heated with Fehling's reagent it forms reddish brown precipitates of cuprous oxide. Fehling's reagent: Fehling solution A (aqueous solution of $CuSO_4$) + Fehling solution B (alkaline solution of sodium potassium tartarate)

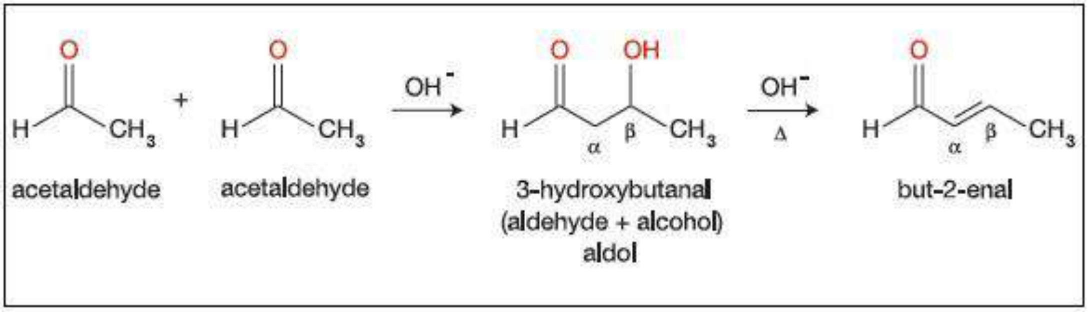
Ketones do not give this test.



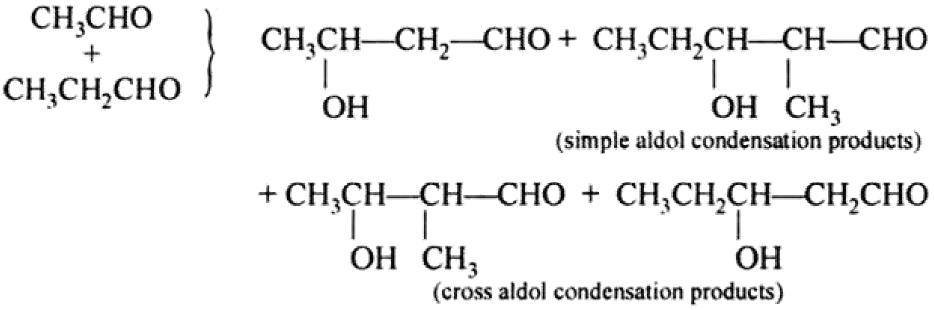
$$R-\overset{O}{\overset{\|}{C}}-H + 2Cu^{2\oplus} + 5OH^{\ominus} \rightarrow R-\overset{O}{\overset{\|}{C}}-O^{\ominus} + Cu_2O + 3H_2O$$

ALDOL CONDENSATION:

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali to form β-hydroxy aldehydes(aldol) or β –hydroxy ketones (ketol).



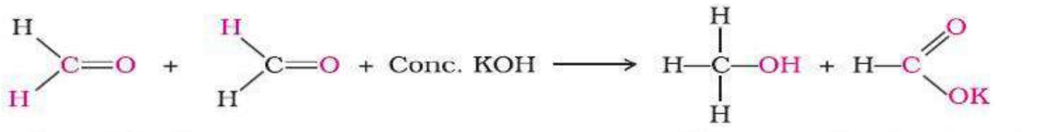
Cross aldol condensation: Aldol condensation between two different aldehydes and ketones is called aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



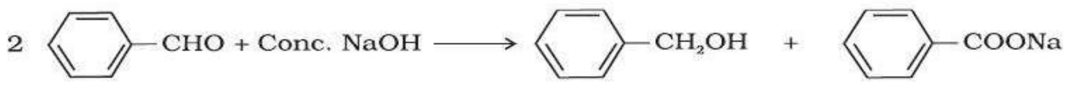
$$\left.\begin{array}{c}CH_3CHO\\+\\CH_3CH_2CHO\end{array}\right\} \underset{OH}{CH_3CH}-CH_2-CHO + CH_3CH_2\underset{OH}{CH}-\underset{CH_3}{CH}-CHO + \underset{OH}{CH_3CH}-\underset{CH_3}{CH}-CHO + CH_3CH_2\underset{OH}{CH}-CH_2CHO$$

Cannizzaro Reaction

Aldehydes which do not contain hydrogen when treated with a concentrated solution of an alkali undergo self oxidation-reduction. As a result, one molecule of aldehyde is reduced to corresponding alcohol while the other molecule is oxidized to the corresponding acid.

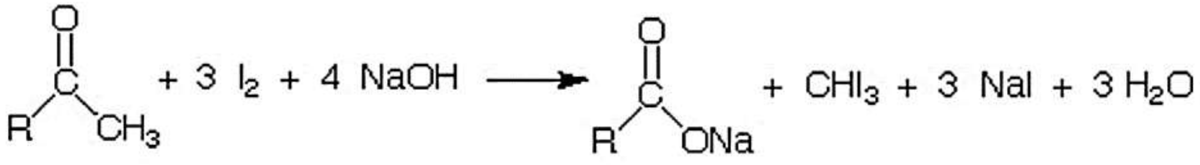


Formaldehyde Methanol Potassium formate



Benzaldehyde Benzyl alcohol Sodium benzoate

Haloform reaction: Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom i.e. methyl ketones are oxidised by sodium hypohalite to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform.



Iodoform Test using Iodine and Sodium Hydroxide

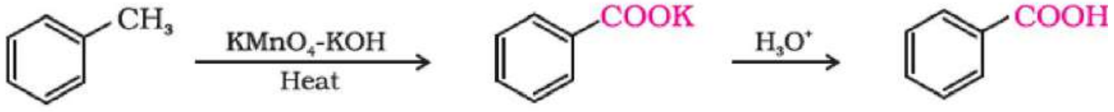
Carboxylic Acids: Carboxylic acids are the compounds containing the carboxyl functional group (-COOH).

Preparation of carboxylic acid:

(i) From alcohols: Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate ($KMnO_4$) in neutral, acidic or alkaline media or by potassium dichromate ($K_2Cr_2O_7$) and chromium trioxide (CrO_3) in acidic media.

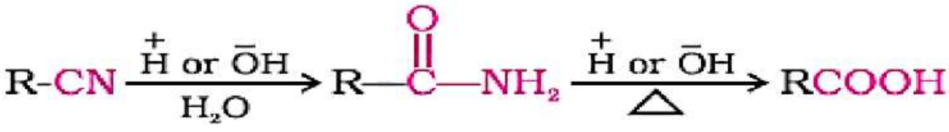
$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

From alkyl benzenes: Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.



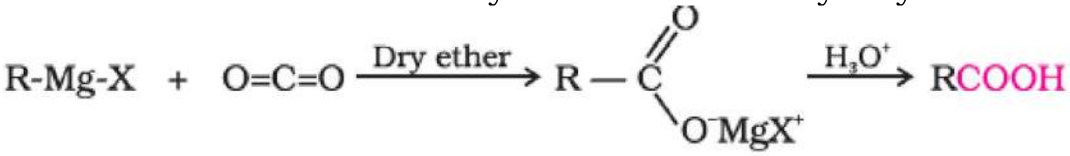
Benzoic acid

From Nitriles: Nitriles on hydrolysis in presence of dilute acids or bases forms amide which on further hydrolysis gives carboxylic acid.

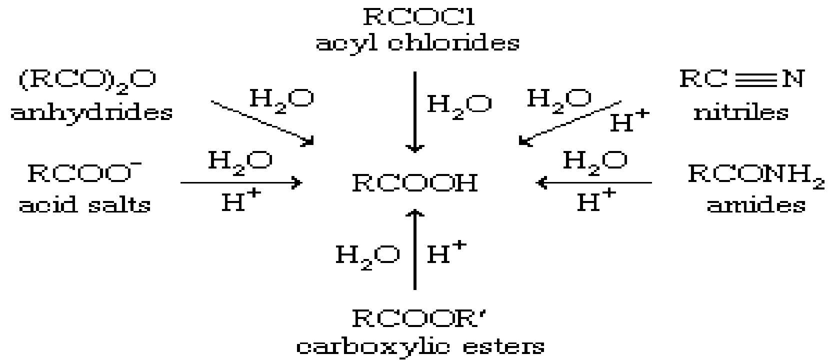


$$R\text{-}CN \xrightarrow[H_2O]{\overset{+}{H}\text{ or }\bar{O}H} R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{\overset{+}{H}\text{ or }\bar{O}H} RCOOH$$

From Grignard reagent: Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids which on hydrolysis forms carboxylic acids.



From acyl halides and anhydrides: Acid chlorides when hydrolysed with water give carboxylic acids. On basic hydrolysis carboxylate ions are formed which on further acidification forms corresponding carboxylic acids. Anhydrides on hydrolysis forms corresponding acid(s)From esters: Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.



Physical properties of carboxylic acids:

(i)Solubility: As the size of alky group increases solubility of carboxylic acid decreases because non-polar part of the acid increases.

(ii)Boiling points: Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to extensive association of carboxylic acid molecules through intermolecular hydrogen bonding.

Acidity of carboxylic acids:

Carboxylic acids are more acidic than phenols. The strength of acid depends on extent of ionization which in turn depends on stability of anion formed.

(i)Effect of electron donating substituents on the acidity of carboxylic acids: Electron donating substituent decreases stability of carboxylate ion by intensifying the negative charge and hence decreases acidity of carboxylic acids.

(ii)Effect of electron withdrawing substituent on the acidity of carboxylic acids: Electron withdrawing group increases the stability of carboxylate ion by delocalizing negative charge and hence, increases acidity of carboxylic acid. The effect of the following groups in increasing acidity order is

$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

Reaction of carboxylic acids:

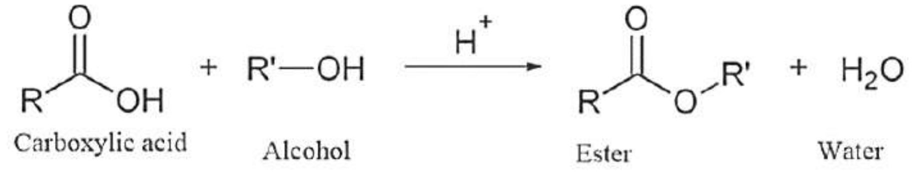
Reaction with Na metal NaOH, $NaHCO_3$

$$2R\text{-}COOH + 2Na \longrightarrow 2R\text{-}CO\bar{O}Na^+ + H_2$$

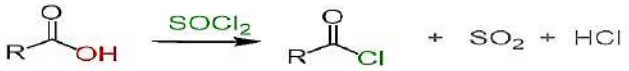
$$R\text{-}COOH + NaOH \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O$$

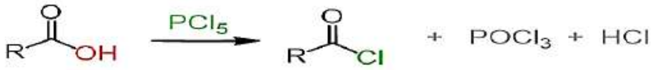
$$R\text{-}COOH + NaHCO_3 \longrightarrow R\text{-}CO\bar{O}Na^+ + H_2O + CO_2$$

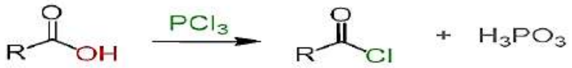
Esterification: Carboxylic acids are esterified with alcohols in the presence of a mineral acid such as concentrated H_2SO_4 or HCl gas as a catalyst.



(iii) Carboxylic acids react with PCl_5, PCl_3 and $SOCl_2$ to form acyl chlorides.







Some Distinguishing tests:

1.		
	Methanal	Ethanal
	It does not give yellow ppt of iodoform with NaOH and I_2	It gives yellow ppt of iodoform with NaOH and I_2
2	Benzaldehyde	Acetophenone
	*It gives silver mirror with Tollen's reagent *It does not give yellow ppt of iodoform with iodine and NaOH or NaOI	*It does not gives silver mirror with Tollen's reagent *It gives yellow ppt of iodoform with Iodine and NaOH or NaOI
3	Methanal	Benzaldehyde
	It gives brick red ppt with Fehling's solution A & B	It does not give brick red ppt with Fehling's solution A & B
4	Propanal	Ethanal
	It does not give yellow ppt of iodoform with NaOH and I_2	It gives yellow ppt of iodoform with NaOH and I_2
5	Phenol	Benzoic Acid
	Does not give brisk effervescence with $NaHCO_3$	Gives brisk effervescence with $NaHCO_3$
6	Acetic acid	Formic acid
	It doesn't give silver mirror with ammonical silver nitrate. It doesn't give brick red ppt with Fehling's solution A & B	It gives silver mirror with Tollen's reagent (ammonical silver nitrate). It gives brick red ppt with Fehling's solution A & B
7	Phenol	Ethanol
	Gives violet coloured solution with neutral $FeCl_3$ solution.	Does not give violet coloured solution with neutral $FeCl_3$ solution.
8	Propanol	Ethanol
	It does not give yellow ppt of iodoform with NaOH and I_2	It gives yellow ppt of iodoform with NaOH and I_2
9	Benzophenone	Acetophenone
	It does not give yellow ppt of iodoform with NaOH and I_2	It gives yellow ppt of iodoform with NaOH and I_2
10	Pentan-3-one	Pentan-2-one
	It does not give yellow ppt of iodoform with NaOH and I_2	It gives yellow ppt of iodoform with NaOH and I_2

MULTIPLE CHOICE QUESTIONS (1 MARKS)

1.) Which aldehyde will give Cannizzaro's reaction?

(a) $CH_3CH_2CH_2CHO$ (b) CH_3CH_2CHCHO

(c) $(CH_3)_3CCHO$ (d) $(CH_3)_2CH_2CH_2CHO$

2.) Carboxylic acids are more acidic than phenol and alcohol because of

(a) Formation of dimers (b) Resonance stabilization of their conjugate base

(c) Highly acidic hydrogen (d) Intermolecular hydrogen bonding

3.) Aldehydes and ketones undergo __________ reactions.

a) electrophilic addition b) electrophilic substitution

c) nucleophilic addition d) nucleophilic substitution

4.) What is the correct order of reactivity of the following towards nucleophilic addition?

a) Methanal > Ethanal > Acetone b) Acetone > Ethanal > Methanal

c) Methanal > Acetone > Ethanal d) Ethanal > Methanal > Acetone

5.) Identify the reagent for the conversion of but-2-ene to ethanal.

a) O_3/H_2O-Zn dust b) H_2O, H_2SO_4, $HgSO_4$

c) PCC d) DIBAL-H

6.) Which of the reactions below can result in ketones?

a) Oxidation of primary alcohols

b) Oxidation of secondary alcohols

c) Dehydrogenation of tertiary alcohols

d) Dehydrogenation of primary alcohols

7.) Which of the following orders of relative strengths of acids is correct?

(a) $ClCH_2COOH > FCH_2COOH > BrCH_2COOH$

(b) $ClCH_2COOH > BrCH_2COOH > FCH_2COOH$

(c) $BrCH_2COOH > ClCH_2COOH > FCH_2COOH$

(d) $FCH_2COOH > ClCH_2COOH > BrCH_2COOH$

8.) The reagent which does not react with both Propanone and Benzaldehyde:

(a) Grignard reagent (b) Tollen's reagent

(c) Zn-Hg amalgam (d)Fehling solution

9.) Which of the following compound will not give $NaHCO_3$ test?

(a)Carbolic acid (b)Formic acid (c) Acetic acid (d) Benzoic acid

10.) 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

Question	1	2	3	4	5	6	7	8	9	10
Answer	c	b	c	a	a	b	b	d	c	a

ASSERTION REASON TYPE QUESTIONS(1MARKS)

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 statements and reason is correct explanation for assertion.

b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

c) Assertion is correct statement but reason is wrong statement.

d) Assertion is wrong statement but reason is correct statement.

11.) Assertion: Methanal, ethanal and propanone are miscible with water in all proportions.

Reason: The lower members of aldehydes and ketones form hydrogen bond with water.

12.) Assertion: Aldehydes are generally more reactive than ketones in nucleophilic addition reactions.

Reason: Sterically, the presence of two relatively large substituents in ketones hinder the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.

13.) Assertion: Sodium hydrogen sulphite adds to aldehydes and ketones to form the addition product.

Reason: Reaction of aldehydes with Sodium hydrogen sulphite is useful for separation and purification of aldehydes.

1**4.) Assertion**: Pk_a of acetic acid is lower than that of phenol

Reason: Phenoxide ion is more resonance stabilized than acetate ion.

15.) Assertion : α-hydrogen atoms of carbonyl compounds are acidic in nature.

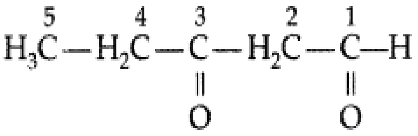
Reason: The strong electron donating effect of the carbonyl group and resonance destabilisation of the conjugate base makes the alpha hydrogen acidic.

Question	11	12	13	14	15
Answer	a	a	b	d	c

VERY SHORT ANSWER TYPE QUESTIONS (1 MARKS)

16) Write the structure of 3-oxopentanal.

Ans:



$$\overset{5}{H_3C}-\overset{4}{H_2C}-\overset{3}{\underset{\underset{O}{\|}}{C}}-\overset{2}{H_2C}-\overset{1}{\underset{\underset{O}{\|}}{C}}-H$$

3-oxopentanal

17) Give a chemical test to distinguish between Benzoic acid and Phenol.

Ans: Benzoic acid forms a brisk effervescence with $NaHCO_3$ solution but phenol does not respond to this test.

18) Formaldehyde does not undergo aldol condensation reaction. Why?

Ans: Formaldehyde does not contain α-hydrogen atom.

19) Aldehydes and Ketones have lower boiling points than corresponding alcohols. Why?

Ans: Aldehydes and ketones have weak intermolecular interactions dipole – dipole interactions whereas alcohols have intermolecular hydrogen bonding.

20) Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions:

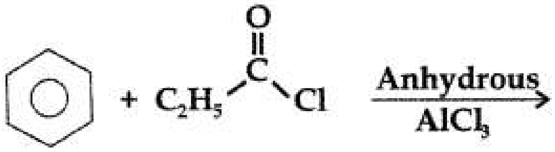
(i)Ethanal, Propanal, Propanone, Butanone.

(ii)Benzaldehyde, *p*-Tolualdehyde, *p*-Nitrobenzaldehyde, Acetophenone.

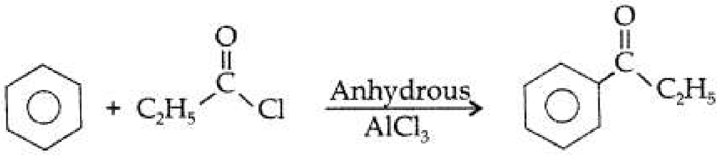
Ans: (i)Butanone<Propanone<Propanal<Ethanal

(ii)Acetophenone < p-Tolualdehyde < Benzaldehyde < p-nitro benzaldehyde

21) Write the structure of the product formed in the following reaction.



Ans:



22) Carboxylic acids do not give characteristic reactions of carbonyl group. Why?
Ans: The carboxylic carbon is less electrophilic due to resonance than the carbonyl carbon.

23) Write the reagents required in the following reactions.

(*i*) $CH_2 = CH—CH_2OH \xrightarrow{?} CH_2 = CH—CHO$

(*ii*) $CH_3—COOH \xrightarrow{?} CH_3—CONH_2$

Ans:

(*i*) $CH_2 = CH—CH_2OH \xrightarrow{PCC} CH_2 = CH—CHO$

(*ii*) $CH_3—COOH \xrightarrow[\Delta]{NH_3} CH_3—CONH_2$

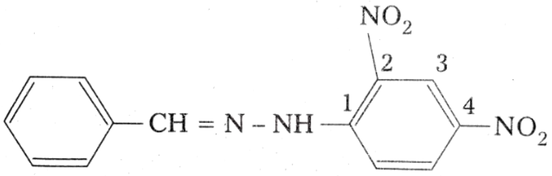
24) Why does benzoic acid not undergo Friedel-Craft reaction?
Ans: – COOH group in C_6H_5COOH is an electron withdrawing group which deactivates the benzene ring. Hence electrophilic substitution becomes difficult.

25) Why Pka of F-CH_2COOH is lower than that of Cl–CH_2COOH?
Ans: Stronger –I effect of fluorine makes F-CH_2COOH to be stronger acid than Cl–CH_2COOH and has less Pka.

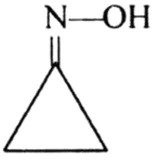
SHORT ANSWER TYPE QUESTIONS (2 MARKS)

26) Draw structures of the following derivatives:
(i) The 2,4-dinitrophenylhydrazone of benzaldehyde
(ii) Cyclopropanone oxime

Ans: (i)



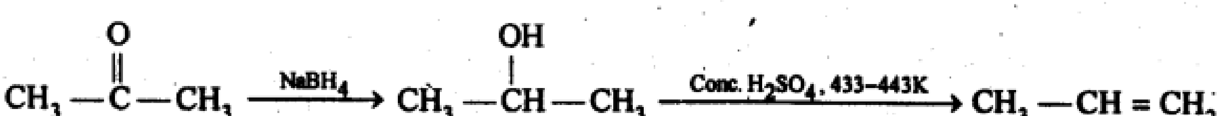
(ii)



27) How will you convert
(i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde

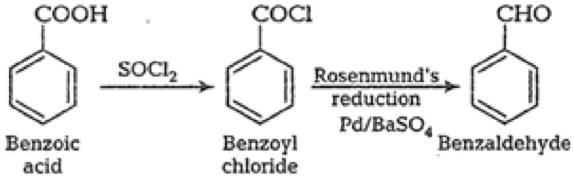
Ans:

(*i*) Propanone to propene:



$$CH_3—\overset{\overset{O}{\|}}{C}—CH_3 \xrightarrow{NaBH_4} CH_3—\overset{\overset{OH}{|}}{CH}—CH_3 \xrightarrow[-H_2O]{Conc.\ H_2SO_4,\ 433–443K} CH_3—CH = CH_2$$

(ii)

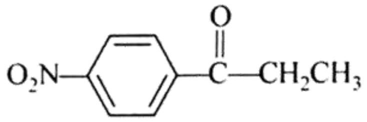


28) Give the structure of the following compounds.

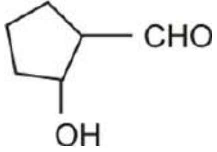
(i) 4-Nitropropiophenone

(ii) 2-Hydroxycyclopentanecarbaldehyde

Ans: (i)



(ii)



29) Explain each of the following.

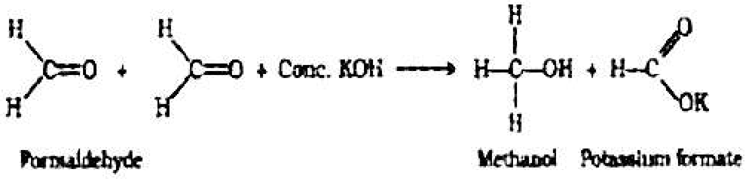
(i) Cyanohydrin (ii) Acetal

Ans: **(i)** Cyanohydrin: gem-Hydroxynitriles, i.e., compounds possessing hydroxyl and cyano groups on the same carbon atom are called cyanohydrins. These are produced by addition of HCN to aldehydes or ketones in a weakly basic medium.

(ii) gem – Di alkoxy compounds in which the two alkoxy groups are present on the terminal carbon atom are called acetals. These are produced by the action of an aldehyde with two equivalents of a monohydric alcohol in presence of dry HCl gas.

30) What happens when Formaldehyde is treated with conc.KOH?

Ans: It undergoes disproportionation to form Methanol and Potassium formate. This is called Cannizzaro reaction.



SHORT ANSWER TYPE QUESTIONS (3MARKS)

31. Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.

(ii) There are two – NH_2 groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

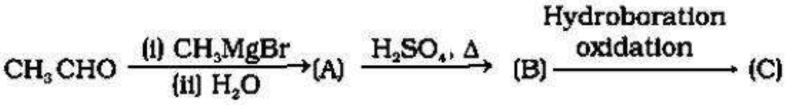
Ans

(i) In 2,2,6-trimethylcyclohexanone due to the presence of three methyl groups nearer to the C = O, the nucleophilic attack by the CN^- ion does not occur due to steric hinderance. Since there is no such steric hindrance in cyclohexanone, therefore, nucleophilic attack by the CN– ion occurs readily and hence cyclohexanone cyanohydrin is obtained in good yield.

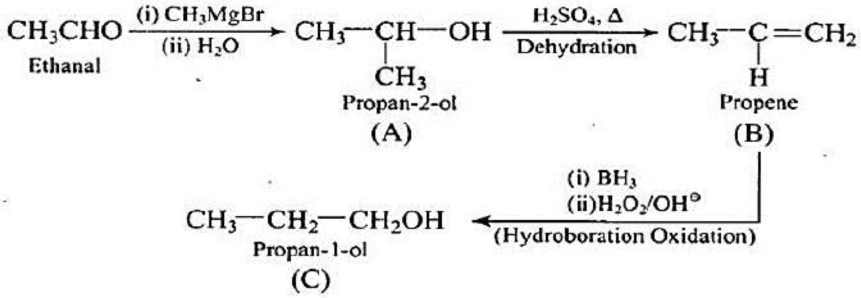
(ii) Although semicarbazide has two – NH_2 groups but one of them (i.e. which is directly attached to C = O) is involved in resonance as shown above. As a result, electron density on N of this -NH_2 group decreases and hence it does not act as a nucleophile. In contrast, the other -NH_2 group (i.e. attached to NH) is not involved in resonance and hence lone pair of electrons present on N atom of this -NH_2 group is available for nucleophilic attack on the C = O group of aldehydes and ketones.

(iii) The formation of esters from a carboxylic acid and an alcohol in presence of an acid catalyst is a reversible reaction. Thus, to shift the equilibrium in the forward direction, the water or the ester formed should be removed as fast as it is formed.

32. Identify the compounds A, B and C in the following reaction.



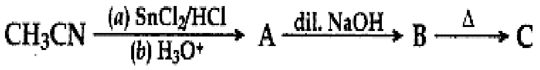
Ans:

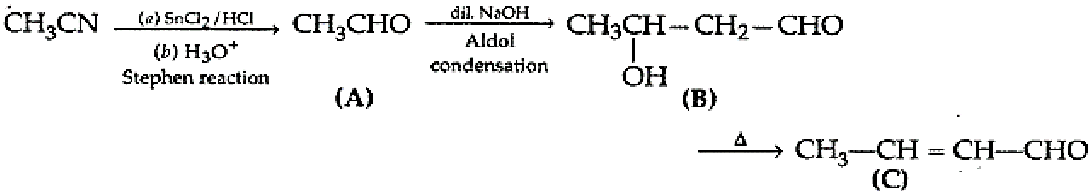


33. Give simple chemical tests to distinguish between the following pairs of compounds.
(i) Propanal and Propanone (ii) Acetophenone and Benzophenone
(iii)Phenol and Benzoic acid

Ans: (i) Tollen's test- Propanal on warming with ammoniacal silver nitrate solution produces bright silver mirror. Propanone does not give this test.
(ii)Iodoform test-Acetophenone gives yellow ppt of iodoform on treating with I_2 and NaOH. Benzophenone does not give this test.
(iii)$NaHCO_3$ test- Benzoic acid gives brisk effervescence when treated with $NaHCO_3$, Phenol does not give this test.

34. Write structures of compounds A, B and C in the following reactions:

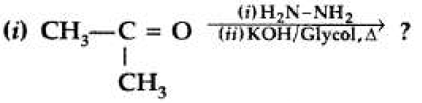


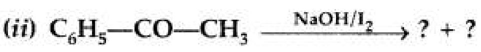


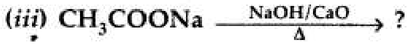
Ans:

A-Ethanal, B- 3-hydroxybutanal, C-But-2-enal

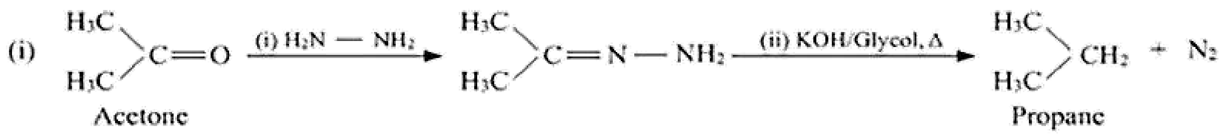
35. Predict the products of the following reactions.

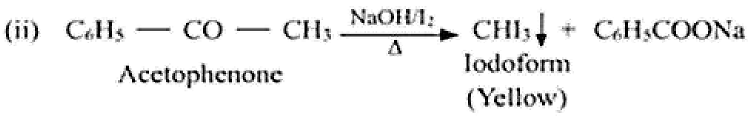


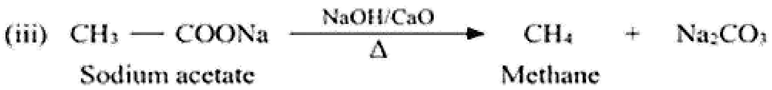




Ans:







Long Answer Type Questions (5 marks each):

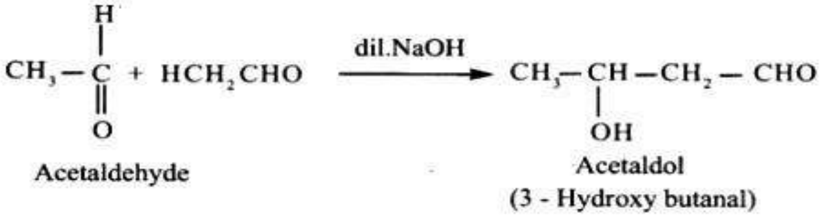
36. Describe the following :

(i) Aldol Condensation (ii)Cannizzaro Reaction

(iii)Clemmensen Reduction (iv)Rosenmund Reduction

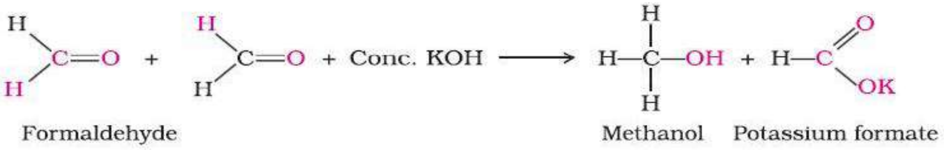
(v) Hell Volhard Zelinsky Reaction.

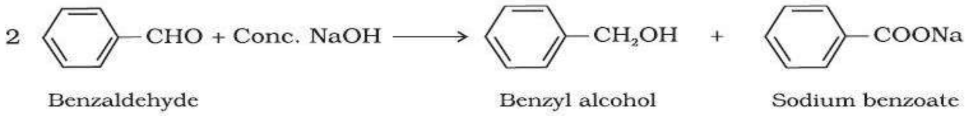
Ans: (i) Aldol Condensation-Aldehydes having α-hydrogen react with a dilute base to give β-hydroxy aldehydes called aldols.



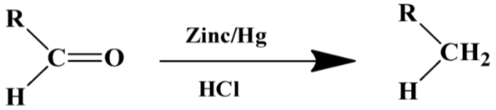
(ii)Cannizzaro reaction:

Aldehydes which do not contain hydrogen when treated with a concentrated solution of an alkali undergo self oxidation-reduction. As a result, one molecule of aldehyde is reduced to corresponding alcohol while the other molecule is oxidized to the corresponding acid.



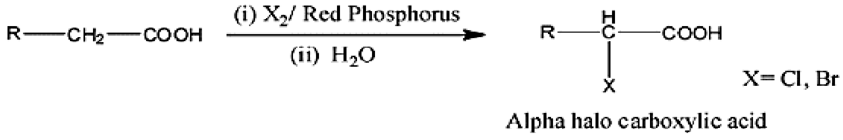


(iii)Clemmensen Reduction: Aldehydes or ketones are reduced to alkanes using hydrochloric acid and zinc amalgam.



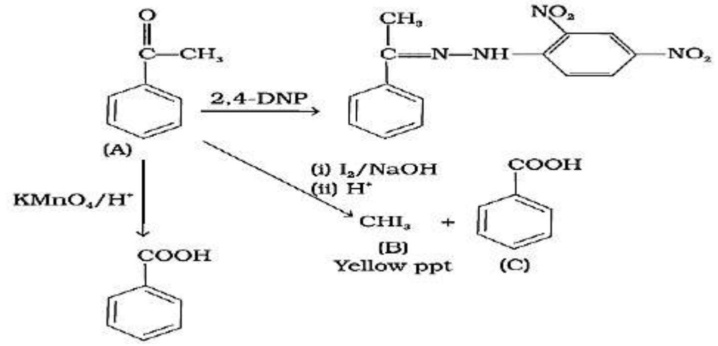
(iv)Rosenmund Reduction: Acyl chloride is hydrogenated in the presence of catalyst – palladium on barium sulphate to produce aldehydes.

(v)Hell Volhard Zelinsky Reaction: It involves the halogenation of a carboxylic acid having alpha hydrogen when treated with Red P and Cl_2 or Br_2.



37. An aromatic compound ‘A’ (Molecular formula C_8H_8O) gives positive 2,4-DNP test. It gives a yellow precipitate of compound ‘B’ on treatment with iodine and sodium hydroxide solution. Compound ‘A’ does not give Tollen’s or Fehling’s test. On drastic oxidation with potassium permanganate, it forms a carboxylic acid ‘C’ (Molecular formula $C_7H_6O_2$), which is also formed along with the yellow compound in the above reaction. Identify A, B and C and write all the reactions involved.

Ans: A-Acetophenone B-Iodoform C- Benzoic acid



Case based; Source based Integrated Questions

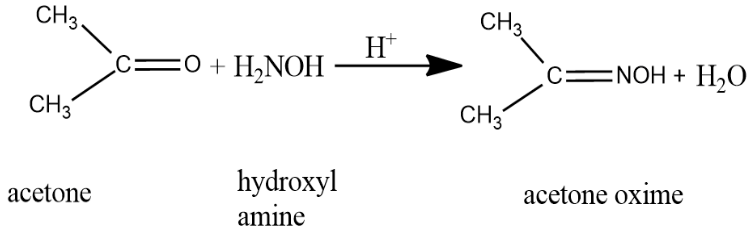
38.) Read the following passage and answer the questions given below the passage.

Reductive alkylation is the term applied to the process of introducing alkyl groups into ammonia or a primary or secondary amine by means of an aldehyde or ketone in the presence of a reducing agent. The present discussion is limited to those reductive alkylations in which the reducing agent is hydrogen and a catalyst or "nascent" hydrogen, usually from a metal acid combination; most of these reductive alkylations have been carried out with hydrogen and a catalyst. The principal variation excluded is that in which the reducing agent is formic acid or one of its derivatives; this modification is known as the Leuckart reaction. The process of reductive alkylation of ammonia consists in the addition of ammonia to a carbonyl compound and reduction of the addition compound or its dehydration product. The reaction usually is carried out in ethanol solution when the reduction is to be affected catalytically Since the primary amine is formed in the presence of the aldehyde it may react in the same way as ammonia, yielding an addition compound, a Schiff's base (RCH= NCH_2R) and finally, a secondary amine. Similarly, the primary amine may react with the imine, forming an addition product which also is reduced to a secondary amine Finally, the secondary amine may react with either the aldehyde or the imine to give products which are reduced to tertiary amines. Similar reactions may occur when the carbonyl compound employed is a ketone

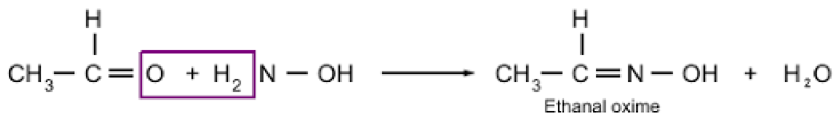
A] Write equations for the following reactions.

(i) Acetone with hydroxyl amine (ii) Ethanal with ammonia

Ans (i)Acetone with hydroxyl amine



(ii) Ethanal with ammonia



$$CH_3-\overset{H}{\overset{|}{C}}=\boxed{O\ +\ H_2}N-OH \longrightarrow CH_3-\overset{H}{\overset{|}{C}}=N-OH\ +\ H_2O$$

Ethanal oxime

B] A compound gives 2,4 DNP test, further it reduces Tollen's reagent. what conclusions can be drawn from this information?

Ans: As the compound gives 2,4-DNP test.it must be an aldehyde or ketone. Further as it gives Tollen's test it is an aldehyde.

C]What type of reaction takes place when aldehydes or ketones are treated with ammonia and its derivatives?

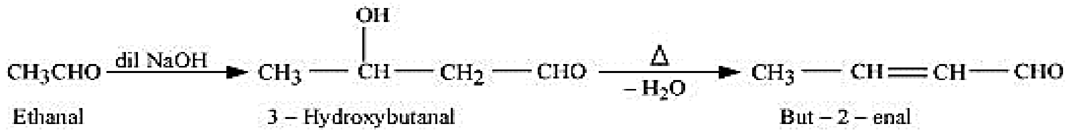
Ans: Nucleophilic addition reaction.

39.) Read the following passage and answer the questions given below the passage.

The addition reaction of enol or enolate to the carbonyl functional group of aldehyde or ketone is known as aldol addition. The b-hydroxy aldehyde or b-hydroxyketone so obtained undergo dehydration in second step to produce a conjugated enone. The first part of reaction is an addition reaction and the second part is an elimination reaction. Carbonyl compound having alpha-hydrogen undergoes aldol condensation reaction. When an aldehyde with no alpha-hydrogen reacts with concentrated aqueous NaOH, half the aldehyde is converted to carboxylic acid salt and other half is converted to an alcohol. In other words, half of the reactant is oxidized and another half is reduced. This reaction is known as Cannizzaro reaction.

A] How will you convert ethanol to But-2-enal?

Ans:

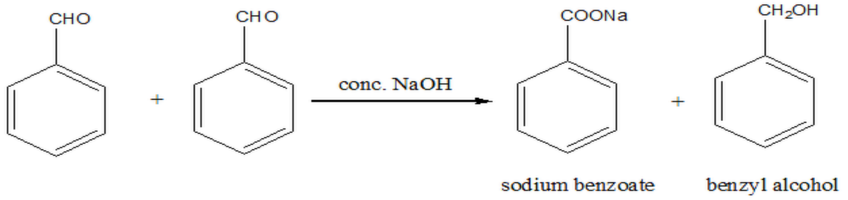


$$CH_3CHO \xrightarrow{\text{dil NaOH}} CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-CHO \xrightarrow[-H_2O]{\Delta} CH_3-CH=CH-CHO$$

B] Name the products of aldol condensation of Propanone and Ethanal.

Ans: 1) But-2-enal 2)2-Methylpent-2-enal
3)Pent-2-enal 4) 2-methyl but -2-enal

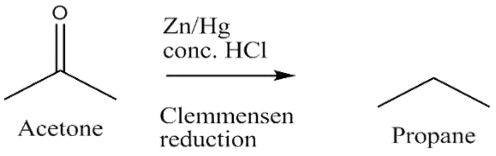
C] What happens when Benzaldehyde is treated with Conc. NaOH?



40.) Read the following passage and answer the questions given below the passage.

The carbonyl group of aldehydes and ketones is reduced to -CH_2- group on treatment with zinc amalgam and concentrated hydrochloric acid [Clemmensen reduction] or with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol (Wolf-Kishner reduction). Aldehydes differ from ketones in their oxidation reactions. Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidising agents, mainly Tollens' reagent and Fehling's reagent also oxidise aldehydes. Ketones are generally oxidised under vigorous conditions, i.e., strong oxidising agents and at elevated temperatures. Their oxidation involves carbon-carbon bond cleavage to afford a mixture of carboxylic acids having lesser number of carbon atoms than the parent ketone.

A] Write a chemical equation to convert Propanone to propane. Mention the name of the reaction.

Ans:  and Wolff –Kishner reduction

B]Name the reagents used in the following conversions?

i) Butan-1-ol to Butanal ii) Ethanal to Ethanoic acid

Ans: i) PCC / CrO_3-H_2SO_4 ii) Acidified $KMnO_4/K_2Cr_2O_7$

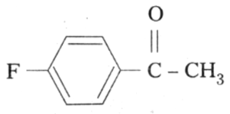
C] You are given two test tubes. One contains aliphatic aldehyde and the other one contains aromatic aldehyde. How will you identify the test tube containing aromatic aldehyde?

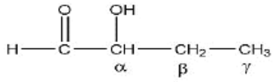
Ans: Both the given compounds are subjected to Fehling's test. The compound which does not give Fehling's test is an aromatic aldehyde

41.) Read the following passage and answer the questions given below the passage.
Aldehydes and ketones are the simplest and most important carbonyl compounds. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones, it is bonded to two carbon atoms. The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending –e with –al and –one respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. The substituents are prefixed in alphabetical order along with numerals indicating their positions in the carbon chain. The same applies to cyclic ketones, where the carbonyl carbon is numbered one. When the aldehyde group is attached to a ring, the suffix carbaldehyde is added after the full name of the cycloalkane. The numbering of the ring carbon atoms starts from the carbon atom attached to the aldehyde group. The name of the simplest aromatic aldehyde carrying the aldehyde group on a benzene ring is benzene carbaldehyde. However, the common name benzaldehyde is also accepted by IUPAC. Other aromatic aldehydes are hence named as substituted benzaldehydes.

A] Write the structures of 4-Fluoroacetophenone & 2-Hydroxybutanal.

Ans:i) ii)





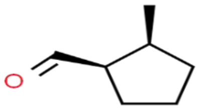
2-hydroxybutanal

B] Write the IUPAC names of the following ketones and aldehydes.

i) $CH_3CH{=}CHCHO$ ii) $CH_3CH_2COCH(C_2H_5)CH_2CH_2Cl$

Ans: i) But-2-en-1-al or But-2-enal ii) 6-Chloro-4-ethylhexan-3-one

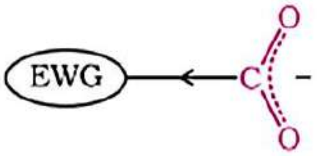
C] Name the compound represented by the formula



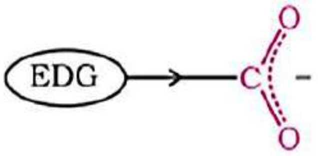
Ans: 2- methylcyclopentane carbaldehyde

42.) Read the following passage and answer the questions given below the passage.

Effect of substituents on the acidity of carboxylic acids: Substituents may affect the stability of the conjugate base and thus, also affect the acidity of the carboxylic acids. Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the conjugate base through delocalisation of the negative charge by inductive and/or resonance effects. Conversely, electron donating groups decrease the acidity by destabilising the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

A] Which is more acid Acrylic acid CH_2=CHCOOH or Propanoic acid ? Why?

Ans: Acrylic acid is more acidic than Propanoic acid. In case of acrylic acid, the carbon atom of the carboxylic group (-COOH) is attached with SP^2hybridised carbon atom which has more s- character (33%) than SP^3hybridised carbon atom (25%), hence SP^2 hybridised carbon atom become more electronegative so the electron density shifts towards SP^2 carbon atom, then due to inductive effect oxygen acquires positive charge hence it becomes easier to remove H^+ ion.

B] Dichloroacetic acid is stronger acid than chloroacetic acid. Why?

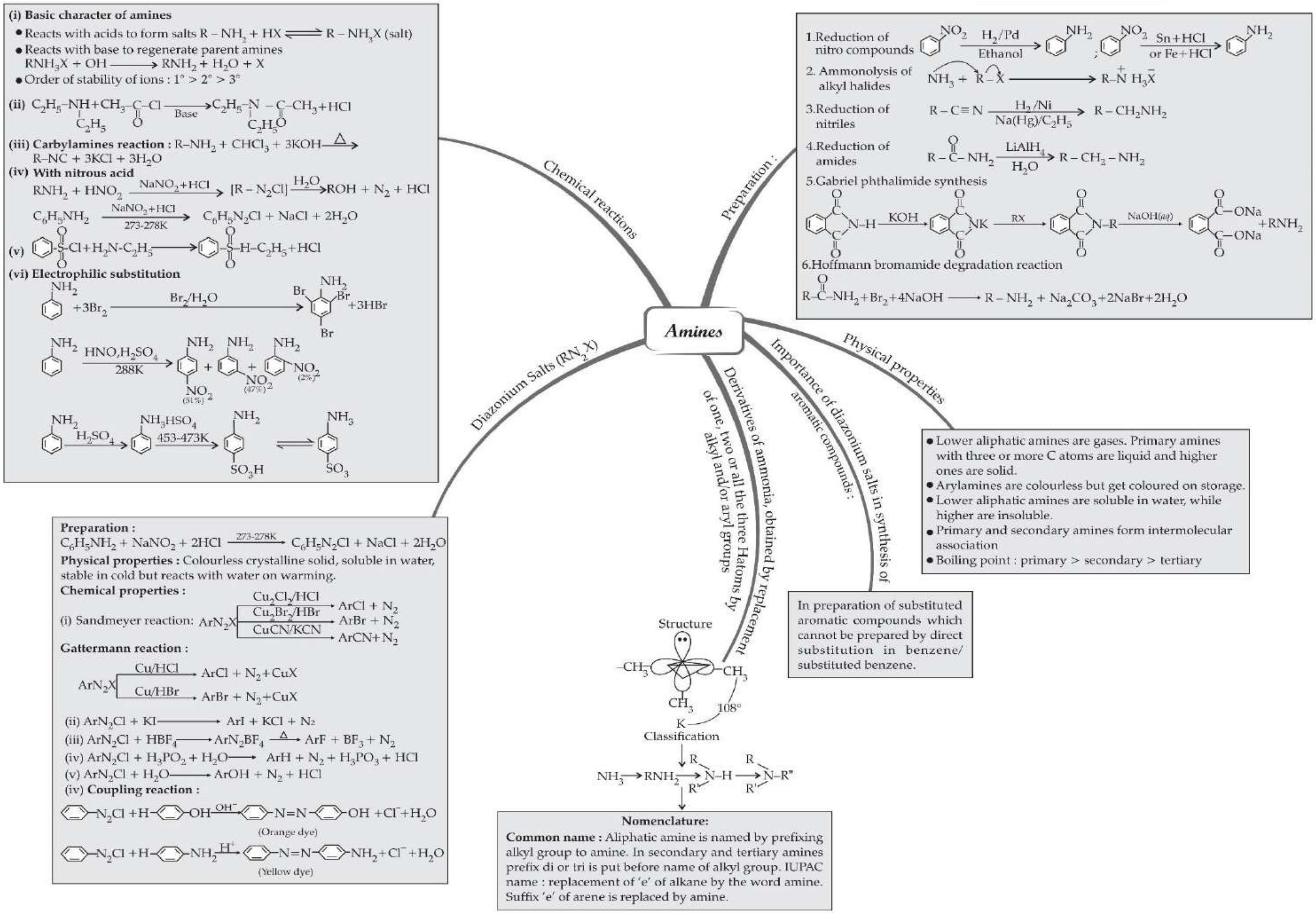
Ans: The more the number of electron withdrawing groups the more is the acidic nature.

C] Arrange the following acids in the increasing order of acidic strength

Benzoic acid, 4- nitrobenzoic acid, 3,4-dinitro benzoic acid,4- methoxy benzoic acid

Ans: 4- methoxy benzoic acid<benzoic acid<4-nitrobenzoic acid<3,4- dinitrobenzoic acid.

MIND MAP : LEARNING MADE SIMPLE



(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines
  $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5-\underset{\substack{|\\C_2H_5}}{NH}+CH_3-\underset{\substack{\|\\O}}{C}-Cl \xrightarrow[\text{Base}]{} C_2H_5-\underset{\substack{|\\C_2H_5}}{N}-\underset{\substack{\|\\O}}{C}-CH_3+HCl$

(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta}$ $R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v) $C_6H_5-\overset{\substack{O\\\|}}{\underset{\substack{\|\\O}}{S}}-Cl+H_2N-C_2H_5 \longrightarrow C_6H_5-\overset{\substack{O\\\|}}{\underset{\substack{\|\\O}}{S}}-H-C_2H_5+HCl$

(vi) Electrophilic substitution

$C_6H_5NH_2 + 3Br_2 \xrightarrow{Br_2/H_2O}$ 2,4,6-tribromoaniline $+ 3HBr$

$C_6H_5NH_2 \xrightarrow[288K]{HNO,H_2SO_4}$ p-NO_2 (51%) + m-NO_2 (47%) + o-NO_2 (2%)

$C_6H_5NH_2 \xrightarrow{H_2SO_4} C_6H_5NH_3HSO_4 \xrightarrow{453\text{-}473K}$ p-$NH_2C_6H_4SO_3H \rightleftharpoons$ p-$NH_3C_6H_4SO_3$

1. Reduction of nitro compounds: $C_6H_5NO_2 \xrightarrow[\text{Ethanol}]{H_2/Pd} C_6H_5NH_2$; $C_6H_5NO_2 \xrightarrow[\text{or } Fe+HCl]{Sn+HCl} C_6H_5NH_2$
2. Ammonolysis of alkyl halides: $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$
3. Reduction of nitriles: $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$
4. Reduction of amides: $R-\overset{\substack{O\\\|}}{C}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$
5. Gabriel phthalimide synthesis: phthalimide (N–H) $\xrightarrow{KOH}$ (NK) $\xrightarrow{RX}$ (N–R) $\xrightarrow{NaOH(aq)}$ $C_6H_4(COONa)_2 + RNH_2$
6. Hoffmann bromamide degradation reaction: $R-\overset{\substack{O\\\|}}{C}-NH_2+Br_2+4NaOH \longrightarrow R-NH_2 + Na_2CO_3+2NaBr+2H_2O$

- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association
- Boiling point : primary > secondary > tertiary

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Nomenclature:

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group. IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Preparation :
$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2Cl + NaCl + 2H_2O$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction: $ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$; $\xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$; $\xrightarrow{CuCN/KCN} ArCN+N_2$

Gattermann reaction :

$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2+CuX$; $\xrightarrow{Cu/HBr} ArBr + N_2+CuX$

(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**

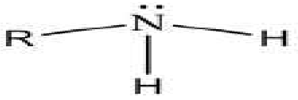
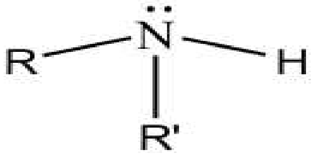
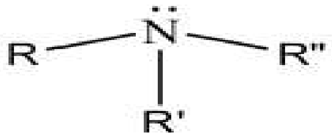
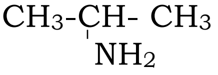
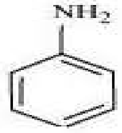
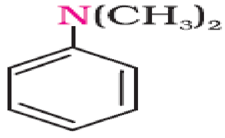
$C_6H_5N_2Cl + H-C_6H_4-OH \xrightarrow{OH^-} C_6H_5-N=N-C_6H_4-OH + Cl^- + H_2O$

$C_6H_5N_2Cl + H-C_6H_4-NH_2 \xrightarrow{H^+} C_6H_5-N=N-C_6H_4-NH_2 + Cl^- + H_2O$

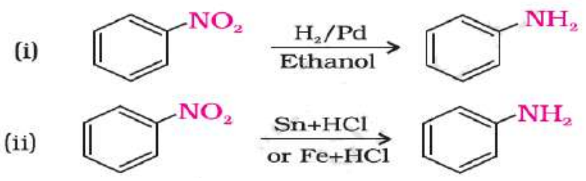
9. AMINES

Quick Revision Points:

Amines are alkyl / aryl derivatives of ammonia. In amines nitrogen atom is sp^3 hybridised and contains one lone pair.

Primary amine (1^0)	Secondary amine (2^0)	Tertiary amine (3^0)
One- H atom is replaced by R/Ar.  IUPAC Name: - Aliphatic amine: Alkanamines Aromatic amine: Benzenamine/Aniline	Two-H atom is replaced by R/Ar. 	Three-H atom is replaced by R/Ar. 
CH_3-NH_2 Methanamine  $CH_3-\underset{NH_2}{CH}-CH_3$ Propan-2-amine	CH_3-NH- CH_3 N-Methylmethanamine	$(CH_3)_3N$ N, N-dimethylmethanamine
 Aniline/benzenamine	CH_3-NH- CH_2- CH_3 N-Methylethanamine CH_3 - CH_2-NH- CH_2- CH_3 N-Ethylethanamine	 N, N-Dimethylbenzenamine

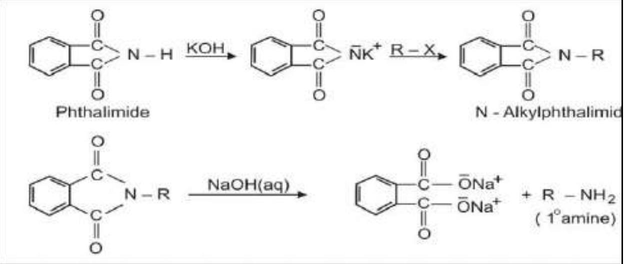
Preparation of Amines:

Reduction of Nitro Compounds gives aliphatic and aromatic primary amines. (Reducing Agents): - • Hydrogen and nickel/ palladium or platinum. • Iron scrap and hydrochloric acid (Fe + HCl). • Tin and hydrochloric acid (Sn + HCl).	
Ammonolysis of alkyl halides: - Reagent: Ethanolic solution of ammonia. Disadvantage: Mixture of amines formed.	$RX \xrightarrow[-HX]{NH_3} RNH_2 \xrightarrow{RX} R_2NH \xrightarrow{RX} R_3N \xrightarrow{RX} R_4N^+X^-$
Reduction of nitriles Reducing agents: - $LiAlH_4$/Catalytic hydrogenation.	$R-CN \xrightarrow{H_2/Ni \text{ or } Na(Hg)/C_2H_5OH} R-CH_2NH_2$
Reduction of Amides:	$CH_3CONH_2 \xrightarrow[H_2O]{LiAll_4} CH_3CH_2NH_2$

Hoffmann bromamide degradation Reaction: An amide is heated with Bromine in aq. solution of NaOH/KOH gives primary amine.

$$R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

The amine formed contains one carbon less than that present in the amide.

Gabriel Phthalimide Synthesis: Only aliphatic primary amines are prepared by this method. Aromatic primary amines cannot be prepared because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.	

Physical properties

In Tertiary amines H-Bonding is not possible due to absence of H atoms.

Hydrogen bonding	$3^0 < 2^0 < 1^0$
Solubility in water	$3^0 < 2^0 < 1^0$
Boiling Point	$3^0 < 2^0 < 1^0$

Boiling point

Alkane < Amine < Alcohol

Chemical reaction and Basic Nature

Amines are Lewis bases due to presence of lone pair.

Larger the value of K_b or smaller the value of pK_b, stronger is the base.

$NH_3 < 1^0 < 2^0 < 3^0$ (gas phase) (due to +I effect)

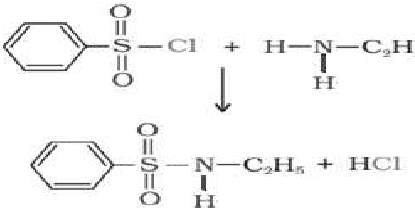
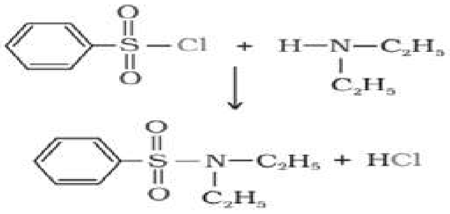
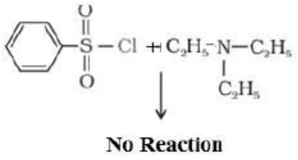
$NH_3 < C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2NH$ (aqueous phase)

$NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ (aqueous phase)

- Aliphatic amines are stronger base than ammonia due to +I effect of alkyl groups.
- Aromatic amines are weaker bases than ammonia due to the electron withdrawing nature of the aryl group**.**

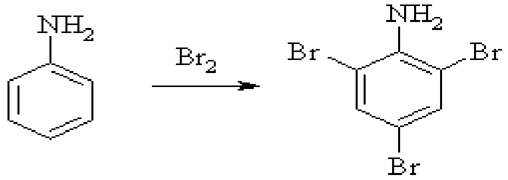
Acetylation: (replacement of H-atom of $–NH_2$ / >N–H group by the acyl group). Reacting agent: stronger base. Benzoylation: (replacement of H-atom of $–NH_2$ / >N–H group by the benzoyl group).	$(C_2H_5)_2NH + CH_3COCl \rightarrow CH_3CON(C_2H_5)_2 + HCl$ $CH_3NH_2 + C_6H_5COCl \rightarrow C_6H_5CONH\text{-}CH_3 + HCl$
Carbylamine reaction (Isocyanide Test) Primary amines react with chloroform and KOH give isocyanides (Carbylamine) which has unpleasant smell (foul smell).	$RNH_2 + CHCl_3 + 3KOH \xrightarrow{HEAT} RNC + 3KCl + 3H_2O$ Secondary and tertiary amines do not show this reaction. It is used as a test for primary amines.
Reaction with nitrous acid (HNO_2) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts (unstable) which liberate nitrogen gas and alcohols. Aromatic amines at low temperatures (273-278 K) forms diazonium salts.	$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [RN_2^+Cl^-] \xrightarrow{H_2O} ROH + N_2 + HCl$ $C_6H_5NH_2 + HNO_2 \xrightarrow{278K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

Reaction with Benzenesulphonyl chloride (Hinsberg's test)($C_6H_5SO_2Cl$)

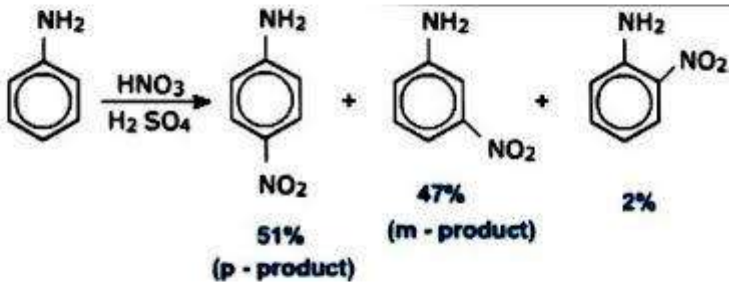
Primary Amine	**Secondary Amine**	**Tertiary Amine**
Primary amines form N-alkylbenzene sulphonamide which is soluble in alkali due to presence of acidic hydrogen at N-atom.	Secondary amines form N, N-dialkylbenzenesulphonamide which is not soluble in alkali due to absence of hydrogen atom at N-atom.	Tertiary amines do not react with Hinsberg's reagent.
		

Electrophilic substitution:

–NH_2 group is ortho and para directing and a powerful activating group.

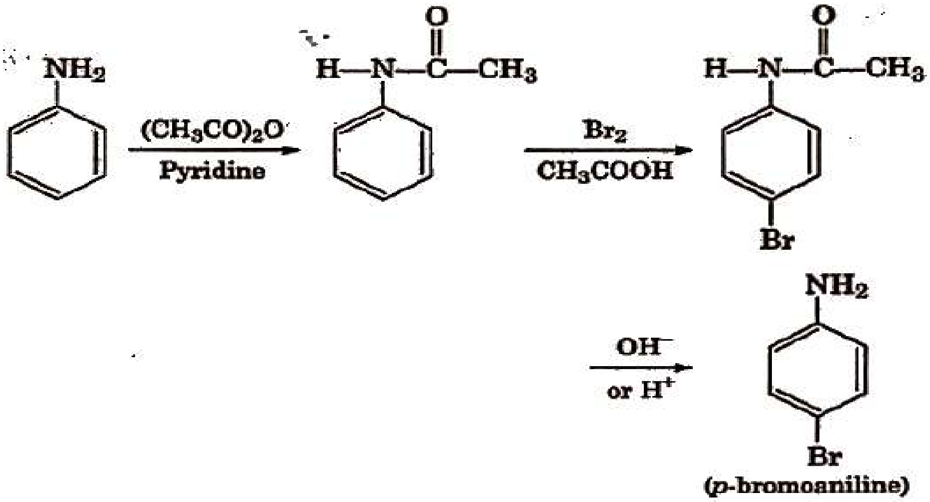


In direct Nitration meta product is formed due to formation of anilinium ion which is meta directing.

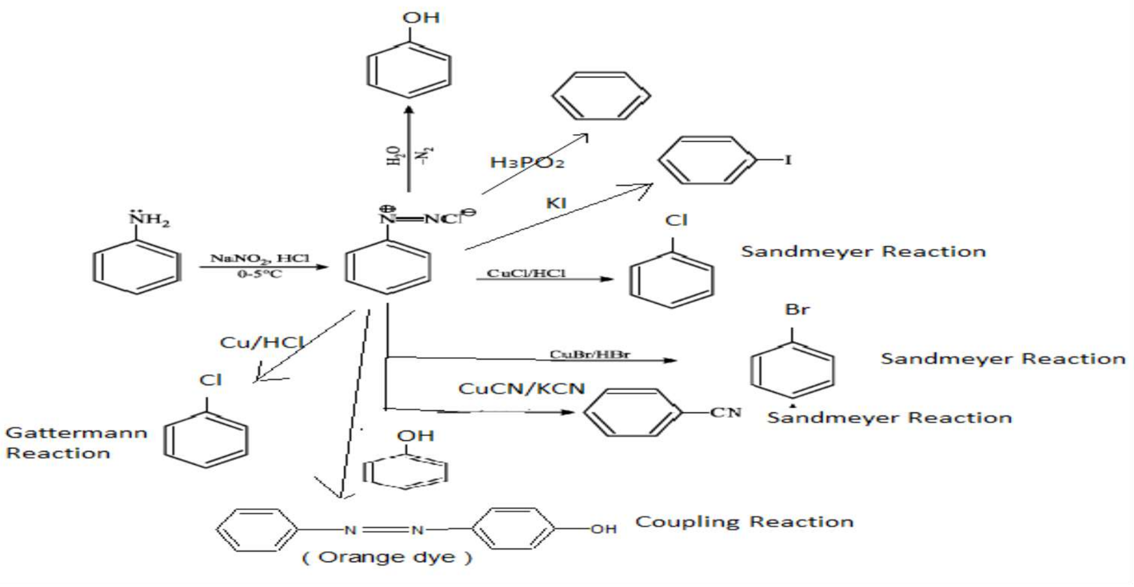


Electrophilic substitution:

Aniline is converted into acetanilide by acetylation with acetic anhydride and then the desired substitution is carried out followed by hydrolysis the lone pair on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of -$NHCOCH_3$ group is less than that of amino group.



Benzene Diazonium Chloride Preparation and Reactions:



MULTIPLE CHOICE QUESTIONS (1 MARKS)

Q: 1 The correct IUPAC name for $CH_3 – CH_2- CH_2- N(CH_3) -C_2H_5$ is

(a) N, N- diethyl propan-1-amine (c) N, N-dimethyl propan-1-amine

(b) N-Ethyl –N-methyl propan-1-amine (d) N-methyl 1- pentanamine

Q: 2 Which of the following statement is not correct?

(a) Primary amines show intermolecular hydrogen bonding.

(b) Secondary amines show intermolecular hydrogen bonding.

(c) Tertiary amines show intermolecular hydrogen bonding.

(d) Amines have lower boiling points as compared to those of alcohols and carboxylic acids of comparable molar masses.

Q: 3 Which of the following statement is correct?

(a) The pK_b of ammonia is more than that of methanamine.

(b) The K_b of ammonia is more than that of methanamine

(c) The pK_b of ammonia is more than that of aniline.

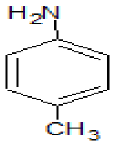
(d) The pK_b of ammonia is less than that of methanamine.

Q: 4 Atharv heated a mixture of primary amine and chloroform with ethanolic potassium hydroxide (KOH) to form isocyanides which has foul smelling. What is the name of the reaction involved in the statement?

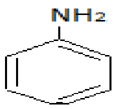
(a) Hoffmann bromide degradation reaction (c) Gabriel Phthalimide reaction

(b) Hinsberg's Test (d) Carbylamine reaction

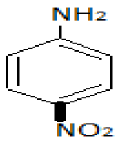
Q: 5 The correct increasing order of basic strength for the following compounds is:



(I)



(II)



(III)

(a) II < III < I (c) III < II < I

(b) III < I < II (d) II < I < II

Q: 6 The reaction $C_6H_5\,N_2Cl \xrightarrow{Cu,HCl} C_6H_5\,Cl + N_2$ **is named as**

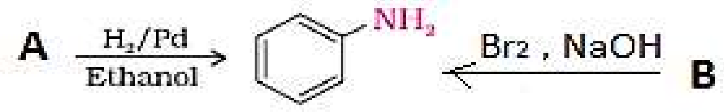
(a) Sandmeyer reaction (b) Gattermann reaction

(c) Claisen reaction (d)Carbylamine reaction

Q: 7 The -NH_2 group is o-, p- directing and strongly activates the aromatic ring. Therefore, aromatic amines undergo electrophilic substitution reactions readily and it is difficult to stop the reaction at the monosubstitution stage. However, sometimes monosubstitution product is required. How can the activating effect of -NH_2 group be controlled to get monosubstitution product?

(a) Protecting -NH_2 group by chlorination with chlorine
(b) Protecting -NH_2 group by nitration with nitric acid
(c) Protecting -NH_2 group by alkylation with alkyl chloride
(d) Protecting -NH_2 group by acetylation with acetic anhydride

Q: 8 A and B in the folowing reactions are:



(a) A = Nitrobenzene, B = Nitrobenzene (c) A=Nitrobenzene,B = Nitrotoluene
(b) A = Nitrobenzene, B = benzamide (d) A = benzamide, B = Nitrobenzene

Q: 9 Gabriel phthalimide reaction is used for the preparation of:

(a) Primary aromatic amine (c) Secondary amine
(b) Primary aliphatic amine (d)Tertiary amine

Q: 10 Hinsberg's reagent is:

(a) Phenylisocyanide (c) benzensulphonyl chloride
(b) p- toluenesulphonic acid (d) o-dichlorobenzene

Question	1	2	3	4	5	6	7	8	9	10
Answer	B	C	A	D	C	B	D	B	C	C

ASSERTION REASON TYPE QUESTIONS(1MARKS)

In the Following questions a statement of Assertion(A) is followed by a statement of Reason(R). Select the most appropriate answer from the options given below:

a. Both A and R are true and R is the correct explanation of A
b. Both A and R are true but R is not the correct explanation of A.
c. A is true but R is false.
d. A is false but R is true.

The question given below consist of an assertion and a reason. Use the following key to choose.

11. Assertion(A): Primary aromatic amines cannot be prepared by Gabriel phthalimide synthesis.
    Reason(R): Aryl halides undergo nucleophilic substitution with anion formed by phthalimide.
12. Assertion(A): Among isomeric amines, 3^0 amines have lowest boiling point.
    Reason(R): Tertiary amines do not have intermolecular association due to absence of H- atoms linked to nitrogen.
13. Assertion(A): Aliphatic amines are stronger bases than ammonia.
    Reason(R): Aromatic amines are weaker bases than ammonia.
14. Assertion(A): Very high amount of HCl is required in reduction of nitro compounds with iron scrap
    Reason(R): $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.
15. Assertion(A): Aniline reacts with bromine water to give 2,4,6-tribromoaniline.
    Reason(R): The -NH_2 group is o-, p- directing and strongly activates the aromatic ring.

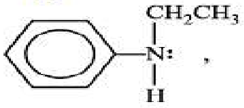
Question	1	2	3	4	5
Answer	c	a	b	d	a

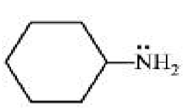
VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

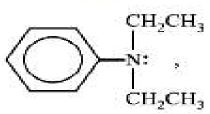
Q: 16 Give the IUPAC name of (i) $H_2N - CH_2 - CH_2 - CH = CH_2$
(ii) $CH_3—NH—CH_2CH_3$.

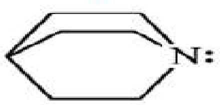
Answer: (i) But-3-en-1-amine (ii) N-methylethanamine

Q: 17 Which of the following are tertiary amines

(i)


(ii)


(iii)


(iv)


Answer: (iii) and (iv) are tertiary amines

Q: 18 Name the IUPAC names of following.

(i) The amine produced by the Hoffmann bromamide degradation of propanamide.
(ii) The product produced after acylation of aniline.

Answer: (i) Ethanamine ($CH_3 - CH_2 - NH_2$)
(ii) N-Phenyl ethanamide ($CH_3CONH- C_6H_5$)

Q: 19 Write the main products of the following reactions:

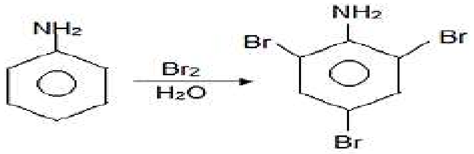
(*i*) $C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{PH=9-10}$
(ii) $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow$

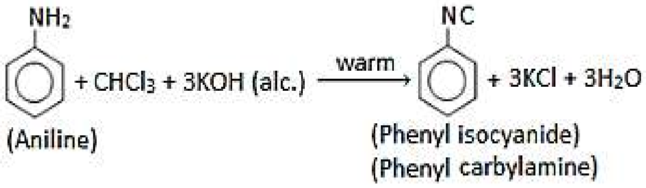
Answer: (i) $C_6H_6 + N_2 + H_3PO_3 + HCl$
(ii) $C_6H_5N=NC_6H_4OH$

Q: 20 Write the chemical equations involved when aniline is treated with the following reagents:

(i) Br_2 water (ii) $CHCl_3$ + KOH

Answer:





Q:21 How will you convert the following:

(*i*) Ethanoic acid to methanamine (*ii)* Benzene diazonium chloride to phenol

Answer:

(i) Ethanoic acid to methanamine

$$CH_3COOH \xrightarrow[\Delta]{NH_3} CH_3CONH_2 \xrightarrow[\text{Hoffmann bromide degradation}]{Br_2/KOH} CH_3NH_2$$

(ii) Benzene diazonium chloride to phenol

$$C_6H_5N_2^+Cl^- + H_2O \rightarrow C_6H_5OH + N_2 + HCl$$

Q: 22 Give the chemical tests to distinguish between the following pairs of compounds:

(i)Ethylamine and Aniline (ii)Aniline and Benzylamine

Answer:

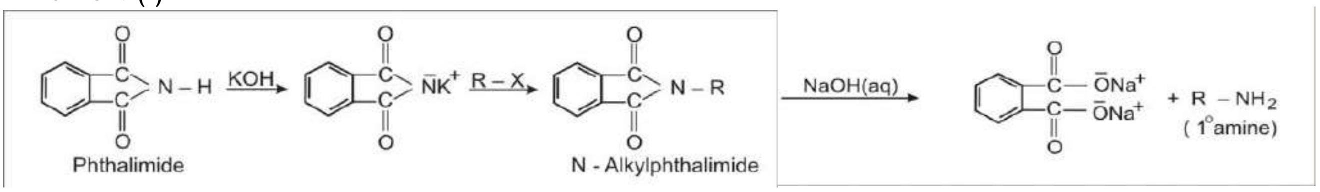
Ethylamine and aniline: Azo-dye test

(i)Aniline reacts with $C_6H_5N_2^+Cl^-$, forms a yellow dye. Ethylamine does not form dye.
(ii) Aniline reacts with $C_6H_5N_2^+Cl^-$, forms a yellow dye. Benzylamine does not form dye.

Q: 23 Write the reactions involved in the following:

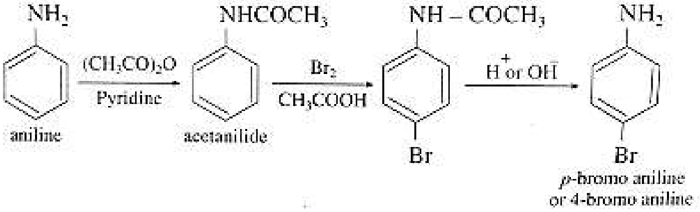
(i) Gabriel phthalimide synthesis (ii) Sandmeyer reaction

Answer: (i)



(ii) $C_6H_5N_2^+X^- + CuCl/HCl \rightarrow C_6H_5Cl + N_2$

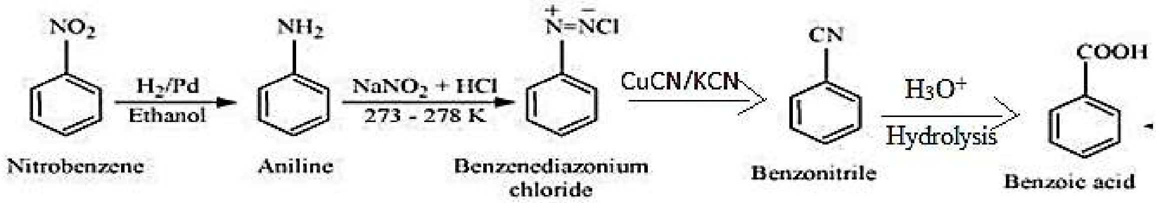
Q: 24 How will you bring about the following conversions?
(*a*) Ethanamine into methanamine (*b*) Aniline into 4-bromoaniline
Answer:
(i) $CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH \xrightarrow{CrO_3,H_2SO_4} CH_3COOH \xrightarrow{NH_{3,\Delta}} CH_3\ CONH_2 \xrightarrow{Br_2,KOH} CH_3NH_2$
(ii)



Q: 25 (i) Arrange the following in increasing order of pK_b values:
$C_6H_5CH_2NH_2$, $C_6H_5NHCH_3$, $C_6H_5NH_2$
(ii) Arrange the following in decreasing order of solubility in water:
$(C_2H_5)_2NH$, $C_2H_5NH_2$, $C_6H_5NH_2$
Answer: (i) $C_6H_5CH_2NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$
(ii) $C_2H_5NH_2 > (C_2H_5)_2NH > C_6H_5NH_2$

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

Q:26 How will you convert the following?
(i) Aniline to chlorobenzene
(ii) Methyl chloride to ethylamine
(iii) Nitrobenzene to benzoic acid
Answer:
(i) $C_6H_5 - NH_2 \xrightarrow{NaNO_2+HCl} C_6H_5N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} C_6H_5Cl$
(ii) $CH_3Cl \xrightarrow{alc.KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$
(iii)



Q: 27 Mr. Krishna, a chemistry teacher gave his class students a sample of an amine "P" having molecular formula $C_4H_{11}N$ to test, identify and write the reaction. The students observed that it reacts with Hinsberg's reagent to form an alkali soluble product. A student Ranu wrote the reaction as follows.

Identify the mistakes committed by Ranu. Write the type of amine in sample "P" and correct chemical equation.
Answer: The formula of Hinsberg's reagent and sample of P were written by Ranu are incorrect. The Sample "P" belongs to primary amine. Therefore, sample "P" is Butanamine. The correct chemical equation is as follows:

Q: 28 Account for the following:
(i) Aniline does not undergo Friedel-Crafts reaction.
(ii) Diazonium salts of aromatic amines are more stable than those of aliphatic amines
(iii) pK_b of methylamine is less than that of aniline.

Answer: (i) Aniline being a Lewis base, reacts with Lewis acid $AlCl_3$ to form a salt. Due to this N atom of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.

(ii) The diazonium salts of aromatic amines are more stable than those of aliphatic amines due to dispersal of the positive charge on the benzene ring.
(iii) In aniline due to resonance the lone pair of electrons on the nitrogen atom are delocalized over the benzene ring. As a result, the electron density on the nitrogen decreases. On the other hand, in methyl amine +I effect of CH_3 increases the electron density on the nitrogen atom. Therefore, aniline is a weaker base than methyl amine and hence its *pKb* value is higher than that of methyl amine

Q: 29 Arrange the following:

(i) CH_3NH_2, $(CH_3)_2NH$, NH_3, $(CH_3)_3N$ [basic strength in gaseous phase]

(ii) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$ [basic strength]

(iii) $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2 [basic strength]

Answer: (i) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(ii) $C_6H_5NH_2 < NH_3 < C_6H_5CH_2NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH$

(iii) $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$

Q: 30 Complete the following reactions:

(i) $CH_3CONH_2 + Br_2 + NaOH \rightarrow$……… $+ Na_2CO_3 + H_2O$

(ii) ……… $+ H_2 \xrightarrow{Pd} CH_3\text{-}CH_2\text{-}NH_2$

(iii) $CH_3CONH_2 \xrightarrow{(i)LiAlH_4(ii)H_2O}$

Answer:

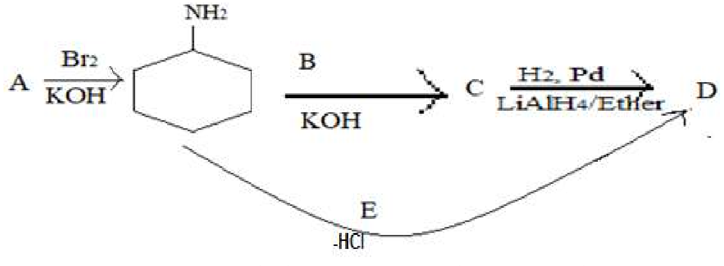
(i) $CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3NH_2. + Na_2CO_3 + 2H_2O + 2NaBr$

(ii) $CH_3\text{-}CH_2\text{-}NO_2 + H_2 \xrightarrow{Pd} CH_3\text{-}CH_2\text{-}NH_2$

(iii) $CH_3CONH_2 \xrightarrow{(i)LiAlH_4(ii)H_2O} CH_3CH_2NH_2$

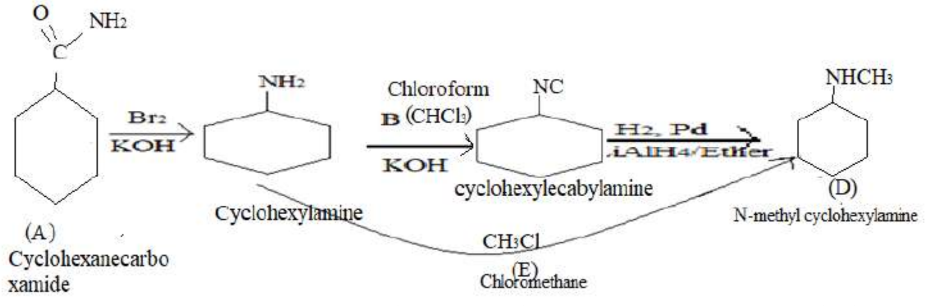
LONG ANSWER TYPE QUESTIONS (5 MARKS

Q: 31 in the following reaction chart identify A, B, C, D and E. Write their IUPAC name and rewrite the following reaction



Answer: A = cyclohexane carboxamide B= Chloroform

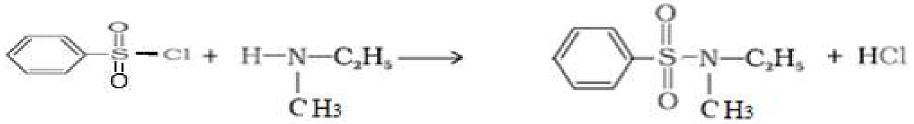
C = cyclohexylcarbylamine D= N- methylcyclohexylamine E = Chloromethane



Q: 32 (i) An amine "X" with formula C_3H_9N reacts with benzenesulphonyl chloride to give a precipitate which is insoluble in alkali. Give the structure and IUPAC name of amine "X". Write the chemical reaction

(ii) How will bring out the following conversions: (A) Aniline to Phenol (B) Aniline to Iodobenzene.

Answer: (i) N methyl ethanamine ($C_2H_5NHCH_3$)



(ii) (a) $C_6H_5-NH_2+HNO_2\xrightarrow{273-278K}C_6H_5-N_2^+Cl^-+NaCl+2H_2O$

$C_6H_5N_2^+Cl^-+H_2O\overset{\Delta}{\rightarrow}C_6H_5OH+N_2+HCl$

(b) $C_6H_5-NH_2+HNO_2\xrightarrow{273-278K}C_6H_5-N_2^+Cl^-+NaCl+2H_2O$

$C_6H_5N_2^+Cl^-+KI\rightarrow C_6H_5I+N_2+KCl$

CASE BASED QUESTIONS

Q 33.Amines are organic bases having the general formula RR'₂N, where R is a hydrocarbon group, 'R' may be H or a hydrocarbon group. As with ammonia, the reaction of amines with water is

$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^-$.

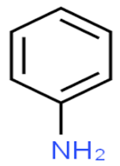
Like all bases, amines form salts when allowed to react with acids.

$CH_3NH_2 + HCl \rightarrow CH_3N^+H_3Cl$

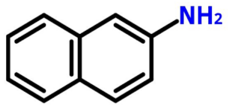
These salts are usually colourless, odourless solids.

Aromatic amines are used mainly in the manufacture of dyes.

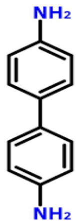
Aniline, the simplest aromatic amine itself is a toxic compound; a number of other aromatic amines such as 2-naphthylamine and benzidine are potent carcinogens.



Aniline



2- naphthylamine



Benzidine

Q(i) Arrange the following in the increasing order of Pk_b value

$C_6H_5NH_2$, $C_2H_5NH_2$, CH_3NH_2, NH_3 .

(ii) Draw the structure of sulphanilic acid

(iii)In cold conditions, aniline is diazotised to form a compound, which is treated with phenol to form a coloured product. Write the necessary equations.

OR

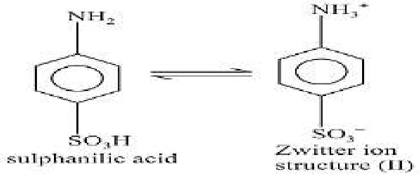
Give reasons

(a) Aniline on nitration gives considerable amount of meta product along with ortho and para.

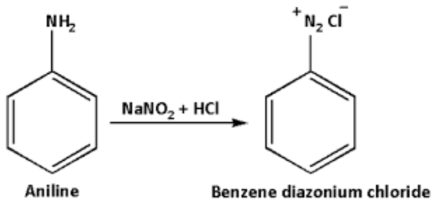
(b) Aniline is less basic than ammonia.

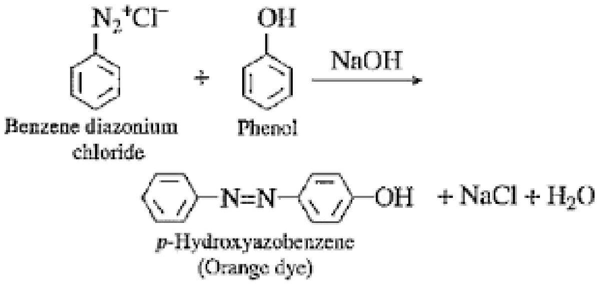
Answers (i) $C_2H_5NH_2$, CH_3NH_2, NH_3, $C_6H_5NH_2$.

(ii)



(iii)

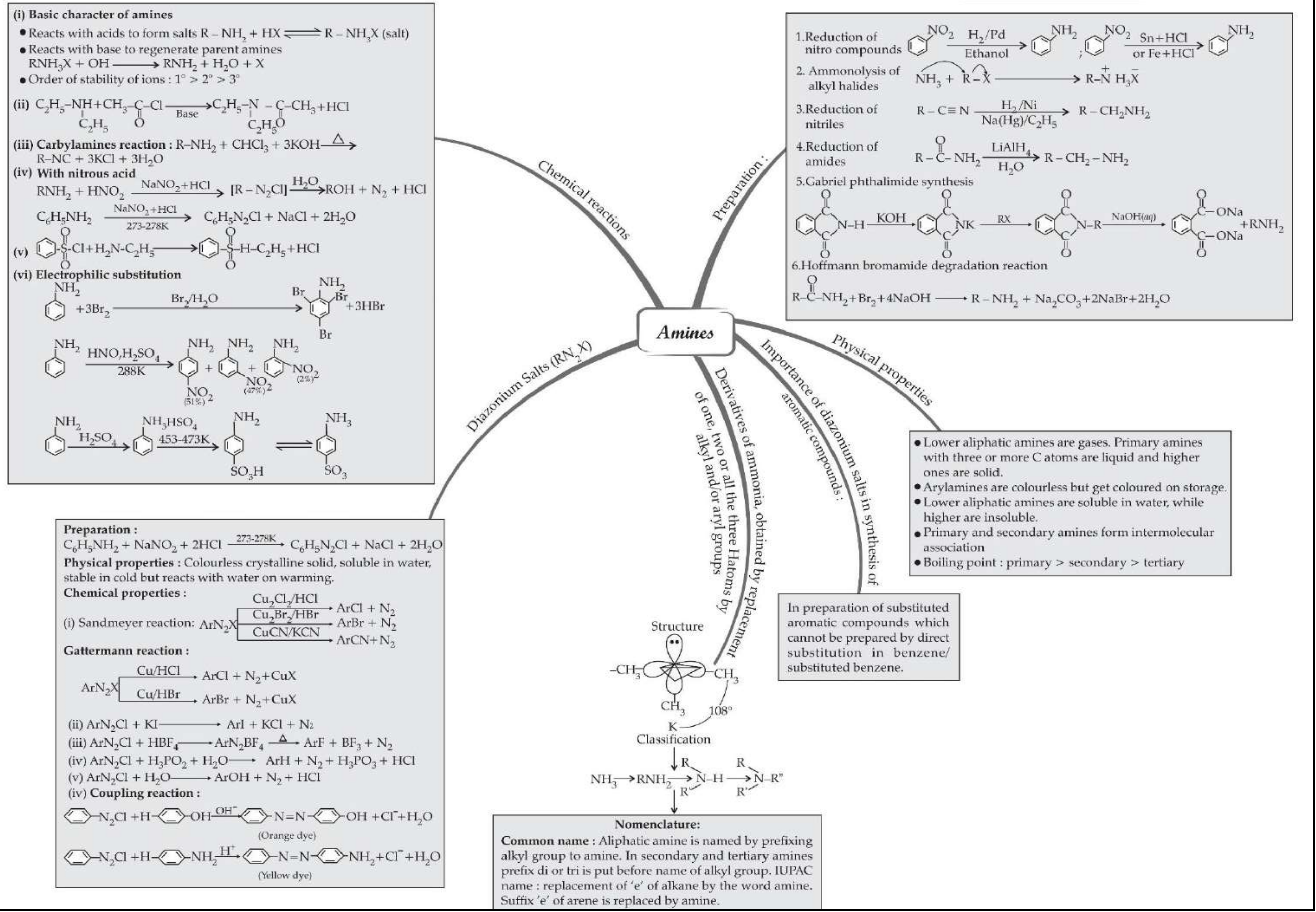




OR

(a)Aniline being basic, reacts with acid to form anilinium ion, which is meta directing.
(b) The lone pair of electrons on N in aniline are not readily available due to delocalization with the benzene ring.

MIND MAP : LEARNING MADE SIMPLE



(i) Basic character of amines

- Reacts with acids to form salts $R-NH_2 + HX \rightleftharpoons R-NH_3X$ (salt)
- Reacts with base to regenerate parent amines
  $RNH_3X + OH \longrightarrow RNH_2 + H_2O + X$
- Order of stability of ions : 1° > 2° > 3°

(ii) $C_2H_5-\underset{C_2H_5}{\underset{|}{N}}H + CH_3-\underset{O}{\underset{\|}{C}}-Cl \xrightarrow[\text{Base}]{} C_2H_5-\underset{C_2H_5}{\underset{|}{N}} - \underset{O}{\underset{\|}{C}}-CH_3 + HCl$

(iii) Carbylamines reaction : $R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-NC + 3KCl + 3H_2O$

(iv) With nitrous acid

$RNH_2 + HNO_2 \xrightarrow{NaNO_2+HCl} [R-N_2Cl] \xrightarrow{H_2O} ROH + N_2 + HCl$

$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2+HCl} C_6H_5N_2Cl + NaCl + 2H_2O$

(v) $C_6H_5-SO_2-Cl + H_2N-C_2H_5 \longrightarrow C_6H_5-SO_2-H-C_2H_5 + HCl$

(vi) Electrophilic substitution

1.Reduction of nitro compounds

2. Ammonolysis of alkyl halides $NH_3 + R-X \longrightarrow R-\overset{+}{N}H_3\overset{-}{X}$

3.Reduction of nitriles $R-C\equiv N \xrightarrow[Na(Hg)/C_2H_5]{H_2/Ni} R-CH_2NH_2$

4.Reduction of amides $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[H_2O]{LiAlH_4} R-CH_2-NH_2$

5.Gabriel phthalimide synthesis

6.Hoffmann bromamide degradation reaction

$R-\overset{O}{\overset{\|}{C}}-NH_2 + Br_2 + 4NaOH \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

- Lower aliphatic amines are gases. Primary amines with three or more C atoms are liquid and higher ones are solid.
- Arylamines are colourless but get coloured on storage.
- Lower aliphatic amines are soluble in water, while higher are insoluble.
- Primary and secondary amines form intermolecular association
- Boiling point : primary > secondary > tertiary

In preparation of substituted aromatic compounds which cannot be prepared by direct substitution in benzene/ substituted benzene.

Nomenclature:

Common name : Aliphatic amine is named by prefixing alkyl group to amine. In secondary and tertiary amines prefix di or tri is put before name of alkyl group. IUPAC name : replacement of 'e' of alkane by the word amine. Suffix 'e' of arene is replaced by amine.

Preparation :

$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{-}278K} C_6H_5N_2Cl + NaCl + 2H_2O$

Physical properties : Colourless crystalline solid, soluble in water, stable in cold but reacts with water on warming.

Chemical properties :

(i) Sandmeyer reaction:

$ArN_2X \xrightarrow{Cu_2Cl_2/HCl} ArCl + N_2$

$ArN_2X \xrightarrow{Cu_2Br_2/HBr} ArBr + N_2$

$ArN_2X \xrightarrow{CuCN/KCN} ArCN + N_2$

Gattermann reaction :

$ArN_2X \xrightarrow{Cu/HCl} ArCl + N_2 + CuX$

$ArN_2X \xrightarrow{Cu/HBr} ArBr + N_2 + CuX$

(ii) $ArN_2Cl + KI \longrightarrow ArI + KCl + N_2$

(iii) $ArN_2Cl + HBF_4 \longrightarrow ArN_2BF_4 \xrightarrow{\Delta} ArF + BF_3 + N_2$

(iv) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow ArH + N_2 + H_3PO_3 + HCl$

(v) $ArN_2Cl + H_2O \longrightarrow ArOH + N_2 + HCl$

(iv) **Coupling reaction :**

10. BIOMOLECULES

Quick Revision Points

KEY POINTS	EXPLANATIONS
Monosaccharides	Cannot be hydrolysed further. eg- glucose, fructose, ribose
Disaccharides	Sucrose (α-D- glucose + β-D-fructose), Maltose(α-D- glucose + α-D- glucose) Lactose (β-D-galactose + β-D-glucose)
Polysaccharides	*Starch* (two components—Amylose and Amylopectin) polymer of α-D- glucose
Amylose	Water soluble,15-20% of starch, unbranched chain , C1– C4 glycosidic linkage.
Amylopectin	Water insoluble, 80-85% of starch, branched chain polymer, C1–C4 & C1–C6 glycosidic linkage
Cellulose	Straight chain polysaccharide of β -D-glucose units/ joined by C1-C4glycosidic linkage (β-link), not digestible by human / constituent of cell wall of plant cells
Glycogen	Highly branched polymer of α-D- glucose .found in liver, muscles and brain.
reducing sugars	Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Eg- maltose and lactose
Non reducing sugars	Aldehydic/ ketonic groups are bonded so cannot reduce Fehling's solution and Tollens' reagent. Eg- Sucrose
Anomers.	The two cyclic hemiacetal forms of glucose differ only in the configuration of the hydroxyl group at C1, called *anomeric carbon* Such isomers, i.e., α –form and β -form, are called anomers.
Invert sugar	Sucrose is dextrorotatory but after hydrolysis gives dextrorotatory glucose and laevorotatory fructose. Since the laevorotation of fructose (–92.4°) is more than dextrorotation of glucose (+ 52.5°), the mixture is laevorotatory. 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
Glycosidic linkage	Linkage between two mono saccharide
Importance of Carbohydrates	Major portion of our food. / used as storage molecules as starch in plants and **glycogen** in animals/. Cell wall of bacteria and plants is made up of cellulose./wood and cloth are cellulose / provide raw materials for many important industries like textiles, paper, lacquers and breweries.
essential amino acids	which cannot be synthesised in the body and must be obtained through diet, eg- Valine, Leucine
Nonessential amino acids	which can be synthesised in the body, eg - Glycine, Alanine
Zwitter ion.	In aqueous solution, amino acids exist as a dipolar ion known as *Zwitter ion.*
peptide linkage	peptide linkage is an amide formed between –COOH group and –NH_2 group of two successive amino acids in peptide chain.
1^0- str. of proteins:	sequence of amino acids that is said to be the primary structure of protein

2^0- str. of proteins:	secondary structure of protein refers to the shape in which a long polypeptide chain can exist. They are found to exist in two types of structures viz. α -helix and β -pleated sheet structure.
Tertiary structure of proteins:	further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular.
Fibrous proteins	Polypeptide chains run parallel, held together by hydrogen and disulphide bonds, fibre– like structure. Water insoluble. Eg- are keratin(in hair, wool, silk) and myosin (present in muscles).
Globular proteins	chains of polypeptides coil around to give a spherical shape. water soluble. Eg-Insulin and albumins
Stab. Forces 2°& 3°	hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction.
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, globules unfold and helix get uncoiled and protein loses its biological activity. This is called **denaturation** of protein. (During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.) eg- The coagulation of egg white on boiling, curdling of milk
Enzymes	Enzymes are essential biological catalysts which are required to catalyse biological reactions, e.g., maltose, lactose, invertase, etc. Almost all the enzymes are globular proteins
Fat soluble vit	These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues
Water soluble vit	B, C. these vitamins must be supplied regularly in diet because they are readily excreted in urine
Vitamins –sources-Deficiency diseases	Vit- A (Fish liver oil, carrots)- Night blindness/Vitamin B_1 (Yeast, milk,)- Beri beri
	Vit-B_2 (Milk, egg white)- Cheilosis/Vit- B_6 (Yeast, milk,)- Convulsions / Vit- B_{12} (Meat, fish,)- Pernicious anaemia
	Vit C(Citrus fruits)- Scurvy, /Vit D(Exposure to sunlight, fish and egg yolk)- Rickets, osteomalacia
	Vit E(wheat oil, sunflower oil)- fragility of RBCs/Vit K(leafy vegetables)- Increased blood clotting time
DNA	pentose sugar (D-2-deoxyribose) +phosphoric acid +nitrogenous bases (A, G, C, T)
RNA	pentose sugar (ribose) + phosphoric acid + nitrogenous bases (A, G, C, U)
Nucleoside / tides	Nucleoside → sugar + base Nucleotides → sugar + base + phosphate
Phosphodiester link	Linkage between two nucleotides in polynucleotides
Functions of Nucleic Acids	DNA reserve genetic information, maintain the identity of different species e is capable of self duplication during cell division, synthesizes protein in the cell.

MULTIPLE CHOICE QUESTIONS (1 MARKS)

1. **α−D (+)-glucose and β−D (+)-glucose are-**

(A) Anomers (B) Epimers (C) Enantiomers (D) Geometrical isomers

2. **Which of the following statements about maltose is incorrect?**

(A) It consists of two glucopyranose units
(B) It is a disaccharide
(C) Glycosidic bond between C1 of one unit and C4 of the other unit
(D) It is a non-reducing sugar

3. **Which of the following acids is a vitamin?**

(A) Aspartic acid (B) Ascorbic acid (C) Adipic acid (D) Saccharic acid

4. **Which of the following statements is not true about glucose?**

(A) It is an aldohexose (B) On heating with HI it forms n-hexane
(C) It is present in Pyranose form (D) It does not give 2,4-DNP test

5. **The helical structure of protein is stabilized by:**

(A) Peptide bond (B) Dipeptide bond (C) Hydrogen bonds (D) Vander Waal's forces

6. **The symbols D and L in the name of Carbohydrate represents**

(A) Dextro rotatory nature
(B) Laevo rotatory nature
(C) The relative configuration of a particular isomer
(D) The optical activity of compounds

7. **DNA and RNA compose of similar-**

(A) Sugar (B) Purines bases (C) Pyrimidines bases (D) Both (A) and (B)

8. **Which of the following is/are example(s) of denaturation of protein?**

(A) Coagulation of egg white (B) Curding of milk
(C) Clotting of blood (D) Both (A) and (B)

9. **What are the hydrolysis products of lactose?**

(A) β–D-galactose and β –D-Glucose (B) α –D-Galactose and α –D-Glucose
(C) α –D-Glucose and β –D-Fructose (D) None of these

10. **Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?**

(A) 5' and 3' (B) 1' and 5' (C) 5' and 5' (D) 3' and 3'

ANSWERS

1. A 2. D 3. B 4. D 5. C 6. C 7. B 8. D 9. A 10.A

ASSERTION REASON TYPE QUESTIONS(1MARKS)

1. **Two statements are given below- one labelled Assertion (A) and the other labelled Reason (R).**

ASSERTION – Vitamin C can't be stored in our body.
REASON – Vitamin C is water soluble and is excreted from the body through urine.
(a) A and R both statements are correct and R is the correct explanation of A.
(b) A and R both statements are correct and R is not the correct explanation of A.
(c) A is correct statement but R is not the correct statement.
(d) A is incorrect statement but R is the correct statement.

2. **Two statements are given below- one labelled Assertion (A) and the other labelled Reason (R).**

ASSERTION – Proteins are polymers of alpha amino acids connected by peptide bonds.
REASON – A tripeptide contains 3 amino acids linked by 3 peptide bonds.
(a) A and R both statements are correct and R is the correct explanation of A.
(b) A and R both statements are correct and R is not the correct explanation of A.
(c) A is correct statement but R is not the correct statement.
(d) A is incorrect statement but R is the correct statement.

3. **Two statements are given below- one labelled Assertion (A) and the other labelled Reason (R).**
   ASSERTION – Change in pH and heating leads to denaturation of proteins.
   REASON – Change in pH and heating cause loss of biological activity of proteins.
   (a) A and R both statements are correct and R is the correct explanation of A.
   (b) A and R both statements are correct and R is not the correct explanation of A.
   (c) A is correct statement but R is not the correct statement.
   (d) A is incorrect statement but R is the correct statement.
4. **Two statements are given below- one labelled Assertion (A) and the other labelled Reason (R).**
   ASSERTION – Adenine and Guanine are the purines present in both nucleic acids.
   REASON – Thiamine and Uracil are the pyrimidine present in DNA.
   (a) A and R both statements are correct and R is the correct explanation of A.
   (b) A and R both statements are correct and R is not the correct explanation of A.
   (c) A is correct statement but R is not the correct statement.
   (d) A is incorrect statement but R is the correct statement.
5. **Two statements are given below- one labelled Assertion (A) and the other labelled Reason (R).**
   ASSERTION – Amylopectin is water soluble and contributes 15-20% of starch.
   REASON – Amylopectin has C_1-C_4 & C_1-C_6 glycosidic linkages.
   (a) A and R both statements are correct and R is the correct explanation of A.
   (b) A and R both statements are correct and R is not the correct explanation of A.
   (c) A is correct statement but R is not the correct statement.
   (d) A is incorrect statement but R is the correct statement.

ANSWERS

1.A 2.B 3.A 4.C 5.D

VERY SHORT ANSWER QUESTIONS (1M)

1. What is the basic structural difference between glucose and fructose?

A. Glucose has aldehyde group whereas fructose has keto group.

2. Name the carbohydrate used as storage molecule to store energy in animals?

A. Glycogen

3. Name the vitamin whose deficiency cause pernicious anemia?

A. Vit B_{12}

4. Write down the vitamin which is responsible for the coagulation of blood?

A. Vit K

5. Give one example each for Fibrous protein and Globular protein.

A. Fibrous protein – Keratin, Globular protein – Insulin

6. What type of linkage is responsible for the formation of proteins?

A. Peptide linkage.

7. Name the unit formed by the attachment of a base to 1^1 positions of sugar.

A. Nucleoside

8. Write the products obtained after hydrolysis of DNA.

A. Pentose sugar, phosphoric acid and Nitrogen containing heterocyclic compounds as bases.

9. Name the base that is found in nucleotide of RNA only ?

A. Uracil

10. Name

a) A major sex hormone produced in males b) The main female sex hormone

A. a) Testosterone
b) Estradiol

SHORT ANSWER QUESTIONS TYPE – 1 (2M)

1. What is the difference between nucleotide and nucleoside?

A. Nucleoside contains ribose or deoxyribose sugar and heterocyclic base. Nucleotide contains phosphoric acid residue along with heterocyclic base and pentose sugar.

2. Name a water-soluble vitamin which is a powerful antioxidant? Give one of its sources.

A. Vit C, citrus fruits like orange, lemon etc.

3. Write 2 differences between RNA and DNA.

A. RNA – a) It has ribose sugar with adenine, uracil, cytosine, guanine as heterocyclic bases.

b) It is single helix.

DNA – a) It has deoxyribose sugar along with adenine, thiamine, cytosine, guanine as heterocyclic bases.

b) It is double helix.

4. What are the two types of secondary structure of proteins? How will you differentiate between them?

A. Alpha – helix and Beta pleated helix structure.

Those polypeptide chains stabilized by intramolecular hydrogen bonds are alpha helix structure.

Beta pleated structure of proteins are stablilised by intermolecular hydrogen bonding.

5. What are polysaccharides? Give two examples.

A. Those carbohydrates which on hydrolysis give large number of monosaccharides. Eg:- Starch, Cellulose.

SHORT ANSWER QUESTION TYPE – 2 (3M)

1. Differentiate between

a) Amylose and Amylopectin

b) Peptide linkage and Glycosidic linkage

c) Fibrous proteins and Globular proteins.

A. a) Amylose is a branched chain polymer of alpha glucose, water soluble. Amylopectin is a branched chain polymer of alpha glucose, water insoluble.

b) The bond CONH between two or more amino acids in polypeptides and proteins is called peptide linkage. The oxide linkage between two or more monosaccharide units in oligosaccharides and polysaccharides is called glycosidic linkage.

c) Fibrous proteins - Thread like structures, insoluble in water. Eg – Keratin, Myosin Globular proteins – Chains of polypeptides coil around spherical shape, soluble in water. Eg – Insulin, Albumin.

2. Define the following with a suitable example.

a) Oligosaccharides

b) Denaturation of proteins

c) Vitamins

A. a) Gives two to ten units of monosaccharides on hydrolysis.

Eg – Lactose, Raffinose

b) On heating or change in pH hydrogen bonds are disturbed, globules unfold and helix get uncoiled and leads to loss of biological activity. Eg – Coagulation of egg white, milk converted to curd.

c) Group of organic compounds which are required in very small amounts for healthy growth and functioning of organism. They cannot be made by organism and so have to be part of our diet. The deficiency of a Vitamin can cause a specific disease. Eg – Fat soluble vitamins – A, D, E, K

Water soluble vitamins – B (except B_{12}), C

3. What are essential and non – essential amino acids? Give two examples of each.

A. Amino acids which cannot be synthesized in the body and must be obtained through diet are known as essential amino acids. Eg – Valine, Leucine

Amino acids which can be synthesized in the body are known as non-essential amino acids. Eg – Alanine, Glutamic acid.

4. Write chemical reactions to show that open structure of D-glucose contains the following

a) Straight chain

b) 5 alcohol groups

c) Aldehyde as carbonyl group

A. a) Glucose when reacted with Red P and HI gives n-hexane. It indicates the presence of straight chain of 6 carbon atoms in glucose. Write equation.

b) On acetylation wit acetic anhydride glucose gives a Pentaacetate. Write equation.

c) Glucose on oxidation with a mild oxidizing agent like bromine water gives gluconic acid containing the same 6 carbon atoms as present in glucose. Write equation.

5. a) Why Vit C cannot be stored in our body?

b) Write the name of Vitamin whose deficiency causes bone deformities in children.

c) Deficiency of which Vitamin cause night blindness.

A. a) Vit C is soluble in water and regularly excreted in urine and hence cannot be stored in body.

b) Vit D

c) Vit A

LONG ANSWER QUESTIONS (5M)

1. Give reasons for the following observations.

a) Amino acids behave like salts rather than simple amines or carboxylic acids.

b) Amino acids show amphoteric behavior.

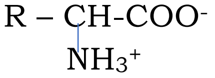
c) The two strands of DNA are complementary to each other.

d) Pentaacetate of glucose does not react with hydroxyl amine.

e) Starch and cellulose both contain glucose units as monomers yet they are structurally different.

A. a) Due to the presence of both acidic (carboxyl group) and basic (amino group) groups in the same molecule.

b) They exist as Zwitter ions in



$R-\underset{\underset{NH_3^+}{|}}{C}H-COO^-$

In Zwitter ionic form amino acids show amphoteric behaviour as they react both with acids and bases.

c) Since there is specific hydrogen bonding between heterocyclic bases, A can form hydrogen bond with T, C can form hydrogen bond with G and vice versa.

d) As glucose forms a six membered ring in which – CHO group combines with – OH group at C5, pentaacetate of glucose does not react with hydroxyl amine due to absence of free – CHO group.

e) The basic structural difference between starch as cellulose is of linkage between the glucose units. In starch there is α- D – glycosidic linkage. Both the components of starch, amylose and amylopectin are polymers of α- D – glycose. On the other hand, cellulose is a linear polymer of β – D- glucose in which C1 of one glucose unit is connected to C4 of the other through β – D- glycosidic linkage.

2. a) Which sugar is called invert sugar? Why is it called so?

b) How can reducing and non-reducing sugars be distinguished? Mention the structural feature characterizing reducing sugars

A. a) Mixture of glucose and fructose is called invert sugar. It is called invert sugar because dextro-rotatory sucrose gives mixture of glucose and fructose on hydrolysis which is laevo-rotatory. Therefore, it is called invert sugar.

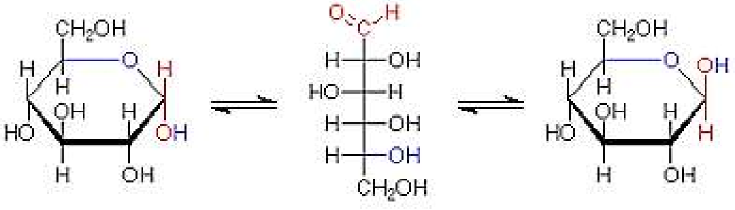
b) Those carbohydrates which reduce Tollens' reagent to give silver mirror or form brick red precipitate with Fehling's solution are called reducing sugars whereas those which do not are non-reducing sugars.

All monosaccharides are reducing sugars due to the presence of aldehyde group or α-keto group. Those disaccharides like sucrose are not reducing sugar because aldehydic and ketonic groups not free. All polysaccharides are non-reducing.

Case Based Questions

1. Read the paragraph carefully and give the answers of the questions followed.

Glucose, Galactose, and fructose have the same chemical formula but they differ in the organization of their atoms. The sugars we have looked at so far are linear molecules (straight chains). That may seem odd because sugars are often drawn as rings. As it turns out both are correct: many five- and six-carbon sugars can exist either as a linear chain or in one or more ring-shaped forms. Cyclic sugars show mutarotation. The optical rotation of the solution depends on the optical rotation of each anomers and their ratio in the solution. Mutarotation was discovered by French chemist Augustin-Pierre Dubrunfaut in 1844, when he noticed that the specific rotation of aqueous sugar solution changes with time. These forms exist in equilibrium with each other, but equilibrium strongly favours the ring forms (particularly in aqueous, or water-based, solution). For instance, in solution, glucose's main configuration is a six-membered ring. Over 99% of glucose is typically found in this form.



(A) (B) (C)

Even when glucose is in a six-membered ring, it can occur in two different forms with different properties. During ring formation, the 'O' from the carbonyl, which is converted to a hydroxyl group, will be trapped either "above" the ring (on the same side as the CH_2OHCH_2OH) or "below" the ring (on the opposite side from this group).

Answer the following questions:

(a) Why D- Glucose does show mutarotation?

(b) What will be the condensation product of glucose and fructose? Which linkage is responsible for condensation of monosaccharides?

(c) Mention the difference in anomeric forms of glucose and evidence to support the cyclic forms of glucose.

OR

(c)Under what conditions glucose is converted to gluconic and saccharic acid? Write chemical reactions.

Answer

(a) D- Glucose shows mutarotation because it undergoes interconversion between its α and β (+) Glucopyranose structures.

(b) Sucrose. Glycosidic linkage

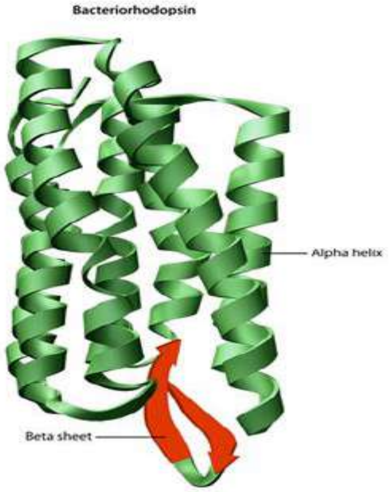
(c) In the α-anomer, the hydroxyl on the anomeric carbon is on the opposite side of the ring from the terminal −CH_2OH group (i.e., pointing down). In the β-anomer, it is on the same side of the ring (pointing up).

Glucose does not give Schiff's test; Hydrogen sulphite addition product is not formed with $NaHSO_3$.The reaction of Pentaacetate of glucose with hydroxylamine does not take place. (any one)

OR

(c) Glucose is converted to gluconic acid by oxidization with bromine water and to saccharic acid when oxidation is carried by conc. HNO_3.

2. **Read the paragraph carefully and give the answers of the questions followed.**



Proteins are the polymers of α -amino acids and they are connected to each other by peptide bond or peptide linkage. Chemically, peptide linkage is an amide formed between–COOH group and –NH_2 group. The reaction between two molecules of similar or different amino acids proceeds through the combination of the amino group of one molecule with the carboxyl group of the other. This results in the elimination of a water molecule and formation of a peptide bond –CO–NH–. The product of the reaction is called a dipeptide because it is made up of two amino acids. For example, when carboxyl group of glycine combines with the amino group of alanine we get a dipeptide, glycylalanine. Structure and shape of proteins can be studied at four different levels, i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

The final shape adopted by a newly synthesized protein is typically the most energetically favourable one. As proteins fold, they test a variety of conformations before reaching their final form, which is unique and compact. Folded proteins are stabilized by thousands of noncovalent bonds between amino acids. In addition, chemical forces between a protein and its immediate environment contribute to protein shape and stability. For example, the proteins that are dissolved in the cell cytoplasm have hydrophilic (water-loving) chemical groups on their surfaces, whereas their hydrophobic (water-averse) elements tend to be tucked inside. In contrast, the proteins that are inserted into the cell membranes display some hydrophobic chemical groups on their surface, specifically in those regions where the protein surface is exposed to membrane lipids. It is important to note, however, that fully folded proteins are not frozen into shape. Rather, the atoms within these proteins remain capable of making small movements.

Answer the following questions:

(a) Name the forces responsible for secondary and tertiary structure.

(b) Where does the water present in the egg go after boiling the egg?

(c) Write one difference between α-helix and β-pleated sheet structure of protein

OR

(c) What is the difference between native protein and denatured protein?

Answer

(a) The forces which are responsible for tertiary structure of proteins are hydrogen bonds, disulphide linkage, Vander walls and electrostatic forces of attraction.

(b) On boiling the water-soluble globular proteins unfold and helix get uncoiled. During this change intermolecular hydrogen bond get disturbed. The water molecule gets attached to the uncoiled proteins molecule through hydrogen bond.

(c) α-Helix structure: The polypeptide chains are held together (stabilized) by Intramolecular H-bonding. β-Pleated sheet structure: The two neighbouring polypeptide chains are held together by intermolecular H-bonding.

OR

(c) Proteins found in a biological system with unique 3D-structure and biological activity is called native protein. When native protein is subjected to physical and chemical change, protein loses its biological activity and is called denatured protein.

3. Read the paragraph carefully and give answers of the questions followed.

Information regarding the sequence of nucleotides in the chain of a nucleic acid is called its primary structure. Nucleic acids have a secondary structure also. James Watson and Francis Crick gave a double strand helix structure for DNA. 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 single stranded helix is present which sometimes folds back on itself. RNA molecules are of three types and they perform different functions. DNA is the chemical basis of heredity and may be regarded as the reserve of genetic information. DNA is exclusively responsible for maintaining the identity of different species of organisms over millions of years. A DNA molecule is capable of self-duplication during cell division and identical DNA strands are transferred to daughter cells.

Answer the following questions:

(a) Name the segment of DNA which acts as the instrumental manual for the synthesis of proteins.

(b) Name the chemical change in DNA that leads to the synthesis of proteins with different amino acids.

(c) (i) Write the sequence of chemicals present in nucleic acids.

(ii) What are the different types of RNA found in the cell?

OR

(c) Write the main functional differences between DNA and RNA. Of the four bases name those which are common to both DNA and RNA.

Answer

3. (a) Gene
   (b) Mutation
   (c) (i)Phosphate- sugar-base
   (ii) m-RNA, t-RNA, r-RNA

OR

(c) DNA is the chemical basis of heredity and RNA molecules are responsible for protein synthesis. Common bases in DNA and RNA Adenine, Guanine and Cytosine.

4. **Read the paragraph carefully and give answers of the questions followed**

An average Indian derives 61 to 64% of energy from consumption of food rich in carbohydrates. A study published in the journal diabetes care has recommended reducing this to 49 to 56% for remission or prevention of type-2 diabetes one of the leading causes of death worldwide. Along with reducing carbohydrates intake the study suggests that one should also increase protein intake. (14-20%) of the total energy consumption. Fats should contribute not more than 21 to 27% of the total energy consumption. In simple words 50% of plate should consist of fruits and green vegetables, 25% carbohydrates of choice, 25% contain food rich in protein. Physically inactive, obese and older individuals as well as presiding in urban locations may require greater reduction in carbohydrate intake. The keto diet, very low-calorie diet is best.

Answer the following questions:

a) **Why do elderly people reduce more intake of carbohydrates than younger people?**
b) **Which carbohydrate are healthier out of polysaccharides, monosaccharides and disaccharides? Give reason.**
c) **i)Which hormone controls blood sugar in our body?**
   ii) Why should diabetic patients do mild exercise like walking every day?

OR

c) **i) Why should protein be increased in diet especially for growing children?**
   ii) Why should our plate have 50% fruits and vegetables.

Answer

a) It is because rate of metabolism is slow in elderly people than younger people.
b) Polysaccharides are healthier because they produce energy slowly.
c) i) Insulin
   ii) It is because rate of metabolism will increase and blood sugar will decrease.

OR

c) i) Proteins are essential for growth and development of body. They strengthen muscles of our body.
   ii) Fruits and vegetables are rich in vitamins, minerals and fibers which help in digestion and keep our body healthy.

5. **Read the paragraph carefully and give answers of the questions followed**

Vitamins are vital for life. A, D, E, K are fat soluble vitamins whereas B_1, B_2, B_3, B_5, B_6, B_7, B_9, C are water soluble vitamins. Vitamin A helps in improving eye sight. Vitamin C prevents scurvy and increases immunity. Vitamin D helps in strong bones and teeth. Our requirement of vitamin D is 15mcg. We get vitamin D from sunlight, eggs, dairy products, orange, oats and mushroom etc. Citrus fruits contain vitamin C. Carrot contains vitamin A. We should include chick pea flour in our diet to prevent inflammation. It has phytonutrients and fibres which have anti-inflammatory properties. It prevents accumulation of fats. It contains Fe, Cu, Mg, fibre, K which are essential to control our wait. It increases our immune system. It contains proteins, amino acids, Mg, vitamin B and P. Pomegranates are good source of vitamin C which our body needs to make collagen. It is rich source of B-complex, vitamin B5 folates pyridoxine and vitamin K. It contains essential minerals like Ca, Cu, Mg and Mn. Pomegranates are rich source of insoluble fibres which help us keep fuller for longer time and regulate bowel function.

Answer the following questions:

a) Why should vitamin B and C must be taken regularly in diet?

b) Which vitamin deficiency causes pernicious anemia? Is it fat or water soluble?

c) i) What is meant by vitamin B-complex?

ii) What is deficiency decease and source of vitamin E

OR

c) i) Which vitamin deficiency leads to bleeding for long time? What is its source?

ii) What is the role of fibre in our body?

Answer

a) It is because vitamin B and C are water soluble and excreted through urine. So it should be taken regularly.

b) Vitamin B_{12}. It is neither fat nor water soluble

c) i) It consists of vitamin B_1, B_2, B_3, B_5, B_6, B_7, B_9 and B_{12}.

ii) Vitamin E deficiency leads to dry skin and loss of reproductive power. Its source is oils like cotton seed oil.

OR

c) i) Vitamin K. It is present in green leafy vegetables.

ii) Fiber helps in digestion and helps to reduce weight.

MIND MAP : LEARNING MADE SIMPLE

Biomolecules

Proteins

(Polymers of α–amino acids)
Amino acids contain $-NH_2$ and $-COOH$ group.

Classification:

- On the basis of relative number of $-NH_2$ and $-COOH$ group
  - (I) Neutral–equal number of $-NH_2$ and $-COOH$ group.
  - (ii) Basic – more number of $-NH_2$ than $-COOH$ group.
  - (iii) Acidic – more number of $-COOH$ than $-NH_2$ group.
- On the basis of place of synthesis
  - (i) Essential – cannot be synthesized in the body.
  - (ii) Non-essential – synthesized in the body.
- On the basis of shape
  - (I) Fibrous – fibre –linke structure
  - (ii) Globular – spherical

Structure : $H_2N-CH_2-\overset{\text{Peptide linkage}}{\boxed{CO-NH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOH$

Denaturation of proteins :
When a protein in its native form is subjected to physical change, globules unfold, helix get uncoiled and protein loses its biological activity.

Carbohydrates

Optically active polyhydroxy aldehydes or ketones or compounds which produce such units on hydrolysis.

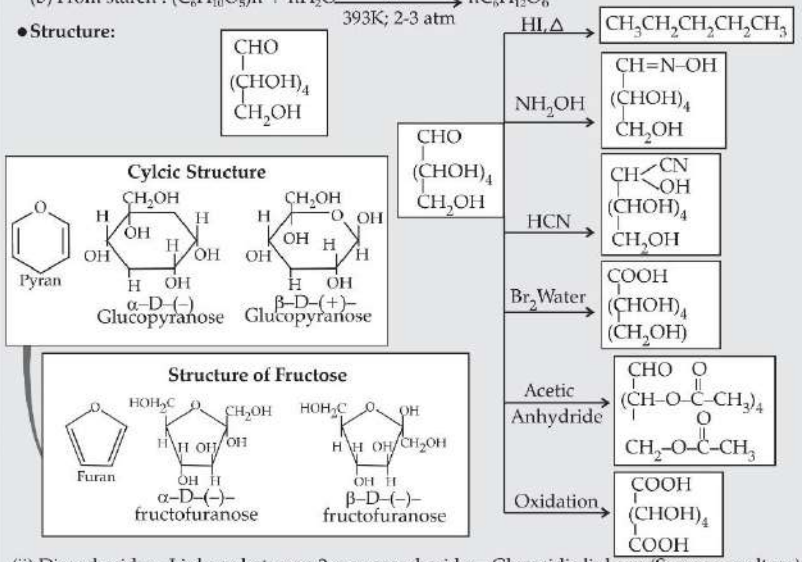
- **Classification:**

(I) Monosaccharides : (Aldehyde group – aldose, keto group –ketose)
Glucose : Preparation :

(a) From sucrose : $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

(b) From starch : $(C_6H_{10}O_5)n + nH_2O \xrightarrow[393K;\ 2\text{-}3\ atm]{H^+} nC_6H_{12}O_6$

- **Structure:**



(ii) Disaccharides : Linkage between 2 monosaccharides– Glycosidic linkage (Sucrose, maltose)
(iii) Polysaccharides : Large number of monosaccharides units joined by glycosidic linkages.
(a) Starch : Polymer of α–glucose with two components amylase and amylopectin
(b) Cellulose
(c) Glycogen

Importance:

- Form a major portion of food.
- As storage molecules.
- Cellulose forms cell wall of bacteria and plants.
- Raw materials for industries like textiles, paper, lacquers and breweries.

Vitamins

Organic compounds required in diet in small amounts to perform specific biological functions for maintenance and growth.
Classification:
(i) Fat soluble : Soluble in fats and oils but insoluble in water. (vitamins A,D,E and K)
(ii) Water soluble : B group and vitamin C are soluble in water.

Enzymes

Globular proteins specific for particular reaction and for particular substrate.
Mechanism : Reduces the magnitude of activation energy

DNA Fingerprinting:Unique sequence of bases on DNA.

Nucleic Acids

Chromosomes : Particles in nucleus responsible for heredity. Chromosomes are made up of proteins and nucleic acid.
Two types : Deoxyribonucleic acid (DNA), ribonucleic acid (RNA)
Composition : In DNA, sugar is β–D–2–deoxyribose whereas in RNA is β–D–ribose. DNA contains A,G,C,T whereas RNA has A,G,C,U.
Structure : –
Nucleoside : Formed by attachment of a base to 1′ of sugar′
Nucleotide : Formed by link to phosphoric acid at 5′ of sugar.

$$-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}-\left[\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}\right]-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-$$

Types of RNA : m–RNA, r–RNA, t–RNA

Biological Functions :

- Chemical basis of heredity.
- Responsible for identity of different species of organisms.
- Nucleic acids are responsible for protein synthesis in cell.

KENDRIYA VIDYALAYA SANGATHAN, BENGALURU REGION
CLASS XII
SAMPLE PAPER-I
CHEMISTRY (THEORY)

BLUEPRINT

S.No.	CHAPTERS	MCQ	A/R	VSA	SA	CASE BASED	LA	TOTAL
		1M	**1M**	**2M**	**3M**	**4M**	**5M**	**70**
1	SOLUTIONS			2 (1)			5 (1)	**7 (2)**
2	ELECTROCHEMISTRY	2(2)			3 (1)	4 (1)		**9 (4)**
3	CHEMICAL KINETICS	1 (1)	1 (1)	2 (1)	3 (1)			**7 (4)**
4	THE d- AND f-BLOCK ELEMENTS	1 (1)	1 (1)				5 (1)	**7 (3)**
5	COORDINATION COMPOUNDS				3 (1)	4 (1)		**7 (2)**
6	HALOALKANES AND HALOARENES	1 (1)		2 (1)	3 (1)			**6 (3)**
7	ALCOHOLS, PHENOLS AND ETHERS	2 (2)	1 (1)		3 (1)			**6 (4)**
8	ALDEHYDES, KETONES AND CARBOXYLIC ACIDS	2 (2)	1(1)	2 (1)	3 (1)			**8 (5)**
9	AMINES	1 (1)					5 (1)	**6 (2)**
10	BIOMOLECULES	2 (2)		2 (1)	3 (1)			**7 (4)**
		12 (12)	**4 (4)**	**10 (5)**	**21 (7)**	**8 (2)**	**15 (3)**	**70 (33)**

Note: - Marks are outside of bracket and number of questions in bracket

KENDRIYA VIDYALAYA SANGATHAN, BENGALURU REGION
CLASS XII
SAMPLE PAPER-I
CHEMISTRY (THEORY)

Time allowed: 3 hours **Maximum marks: 70**

General Instructions:

Read the following instructions carefully and follow them:

(i) This question paper contains 33 questions. All questions are compulsory.
(ii) Question paper is divided into FIVE sections - Section A, B, C, D and E.
(iii) Section A - question number 1 to 16 are multiple choice type questions. Each question carries 1 mark.
(iv) Section B - question number 17 to 21 are very short answer type questions. Each question carries 2 marks.
(v) Section C - question number 22 to 28 are short answer type questions. Each question carries 3 marks.
(vi) Section D - question number 29 and 30 are case-based questions. Each question carries 4 marks.
(vii) Section E- question number 31 to 33 are long answer type questions. Each question carries 5 marks.
(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the Sections, except Section -A.
(ix) Use of calculator is NOT allowed.

SECTION-A

16x1=16

Question No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

1. On increasing temperature,
   (a) ionic conductance increases and electronic conductance decreases.
   (b) ionic conductance decreases and electronic conductance increases.
   (c) both ionic and electronic conductance increase.
   (d) both ionic and electronic conductance decrease.

2. What is the correct order of reactivity of alcohols in the following reaction?
   $$R—OH + HCl \xrightarrow{ZnCl_2} R—Cl + H_2O$$
   (a) 1° > 2° > 3° (b) 1° < 2° > 3°
   (c) 3° > 2° > 1° (d) 3° > 1° > 2°

3. Which cell will measure standard electrode potential of copper electrode?
   (a) $Pt(s) | H_2 (g, 0.1\ bar) | H^+ (aq., 1\ M) || Cu^{2+} (aq., 1M) | Cu(s)$
   (b) $Pt(s) | H_2 (g, 1\ bar) | H^+ (aq., 1\ M) || Cu^{2+} (aq., 2M) | Cu(s)$
   (c) $Pt(s) | H_2 (g, 1\ bar) | H^+ (aq., 1\ M) || Cu^{2+} (aq., 1M) | Cu(s)$
   (d) $Pt(s) | H_2 (g, 1\ bar) | H^+ (aq., 0.1\ M) || Cu^{2+} (aq., 1M) | Cu(s)$

4. Phenol is less acidic than
   (a) Ethanol (b) *o*-nitrophenol
   (c) *o*-methylphenol (d) *o*-methoxyphenol

5. The unit of rate and rate constant are same for a reaction of –
(a) zero order (b) first order
(c) Second order (d) third order

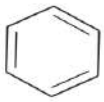
6. Formic acid and ethanoic acid can be distinguished by:
(a) Sod. Bicarbonate test (b) Tollen's test
(c) Iodoform test (d) Lucas test

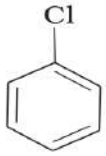
7. In which of the following pairs, both the ions are coloured in aqueous solutions? [Atomic no of Sc = 21, Ti = 22, Ni = 28, Co = 27, Cu = 29]
(a) Sc^{3+}, Ti (b) Sc^{3+}, Co^{2+}
(c) Ni^{2+}, Cu^{+} (d) Ni^{2+}, Ti^{3+}

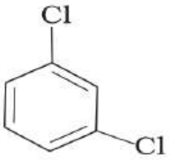
8. In Clemmensen's Reduction, carbonyl compound is treated with __________.
(a) Zn-Hg amalgam + HCl (b) Na-Hg amalgam + HCl
(c) Zn-Hg amalgam + HNO_3 (d) Na-Hg amalgam + HNO_3

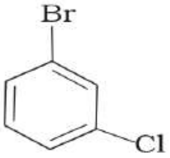
9. Which of the following statements is not true about glucose?
(a) It is an aldohexose. (b) On heating with HI it forms n-hexane.
(c) It is present in furanose form. (d) It does not give 2,4-DNP test

10. Arrange the following compounds in the increasing order of their densities.

(a)


(b)


(c)


(d)


(a) (a) < (b) < (c) < (d) (b) (a) < (c) < (d) < (b)
(c) (d) < (c) < (b) < (a) (d) (b) < (d) < (c) < (a)

11. Curdling of milk is an example of
(a) breaking of peptide linkage. (b) breaking of protein into amino acids.
(c) hydrolysis of lactose. (d) denaturation of protein.

12. The IUPAC name of $CH_3–CH_2-CH_2-N(CH_3)-C_2H_5$ is
(c) N, N-diethylpropan-1-amine (b) N, N-dimethylpropan-1-amine
(c) N-Ethyl–N-methylpropan-1-amine (d) N-methyl-1-pentanamine

For questions number 13 to 16, two statements are given one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below:

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
(C) Assertion (A) is true, but Reason (R) is false.
(D) Assertion (A) is false, but Reason (R) is true.

13. **Assertion (A)** : The solubility of aldehydes and ketones in water decreases with increase of size of the alkyl group
Reason (R) : Alkyl groups are electron releasing groups

14. **Assertion (A)** : Transition metals have high melting point.
Reason (R) : Transition metals have completely filled d-orbitals.

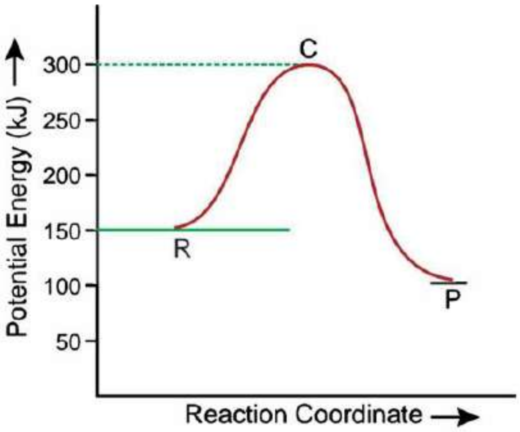
15. **Assertion (A)** : All collisions of reactant molecules lead to product formation.
Reason (R) : Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.

16. **Assertion (A)** : $(CH_3)_3C\text{-}O\text{-}CH_3$ gives $(CH_3)_3$ C-I and CH_3OH on treatment with HI.
Reason (R) : The reaction occurs by S_N1 mechanism.

SECTION - B

17. (i) Why is an increase in temperature observed on mixing chloroform and acetone?
(ii) Why does sodium chloride solution freeze at a lower temperature than water?

18. Answer the following questions on the basis of the given plot of potential energy vs reaction coordinate:



(i) What is the threshold energy for the reaction?
(ii) What is the activation energy for forward reaction?
(iii) What is the activation energy for backward reaction?
(iv) What is enthalpy change for the forward reaction?

19. Give reasons:
(i) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length in CH_3-Cl.
(ii) S_N1 reactions are accompanied by racemisation in optically active alkyl halides.

20. Write the reagents used in the following reactions:
(i) $C_6H_5\text{-}CO\text{-}CH_3 \longrightarrow C_6H_5\text{-}CH_2\text{-}CH_3$
(ii) $CH_3COOH \longrightarrow CH_3\text{-}COCl$

OR

Arrange the following compounds in increasing order of their property as indicated:
(i) CH_3COCH_3, $C_6H_5\text{-}CO\text{-}C_6H_5$, CH_3CHO (reactivity towards nucleophilic addition reaction)
(ii) $Cl_2CH\text{-}COOH$, $Cl\text{-}CH_2\text{-}COOH$, $CCl_3\text{-}COOH$ (acidic character).

21. Write the reactions involved when D-glucose is treated with the following reagents:
(i) HCN (ii) Br_2 water

SECTION – C

22. From the following molar conductivities at infinite dilution, calculate the limiting molar conductivity, Λ_m^0 for NH_4OH. (3m)
Λ_m^0 for $Ba(OH)_2 = 457.6\ \Omega^{-1}\ cm^2\ mol^{-1}$
Λ_m^0 for $BaCl_2 = 240.6\ \Omega^{-1}\ cm^2\ mol^{-1}$
Λ_m^0 for $NH_4Cl = 129.8\ \Omega^{-1}\ cm^2\ mol^{-1}$

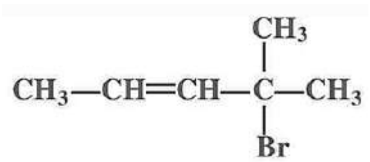
23. (A), (B) and (C) are three non-cyclic functional isomers of a carbonyl compound with molecular formula C_4H_8O. Isomers (A) and (C) give positive Tollens' test whereas isomer (B) does not give Tollens' test but gives positive Iodoform test. Isomers (A) and (B) on reduction with Zn(Hg)/conc. HCl give the same product (D).
    (i) Write the structures of (A), (B), (C) and (D).
    (ii) Out of (A), (B) and (C) isomers, which one is least reactive towards addition of HCN? (2+1)

24. Define the following terms:
    (i) Pseudo first order reaction
    (ii) Half-life period of a reaction
    (iii) Molecularity of a reaction. (1+1+1)

25. Write chemical equations for the following reactions: **(Any three)** (1+1+1)
    (a) Hydroboration - oxidation reaction
    (b) Williamson Synthesis
    (c) Friedel-Crafts Alkylation of Anisole
    (d) Reimer-Tiemann Reaction

26. (i) What type of isomerism is shown by the complex $[Cr(H_2O)_6]Cl_3$? 1
    (ii) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o > P$. 1
    (iii) Write the hybridisation and shape of $[CoF_6]^{3-}$ (Atomic number of Co = 27). 1

27. (i) Write equation for preparation of 1-iodobutane from 1-chlorobutane. 1
    (ii) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction? 1
    (iii) Give IUPAC name of- 1



$$CH_3{-}CH{=}CH{-}\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}{-}CH_3$$

28. Differentiate between:
    (a) Native protein and denaturated protein 1
    (b) RNA and DNA 1
    (c) Essential amino acids and non-essential amino acids. 1

SECTION – D

The following questions are case based. Read the passage carefully and answer the questions that follow.

29. Coordination compounds are the compounds in which the central metal atom is linked to a number of ions or neutral molecules by coordinate bonds and the donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond with it are called ligands. Coordination number is the number of atoms or ions immediately surrounding a central atom in a complex or a crystal.

Coordination number of Ni^{2+} is 4 and it forms two complexes A and B as given below:

$NiCl_2 + KCN \rightarrow A$ (Cyano complex)

$NiCl_2 + KCl \rightarrow B$ (Chloro complex)

(i) Which of the following is the correct IUPAC name of complex A? 1

(a) Potassium tetracyanonickelate (I)
(b) Potassium tetranitrilenickelate (II)
(c) Potassium tetracyanonickelate (III)
(d) Potassium tetracyanonickelate (II)

(ii) The correct formula of the complex B will be 1

(a) $K_2[NiCl_4]$ (b) $K_2[Ni(CN)]$
(c) $K_3[NiCl_4]$ (d) $K[NiCl_4]$

(iii) The magnetic nature of A is 1

(a) paramagnetic (b) diamagnetic
(c) ferrimagnetic (d) ferromagnetic

(iv) The state of hybridisation of the complex B is 1

(a) sp (b) sp^2
(c) sp^3 (d) sp^3d^2

OR

The geometry of the complex A is

(a) tetrahedral (b) trigonal planar
(c) square planar (d) trigonal bipyramidal

30. In a galvanic cell, chemical energy of a redox reaction is converted into electrical energy, whereas in an electrolytic cell the redox reaction occurs on passing electricity. The simplest galvanic cell is in which Zn rod is placed in a solution of $ZnSO_4$, and Cu rod is placed in a solution of $CuSO_4$.The two rods are connected by a metallic wire through a voltmeter. The two solutions are joined by a salt bridge. The difference between the two electrode potentials of the two electrodes is known as electromotive force. In the process of electrolysis, the decomposition of a substance takes place by passing an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

Answer the following questions:

(a) What is the function of a salt bridge in a galvanic cell? 1

(b) When does galvanic cell behave like an electrolytic cell? 1

(c) Can copper sulphate solution be stored in a pot made of zinc? 2
Explain with the help of the value of E^{θ}_{cell}.
(E^{θ} $Cu^{2+}/Cu = 0.34V$) (E^{θ} $Zn^{2+}/Zn = - 0.76V$)

OR

(c) How much charge in terms of Faraday is required for the following: 2

(i) 1 mol of MnO_4^- to Mn^{2+}

(ii) 1mol of H_2O to O_2

31. (i) Define azeotropes. 1

(ii) Out of two 0.1 molal aqueous solutions of glucose and of potassium chloride, which one will have a higher boiling point. 1

(iii) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25 ^{0}C assuming it to be completely dissociated. (Atomic masses K = 39 u, S = 32 1, 0 = 16 u). 3

OR

(i) What are isotonic solutions? 1

(ii) Identify which liquid will have a higher vapour pressure at 90°C if the boiling points of two liquids A and B are 140°C and 180°C, respectively. 1

(iii) Calculate the boiling point of solution when 2 g of Na_2SO_4 (Molar mass = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation. (K_b for water = 0.52 K kg mol^{-1}).

32. Assign reasons for the following (Answer any **FIVE**).

a) The enthalpies of atomisation of transition elements are high.

b) The transition metals and many of their compounds act as good catalysts.

c) From element to element, the actinoid contraction is greater than the lanthanoid contraction.

d) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that of Cr^{3+}/Cr^{2+}.

e) Scandium (Z = 21) does not exhibit variable oxidation states and yet it is regarded as a transition element.

f) Ce^{4+} is used as an oxidising agent in volumetric analysis.

g) Zn^{2+} salts are white while Cu^{2+} salts are blue.

33. (i) Write the structures of main products when aniline reacts with the following reagents:

(a) Br_2 water (b) HCI (c) $(CH_3CO)_2O$/pyridine

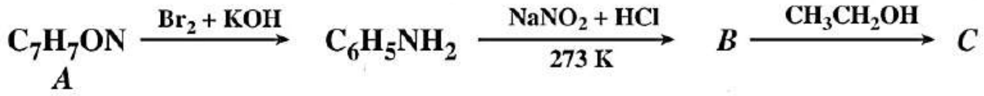
(ii) Arrange the following in the increasing order of their boiling point:

$C_2H_5NH_2$, C_2H_5OH, $(CH_3)_3N$

(iii) Give a simple chemical test to distinguish between: $(CH_3)_2NH$ and $(CH_3)_3N$

OR

(i) An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B and C.



$$\underset{A}{C_7H_7ON} \xrightarrow{Br_2 + KOH} C_6H_5NH_2 \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{CH_3CH_2OH} C$$

(ii) Arrange the following in increasing order of their basic strength:

$C_6H_5NH_2$, $CH_3—CH_2—NH_2$, CH_3-NH-CH_3

(iii) Give one chemical test to distinguish between: Aniline and benzylamine.

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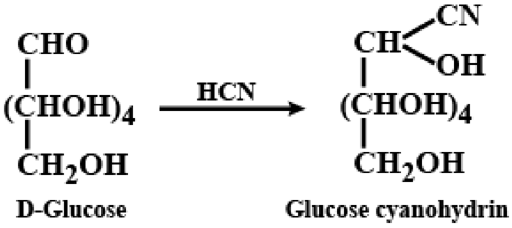
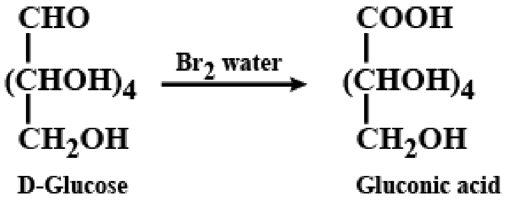
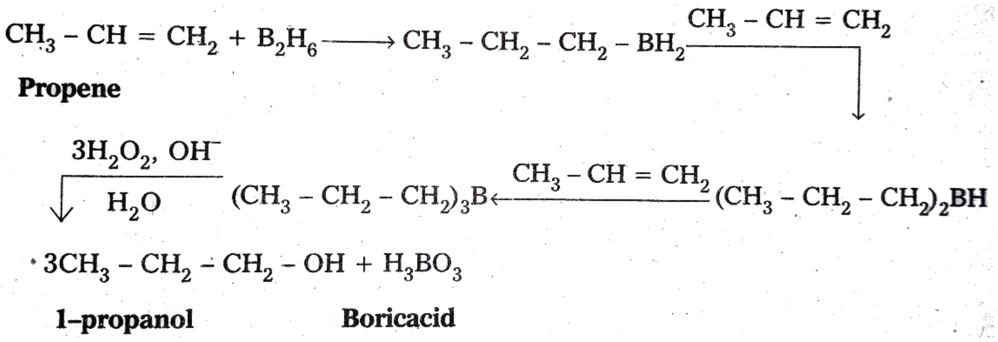
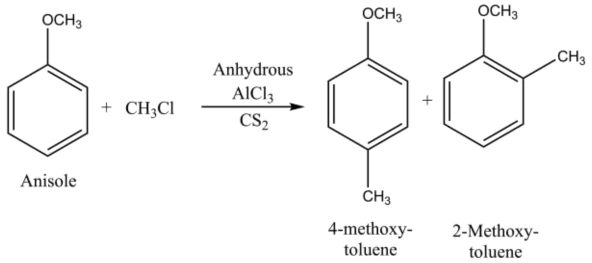
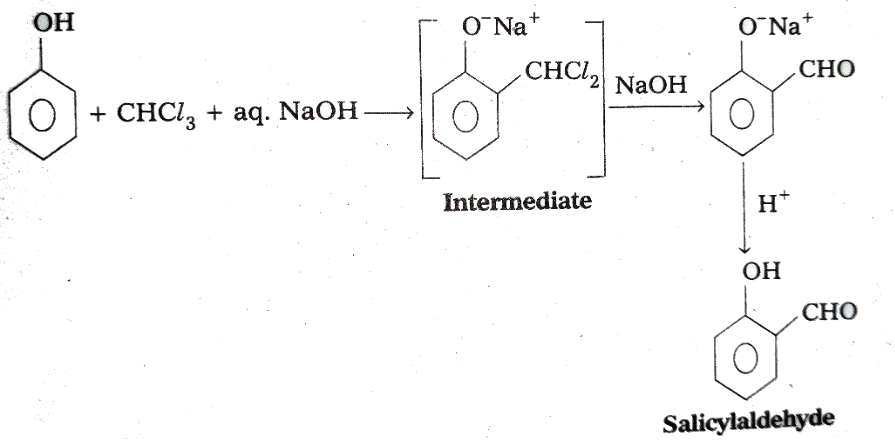
KENDRIYA VIDYALAYA SANGATHAN, BENGALURU REGION
CLASS XII
CHEMISTRY (THEORY)

Time allowed: 3 hours **Maximum marks: 70**

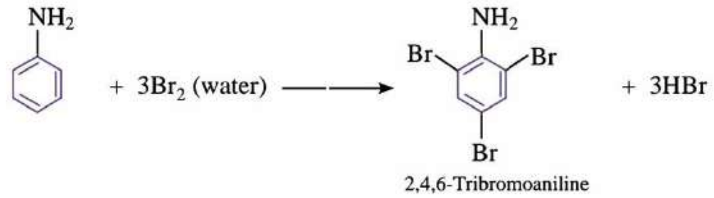
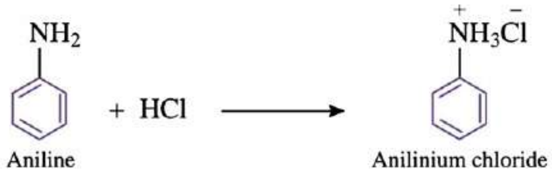
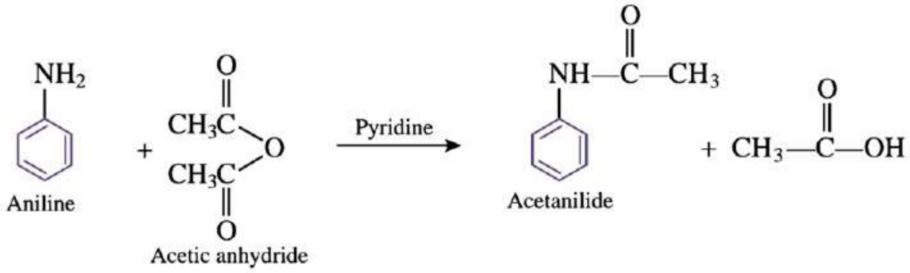
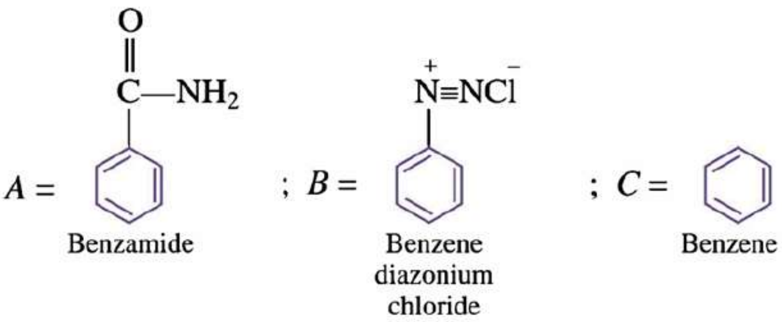
MARKING SCHEME

Q.No	Expected answer/ Value points	Marks
	SECTION - A	
1	a	1
2	c	1
3	c	1
4	b	1
5	a	1
6	b	1
7	d	1
8	a	1
9	c	1
10	a	1
11	d	1
12	c	1
13	b	1
14	c	1
15	d	1
16	a	1
	SECTION - B	
17	(i) The bonds between chloroform molecules and molecules of acetone are dipole-dipole interactions but on mixing, the chloroform and acetone molecules, they start forming hydrogen bonds which are stronger bonds resulting in the release of energy. This gives rise to an increase in temperature. (ii) When a non-volatile solute is dissolved in a solvent, the vapour pressure decreases. As a result, the solvent freezes at a lower temperature.	1 1
18	(i) Threshold energy for the reaction = 300 $kJmol^{-1}$ (ii) Activation energy for the forward reaction= 150 $kJmol^{-1}$ (iii) Activation energy for the backward reaction = 200 $kJmol^{-1}$ (iv) enthalpy change for the forward reaction= - 50 $kJmol^{-1}$	½ ½ ½ ½
19	(i) In chlorobenzene, C - Cl bond acquires partial double bond character while in methyl chloride, C-CI bond has pure single bond character. As a result, C-Cl bond in chlorobenzene is shorter than methyl chloride. (ii) Carbocations are intermediate in S_N1 reactions. Carbocations being sp^2 hybridised are planar species, therefore, attack of nucleophile on it can occur from both front and rear with almost equal ease giving a racemic mixture.	1 1

20	(i) Zn-Hg, conc. HCl or H_2NNH_2 and KOH/ethylene glycol, Heat (ii) PCl_5 or $SOC1_2$ OR (i) $C_6H_5-CO-C_6H_5 < CH_3COCH_3 < CH_3CHO$ (ii) $Cl-CH_2-COOH < Cl_2-CH-COOH < CC1_3-COOH$	1 1 1 1
21	 	1 1
SECTION - C		
22	$\Lambda^o_{m(NH_4OH)} = \lambda^o_{NH_4^+} + \lambda^o_{OH^-}$ $= (\lambda^o_{NH_4^+} + \lambda^o_{Cl^-}) + \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{OH^-}) - \frac{1}{2}(\lambda^o_{Ba^{2+}} + 2\lambda^o_{Cl^-})$ $= \Lambda^o_{m(NH_4Cl)} + \frac{1}{2}[\Lambda^o_{m(Ba(OH)_2)}] - \frac{1}{2}[\Lambda^o_{m(BaCl_2)}]$ $= 129.8 + \frac{1}{2} \times 457.6 - \frac{1}{2} \times 240.6$ $= \mathbf{238.3\ ohm^{-1}\ cm^2\ mol^{-1}}$	 1 1 1
23	(i) A= $CH_3CH_2CH_2CHO$ B= $CH_3CH_2COCH_3$ C= $(CH_3)_2CH-CHO$ D= $CH_3CH_2CH_2CH_3$ (ii) B= $CH_3CH_2COCH_3$	½ ½ ½ ½ 1
24	Correct definitions.	1+1+1
252	(Any three) (a) Hydroboration - oxidation reaction  (b) Williamson Synthesis R-X + R'ONa → R-O-R' + NaX	1+1+1

	(c) Friedel-Crafts Alkylation of Anisole  (d) Reimer-Tiemann Reaction  	
26	(i) Hydration isomerism (ii) $t_{2g}^4\ e_g^0$ (iii) Hybridisation: sp^3d^2, Shape: Octahedral	1 1 ½ +½
27	(i) $CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2CH_2CH_2{-}I + NaCl$ (ii) 2-bromo-2-methylbutane (iii) 4-Bromo-4-methylpent-2-ene	1 1 1
28	(a) Protein found in a biological system with unique three-dimensional structure and biological activity is called native protein. When a protein in its native form is subjected to change such as change in temperature, change in pH, its 2° and 3° structures are destroyed and it loses its biological activity. The protein thus formed is called denatured protein. (b) RNA is single stranded nucleic acid containing D-ribose sugar and N- bases such as adenine, guanine, cytosine and uracil. DNA is double stranded nucleic acid containing 2-deoxy-D-ribose sugar and N- bases such as adenine, guanine, cytosine and thymine. (c) Amino acids which are not synthesized by the human body are known as essential amino acids. On the other hand, amino acids which are needed for health and growth of human beings and are synthesized by the human body are called non-essential amino acids.	1 1 1
SECTION - D		
29	(i) (d) Potassium tetracyanonickelate (II) (ii) (a) $K_2[NiCl_4]$ (iii) (b) diamagnetic (iv) (c) sp^3 OR (c) square planar	1 1 1 1
30	a) maintain electrical neutrality within the internal circuit/ helps in preventing the cell from taking its reaction to equilibrium. b) When an external voltage, greater than the cell potential is applied.	1 1

	c) No. Zinc is more reactive than copper. Thus, if we will store copper sulphate solution in zinc pot then zinc will displace copper from its solution. The following reaction will take place:- $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$.	1 1
	OR (i) 5F (ii) 2F	1 1
31	(i) Mixtures having same composition in liquid and vapour phase, boil at a constant temperature and cannot be separated by fractional distillation.	1
	(ii) 0.1 m KCl	1
	(iii) Since K_2SO_4 dissociates completely as $K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$ $i = \frac{\text{Number of moles of particles after dissociation}}{\text{Number of moles of particles before dissociation}} = \frac{3}{1} = 3$	1
	Applying van't Hoff equation, $\pi = \frac{i \times W_B \times R \times T}{M_B \times V}$ $= \frac{3 \times 0.025 \text{ g} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{174 \text{ g mol}^{-1} \times 2 \text{ L}}$	1
	$= \mathbf{5.27 \times 10^{-3} \text{ atm}}$	1
	OR	
	(i) Solutions having same osmotic pressure.	1
	(ii) Liquid A	1
	(iii) $i = \frac{3}{1} = 3 \left(Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}\right)$	1
	Given, $W_B = 2$ g, $W_A = 50$ g, $M_B = 142$ g mol^{-1}, $K_b = 0.52$ K kg mol^{-1} Substituting the values in the expression, $\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$ $\Delta T_b = \frac{3 \times 0.52 \times 2 \times 1000}{142 \times 50} = 0.439 \text{ K}$	1
	So, boiling point of solution, $T_b = T_b^0 + \Delta T_b = 373.15 \text{ K} + 0.439 \text{ K} = \mathbf{373.589 \text{ K}}$	1
32	(Any Five) a) This is because transition metals have strong metallic bonds as they have a large number of unpaired electrons. b) Because of their variable oxidation states, transition metals form unstable intermediate compounds. c) This is due to poorer shielding by 5f-electrons in actinoids than that by 4f-electrons in the lanthanoids. d) This is due to much larger third ionisation energy of Mn as Mn^{2+} is very stable on account of stable d^3 configuration. e) Sc has partially filled d-orbitals in the ground state ($3d^1 4s^2$). f) Ce^{4+} has the tendency to attain +3 oxidation state which is more stable.	5x1= 5

	g) Zn^{2+} ion has all its orbitals completely filled whereas in Cu^{2+} ion there is one half-filled 3d-orbital. Therefore, due to d-d transition Cu^{2+} has a tendency to form coloured salts whereas Zn^{2+} has no such tendency.	
33	(i)	
	(a) 	1
	(b) 	1
	(c) 	1
	ii) $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$	1
	(i) By Hinsberg's reagent test – Brief explanation.	1
	OR	
	(ii)	
		1+1+1
	(iii) $C_6H_5NH_2 < CH_3—CH_2—NH_2 < CH_3\text{-}NH\text{-}CH_3$	1
	(iv) Azo dye test	1

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KENDRIYA VIDYALAYA SANGATHAN, BENGALURU REGION
CLASS XII
SAMPLE PAPER-II
CHEMISTRY (THEORY)

Sl. No.	NAME OF THE CHAPTER	MCQ	A & R	SA – I	SA - 2	CBQ	LA	Total
		1 Mark	1 Mark	2 Marks	3 Marks	4 Marks	5 Marks	
1	**Solutions**	---	---	2(1)	---	---	5(1)	**7(2)**
2	**Electrochemistry**	1(1)	1(1)	---	3(1)	4(1)	---	**9(4)**
3	**Chemical Kinetics**	1(2)	---	2(1)	3(1)	---	---	**7(4)**
4	**d and f Block Elements**	1(2)	---	---	---	---	5(1)	**7(3)**
5	**Coordination Compounds**	---	---	---	3(1)	4(1)	---	**7(2)**
6	**Haloalkanes and Haloarenes**	1(2)	1(1)	---	3(1)	---	---	**6(4)**
7	**Alcohols, Phenols and Ethers**	1(1)	---	2(1)	3(1)	---	---	**6(3)**
8	**Aldehydes, Ketones and Carboxylic Acids**	1(2)	1(1)	2(1)	3(1)	---	---	**8(5)**
9	**Amines**	1(1)	---	---	---	---	5(1)	**6(2)**
10	**Biomolecules**	1(1)	1(1)	2(1)	3(1)	---	---	**7(4)**
TOTAL		**1 (12)**	**1(4)**	**2(5)**	**3(7)**	**4(2)**	**5(3)**	**70(33)**

Note: 1. Number outside the bracket indicates marks of each question and the number enclosed within bracket denotes number of questions.
2. Prepared as per CBSE CLASS XII CHEMISTRY SQP 2023-24.

KENDRIYA VIDYALAYA SANGATHAN, BENGALURU REGION
CLASS XII
SAMPLE PAPER-II
CHEMISTRY (THEORY)

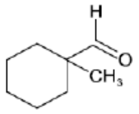
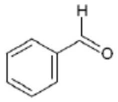
Max. Marks: 70 **Time: 3**
Hours

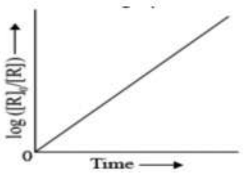
General Instructions:

a) There are 33 questions in this question paper with internal choice.
b) Section A consists of 16 multiple-choice questions carrying 1 mark each.
c) Section B consists of 5 very short answer questions carrying 2 marks each.
d) Section C consists of 7 short answer questions carrying 3 marks each.
e) Section D consists of 2 case-based questions carrying 4 marks each.
f) Section E consists of 3 long answer questions carrying 5 marks each.
g) All questions are compulsory.
h) Use of log tables and calculators is not allowed.

SECTION A

The following questions are multiple-choice questions with one correct answer. Each question carries 1 mark. There is no internal choice in this section.

1.	Which of the following statement is not true about glucose? (a) It is an aldohexose (b) On heating with HI it forms n-hexane (c) It is present in pyranose form (d)It forms orange precipitate with 2,4-DNP	1
2.	Write the IUPAC name of the product of the following reaction $C_6H_5N_2Cl + H_2O \rightarrow$ (a)Chlorobenzene (b) Bromobenzene (c) p-chlorophenol (d) Phenol	1
3.	Which of the following lanthanoids show +4 oxidation state besides the characteristic oxidation state +3 of lanthanoids? (a) Ce (b) Eu (c) Tb (d) Dy	1
4.	If 96500 coulomb electricity is passed through $CuSO_4$ solution, it will liberate (At. Wt of Cu=63.5g/mol) (a) 63.5 g of Cu (b) 31.75 g of Cu (c) 127 g of Cu (d) 100 g of Cu	1
5.	What is the correct order of reactivity of alcohols in the following reaction? $R—OH + HCl \rightarrow R—Cl + H_2O$ (a) 1° > 2° > 3° (b) 1° < 2° > 3° (c) 3° > 2° > 1° (d) 3° > 1° > 2°	1
6.	Which of the following aldehydes doesn't undergo Cannizzaro's reaction? (a)  (b)  (c) HCHO (d) CH_3CHO	1
7.	Which of the following expressions is correct for the rate of reaction given below? $5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$ (a) $\frac{\Delta[Br^-]}{\Delta t} = 5\frac{\Delta[H^+]}{\Delta t}$ (b) $\frac{\Delta[Br^-]}{\Delta t} = \frac{6}{5}\frac{\Delta[H^+]}{\Delta t}$ (c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$ (d) $\frac{\Delta[Br^-]}{\Delta t} = 6\frac{\Delta[H^+]}{\Delta t}$	1
8.	Iodoform is used as an (a) antiseptic (b) analgesic (c) anesthetic (d) antipyretic	1
9.	Which of the following compounds has –Cl in arylic position? (a) Ethyl chloride (b) Chlorobenzene (c) Vinyl chloride (d) Benzyl chloride	1
10.	The reagent which does not react with both Propanone and Benzaldehyde: (a) Grignard reagent (b) Tollen's reagent (c) Zn-Hg /Conc.HCl (d)Fehling solution	1

11.	$KMnO_4$ is acidified using H_2SO_4 in titrations and HCl is not used because (a) H_2SO_4 is stronger acid than HCl (b) HCl is oxidised to Cl_2 by $KMnO_4$ (c) H_2SO_4 is dibasic acid (d) rate of reaction is faster in presence of H_2SO_4	1
12.	The slope of the following graph is  (a) $\frac{k}{2.303}$ (b) $\frac{2.303}{k}$ (c) k (d) $\frac{1}{k}$	1

For question number 13 to 16 two statements labelled as Assertion (A) and Reason (R

Select the most appropriate answer from the options given below:

(a) ***Both A and R are true and R is the correct explanation of A***
(b) ***Both A and R are true but R is not the correct explanation of A.***
(c) ***A is true but R is false.***
(d) ***A is false but R is true.***

13.	Assertion: Conductivity of a solution decreases with decrease in concentration. Reason: The number of ions per unit volume of solution decreases.	1
14.	Assertion : D(+)Glucose is dextrorotatory in nature. Reason : 'D' represents its dextrorotatory nature.	1
15.	Assertion: Aryl halides undergo nucleophilic substitution reactions more easily. Reason: The carbon halogen bond in aryl halides has partial double bond character.	1
16.	Assertion: Sodium hydrogen sulphite adds to aldehydes and ketones to form the addition product. Reason: Reaction of aldehydes with Sodium hydrogen sulphite is useful for separation and purification of aldehydes.	1

SECTION B

This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17.	(a). Define molality. (b). Give an example for Solid-Solid solution	1 1
18.	What happens when (i) Phenol reacts with bromine water? (ii) Anisole reacts with HI? Write the chemical equations involved in the above reactions.	 1 1
19.	Name the nitrogenous bases present in RNA. Which one of these is not present in DNA?	1+1
20.	Arrange the following compounds in increasing order of property mentioned within brackets. (a)CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$ (boiling point) (b)Ethanal, Propanal, Propanone, Butanone (reactivity towards nucleophilic addition reaction)	1+1
21.	A first order reaction has rate constant of $1{\cdot}15 \times 10^{-3}\ s^{-1}$. How long will 5 g of this reactant take to reduce to 3g? (log 5 = 0.6990 , log 3=0.4771)	2

SECTION C

This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 marks each

22.	Write Nernst equation for the cell in which the following reaction takes place $Mg(s) + 2Ag^{+}(0.0001M) \rightarrow Mg^{2+}(0.130M) + 2Ag(s)$ Calculate its E_{Cell} if $E^{O}_{Mg^{2+}/Mg}$ = -2.36 V and $E^{O}_{Ag^{1+}/Ag}$ = 0.81 V (log 13=1.114)	3
23.	(a) Identify the chiral molecule in the following pair: (i) 3-methylbutan-2-ol (ii) 2,4-dimethylbutan-3-ol (b) Write the structure of the product when Chlorobenzene is treated with methyl chloride in the presence of sodium metal and dry ether. (c) Write the structure of the alkene formed by dehydrohalogenation of 1-bromo-1- methylcyclohexane with alcoholic KOH	1 1 1
24.	(a) Draw the Geometrical isomers of [$Pt(en)_2Cl_2]^{2+}$ and name the optically active isomer. (b) On the basis of crystal field theory write the electronic configuration for d^5 ion for which $\Delta o < P$	2 1
25.	(a) Draw the Zwitter ion structure of Alanine $CH_3CH(COOH)(NH_2)$ (b) Lysine is an essential amino acid. Give reason. (c) Give differences between Fibrous and Globular protein (or) (c) Define denaturation of protein. Name the structure of protein that remains intact after denaturation	1 1 1
26.	(a) pK_a of chloroacetic acid is smaller than acetic acid. Give reason. (b) Write chemical reaction for : i) HVZ reaction ii) Gattermann-Koch reaction	1 2
27.	(a) Explain the mechanism of dehydration of ethanol to ethene. (b) write the chemical equation for the conversion of Ethyl magnesium chloride to propanol	2 1
28.	(a) The rate constants of a reaction at 200K and 500K are $0.02s^{-1}$ and $0.20s^{-1}$ respectively. Calculate the value of Ea (Given 2.303R = 19.15 $JK^{-1}mol^{-1}$) (b) Define Collision frequency.	2 1

SECTION D

The following questions are case-based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

29.	Coordination compounds contain a metallic element as the central atom and are therefore referred to as metal complexes. These types of coordination complexes generally consist of a transition element as the central atom. It can be noted that the central atom in these complexes is called the coordination centre. A chemical compound in which the central ion or atom (or the coordination centre) is bound to a set number of atoms, molecules, or ions is called a coordination entity. Some examples of such coordination entities include $[CoCl_3(NH_3)_3]$ and $[Fe(CN)_6]^{4-}$. In coordination compounds, the central atoms or ions are typically Lewis Acids and can, therefore, act as electron-pair acceptors. The atoms, molecules, or ions that are bound to the coordination centre or the central atom/ion are referred to as ligands. These ligands can either be a simple ion or molecule, such as Cl^- or NH_3 or in the form of relatively large molecules, such as ethane-1,2-diamine (NH_2-	

CH_2-CH_2-NH_2). The coordination sphere is the non-ionizable part of a complex compound, which consists of a central transition metal ion surrounded by neighbouring atoms or groups enclosed in a square bracket.

(a) Write down the formula of: Tetraamineaquachloridocobalt(III) chloride. 1

(b) Calculate the coordination number of Co in $[Co(en)_3]^{3+}$. 1

(c) Give Chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. 2

(or)

Describe the shape and magnetic behaviour of the complex $[Co(NH_3)_6]^{3+}$. (At.no. of Cu=29) 2

30\. Electricity can be produced when electrons move from one element to another in certain types of reactions (such as redox reactions). Typically, electrochemistry deals with the overall reactions when multiple redox reactions occur simultaneously, connected via some external electric current and a suitable electrolyte. In other words, electrochemistry is also concerned with chemical phenomena that involve charge separation (as seen commonly in liquids such as solutions). The dissociation of charge often involves charge transfer that occurs homogeneously or heterogeneously between different chemical species. A spontaneous chemical process is one which can take place on its own, and in such a process, the Gibbs free energy of a system decreases. In electrochemistry, spontaneous reaction (redox reaction) results in the conversion of chemical energy into electrical energy. The reverse process is also possible where a non-spontaneous chemical reaction occurs by supplying electricity. These interconversions are carried out in equipment called an electrochemical cell.

(a) Name the electrochemical cell generally used in hearing aids. 1

(b) Λm of CH_3COOH increases drastically while that of CH_3COONa increases gradually on dilution. Explain 1

(or)

Can copper sulphate solution be stored in zinc pot? Explain. 1

$(E^0_{zn^{2+}/zn} = -0.76V, E^0_{Cu^{2+}/Cu} = 0.34V)$

(c) The standard electrode potential for Daniell cell is 1.1 V. Calculate the standard Gibbs energy for the cell reaction. (F = 96,500 C mol^{-1}) 2

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

31\. Attempt any five of the following: 1x5

(a) Which of the following ions will have a magnetic moment value of 1.73 BM.

Sc^{3+}, Ti^{3+}, Ti^{2+}, Cu^{2+}, Zn^{2+}

(b) In order to protect iron from corrosion, which one will you prefer as a sacrificial electrode, Ni or Zn? Why? (Given standard electrode potentials of Ni, Fe and Zn are -0.25 V, -0.44 V and -0.76 V respectively.)

(c) The second ionization enthalpies of chromium and manganese are 1592 and 1509 kJ/mol respectively. Explain the lower value of Mn.

(d) Give two similarities in the properties of Sc and Zn.

(e) What is actinoid contraction? What causes actinoid contraction?

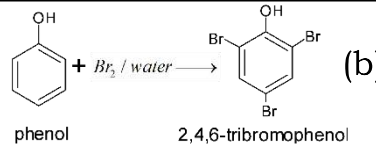
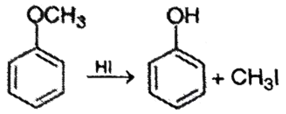
(f) The transition metals and their compounds act as good catalysts. Give reason

(g) Write the ionic equation for reaction of KI with acidified $KMnO_4$.

32.	(a) How will you convert the following : (i) Benzoic acid to aniline (ii) Aniline to p-bromoaniline	2
	(b) Why aniline does not give Friedel-Crafts reaction?	1
	(c)Arrange the following in the increasing order of their pK_b values : $C_6H_5NH_2$, NH_3, $C_2H_5NH_2$, $(CH_3)_3N$	1
	(d) Give a test to distinguish between $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$.	1
	(or)	
	(a) An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.	3
	(b) Explain with equation Gabriel Phthalimide reaction for the preparation of primary amines.	2
33.	(a) State Henry's law.	1
	(b) Give two differences between ideal and non-ideal solution.	1
	(c) Calculate the boiling point of solution when 4g of $MgSO_4$ (Molar mass:120g/mol) is dissolved in 100g of water, assuming $MgSO_4$ undergoes complete ionization. [K_b for water =0.52 K kg mol^{-1}]	3
	(or)	
	(a) Define azeotropic mixture.	1
	(b) What happens when red blood cells are placed in 0.1 %(m/v) NaCl solution?	1
	(c) The Vapour pressure of water at 20°C is 17.5 mm Hg. Calculate the vapour pressure of water at 20°C when 25 g of glucose (Molar mass = 180 g mol^{-1}) is dissolved in 150 g of water.	3

KENDRIYA VIDYALAYA SANGATHAN BENGALURU REGION
MARKING SCHEME

Subject : Chemistry (043)
Class : XII

1.	(d)It forms orange precipitate with 2,4-DNP	1
2.	(d) Phenol	1
3.	(a) Ce	1
4.	(b) 31.75 g of Cu	1
5.	(c) 3° > 2° > 1°	1
6.	(d) CH_3CHO	1
7.	(c) $\frac{\Delta[Br^-]}{\Delta t} = \frac{5}{6}\frac{\Delta[H^+]}{\Delta t}$	1
8.	(a) antiseptic	1
9.	(b) Chlorobenzene	1
10.	(d)Fehling solution	1
11.	(b) HCl is oxidised to Cl_2 by $KMnO_4$	1
12.	(a) $\frac{k}{2.303}$	1
13.	(a) Both A and R are true and R is the correct explanation of A	1
14.	(c) A is true but R is false.	1
15.	(d) A is false but R is true.	1
16.	(b) Both A and R are true but R is not the correct explanation of A.	1
17.	(a) Number of moles of solute dissolved per kilogram of solvent/ any suitable definition (b) Copper and Gold / any suitable example	1 1
18.	(a)  (b) 	1+ 1
19.	adenine, cytosine, uracil, and guanine. (if all bases are correct 1 mark) uracil	1 1
20.	(a) $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$ (b) Butanone < Propanone < Propanal < Ethanal	1 1
21.	first order reaction, $t = \frac{2.303}{k}\log\frac{[R]_0}{[R]}$ $t = \frac{2.303}{(1.15\times10^{-3}s^{-1})}\times\log\frac{(5 g)}{(3 g)}$ $= \frac{2.303}{(1.15\times10^{-3}s^{-1})}(\log 5 - \log 3)$ $= \frac{2.303}{(1.15\times10^{-3}s^{-1})}(0.6990 - 0.4771)$ $= 2.0\times10^3 \times 0.2219 s = 443.8 s$	$\frac{1}{2}$ $\frac{1}{2}$ 1

<table>
<tr><td>22.</td><td>

E^0_{cell} = 0.81 –(-2.36) = 3.17V

$$E_{(cell)} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Mg^{2+}]}{[Ag^+]^2}$$

$$E_{cell} = 3.17\ V - \frac{0.0591}{2}\log\left[\frac{0.130}{(0.0001)^2}\right]$$

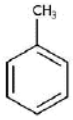
$$E_{cell} = 3.17\ V - \frac{0.059\ V}{2}\times 7.114$$

$$E_{cell} = 3.17\ V - 0.21\ V$$

$$E_{cell} = +2.96\ V.$$

</td><td>$\frac{1}{2}$
1
$\frac{1}{2}$
$\frac{1}{2}$
$\frac{1}{2}$</td></tr>
<tr><td>23.</td><td>

(a) 3-methyl butan-2-ol

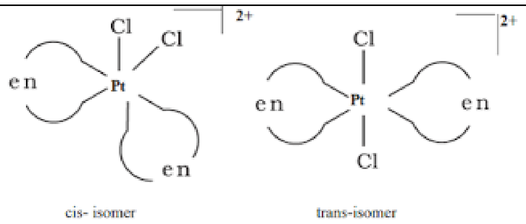


(b) Toluene

(c) 1- methylcyclohexene

</td><td>1
1
1</td></tr>
<tr><td>24.</td><td>

(a)



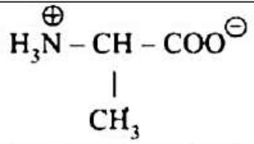
cis- isomer trans-isomer

Cis isomer is optically active

(b) $t_{2g}^3 e_g^2$

</td><td>$\frac{1}{2}$ + $\frac{1}{2}$
1</td></tr>
<tr><td>25.</td><td>

(a)



$$H_3\overset{\oplus}{N}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COO^{\ominus}$$

(b) Lysine is not synthesised by human body and must be obtained through diet.

(c) any two difference

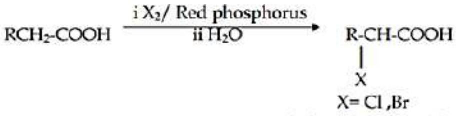
<table>
<tr><th>Fibrous protein</th><th>Globular protein</th></tr>
<tr><td>They have fibre – like structure</td><td>chains of polypeptides coil around to give a spherical shape</td></tr>
<tr><td>Generally insoluble in water</td><td>Generally soluble in water</td></tr>
</table>

(or)

When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, protein loses its biological activity. Primary structure remains intact.

</td><td>1
1
2
2</td></tr>
<tr><td>26.</td><td>

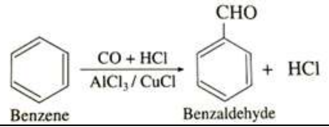
(a) Chloroacetic acid is strong acid than acetic acid due to –I effect of Cl atom which increases the stability of conjugate ion.

(b) 

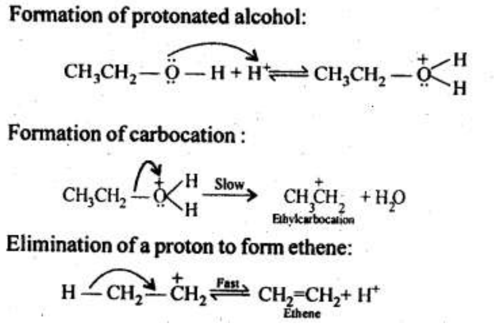
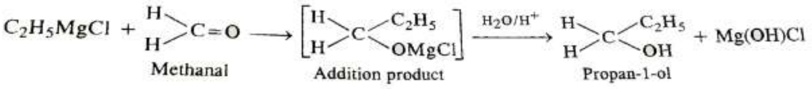
or any specific reaction

'oxylic acids

(c)



</td><td>1
1
1</td></tr>
</table>

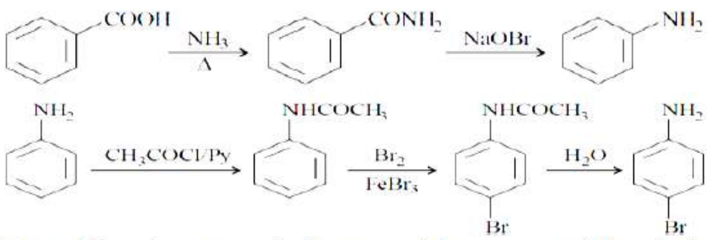
27.	(a)  (b)  	$\frac{1}{2}$ 1 $\frac{1}{2}$ 1
28.	(a) $\log\left(\frac{k_2}{k_1}\right)=\frac{E_a}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$ $\log\frac{0.20}{0.02}=\frac{E_a}{2.303R}\left[\frac{1}{200}-\frac{1}{500}\right]$ $\log 10=\frac{E_a}{19.15}\left(\frac{300}{200\times 500}\right)$ $E_a=\frac{19.15\times 200\times 500}{300}=6383\ \text{J/mol}$ (a) The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z)	$\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ 1
29.	a. $[Co(NH_3)_4(H_2O)Cl]Cl_2$ b. Coordination number of Co=6 c. Aqueous solution of $[Co(NH_3)_5Br]SO_4$ gives white precipitate when $BaCl_2$ solution is added to it and no reaction in case of $[Co(NH_3)_5SO_4]Br$ due to absence of SO_4^{2-} *ions*. / Aqueous solution of $[Co(NH_3)_5SO_4]Br$ gives yellow precipitate when dil. HNO_3 and $AgNO_3$ solution is added to it and no reaction in case of $[Co(NH_3)_5Br]SO_4$ due to absence of Br^- *ions* / any suitable test (or) Hybridization: d^2sp^3 Shape: Octahedral Magnetic behaviour: Diamagnetic	1 1 1+ 1 $\frac{1}{2}$ + $\frac{1}{2}$ 1
30.	a. Mercury cell. b. Because CH_3COOH is a weak electrolyte and degree of dissociation/ionization increases with dilution/ any suitable reason (or) No. Copper in copper sulphate is displaced by zinc. c. Given : E° = 1.1V, F = 96,500 C mol^{-1}, n = 2 $Zn + Cu^{2+} \rightleftharpoons Cu + Zn^{2+}$ Using $\Delta G° = -nFE° = -2 \times 96500 \times 1.1 = 212,300\ Jmol^{-1}$	1 1 2
31.	(a) Both Ti^{3+} and Cu^{2+} have 1 unpaired electron, so the magnetic moment for both will be 1.73 BM (b) Zn, it has a more negative electrode potential so will corrode itself in place of iron. (c) Mn^+ has $3d^54s^1$ configuration and configuration of Cr^+ is $3d^5$, therefore, ionisation enthalpy of Mn^+ is lower than Cr^+. (d) Sc and Zn both form colourless compound and are diamagnetic.	

(e) The decrease in the atomic and ionic radii with increase in atomic number of actinoids due to poor shielding effect of 5f electron.

(f) their ability to adopt multiple oxidation states and to form complexes (any correct reason)

(g) $10I^- + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

32. (a)



1

1

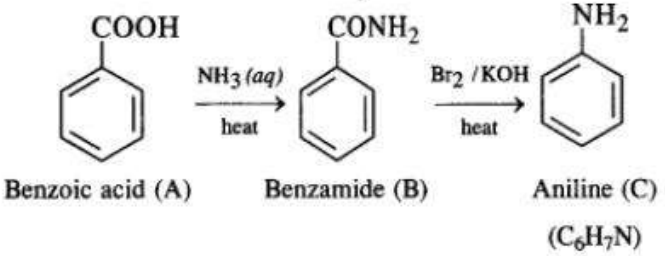
(b) Aniline is a Lewis base and it reacts with $AlCl_3$ to form a salt & N of aniline acquires positive charge with $AlCl_3$ and hence is a deactivating group.

(c) $C_2H_5NH_2 < (CH_3)_3N < NH_3 < C_6H_5NH_2$ 1

(d) Add Hinsberg reagent (benzene sulphonyl chloride) to both the compounds. $CH_3CH_2NH_2$ gives ppt. that is soluble in alkali while the ppt. formed by $(CH_3CH_2)_2NH$ is insoluble in alkali. 1

(or) 1

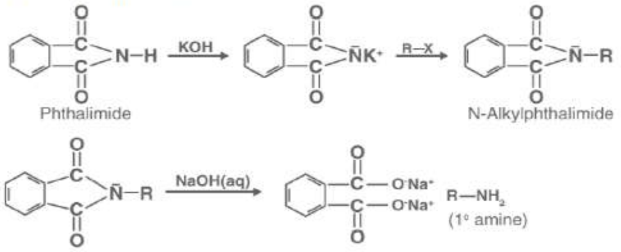
(a) 'B' upon heating with Br_2 and KOH forms a compound 'C'. The compound 'B' is expected to be an acid amide. Since 'B' has been formed upon heating compound 'A' with aqueous ammonia, the compound 'A' is an aromatic acid. It is benzoic acid. The reactions involved are given as follows:



1x 3

(b)

Gabriel Pthalamide reaction.



2

33. (a) the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution / "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution" 1

(b)

Ideal solution	Non ideal solution
obey Raoult's law	do not obey Raoult's law
$\Delta H_{mix} = 0$	$\Delta H_{mix} \neq 0$

(any two differences)

$\frac{1}{2} + \frac{1}{2}$

	(c) $\Delta T_b = i \times K_b \times m$ For $MgSO_4$,i=2 Molality of solution=$\frac{4X\,10}{120}$=1/3m $\Delta T_b = 2 \times 0.52 \times 1/3 = 0.347$ Boiling point of solution= 100+0.347=100.347^{0}C (Or) (a) The binary mixtures of liquids having same composition in liquid and vapour phase and boil at a constant temperature are called azeotropic mixture. (b) Water from NaCl solution passes into cells &they swell (c) $\frac{p_1^0 - p_1}{p_1^0} = x_2$ $n_2 = \frac{25}{180} = 0.139 \quad n_1 = \frac{450}{18} = 25$ $\frac{17.5 - p_1}{17.5} = \frac{0.139}{0.139+25}$ $\frac{17.5 - p_1}{17.5} = 0.0055$ $p_1 = 17.403$ mm Hg (correct unit ½ mark)	½ ½ 1 ½ ½ 1 1 1 ½ ½ 1

CLASS XII
SAMPLE PAPER-III
CHEMISTRY (THEORY)

S.No	Chapter	MCQ	A/R	VSA I	SA I	Case Based	LA	Total wt
		1 Marks	1 Marks	2 Marks	3 Marks	4 Marks	5 Marks	
1	**Solutions**			1			1	2(7)
2	**Electrochemistry**	1	1		1	1		4(9)
3	**Chemical Kinetics**	2		1	1			4(7)
4	**d -and f -Block Elements**	2					1	2(7)
5	**Coordination Compounds**				1	1		2(7)
6	**Haloalkanes and Haloarenes**	1		1	1			4(6)
7	**Alcohols, Phenols and Ethers**	2	1		1			3(6)
8	**Aldehydes, Ketones and Carboxylic Acids**	2	1	1	1			3(8)
9	**Amines**	1					1	3(6)
10	**Biomolecules**	1	1	1	1			4(7)
	Total	12 (1)	4(1)	5(2)	7(3)	2(4)	3(5)	33(70)

CLASS XII
SAMPLE PAPER-III
CHEMISTRY (THEORY)

Time allowed : 3 Hrs **Maximum Marks : 70**

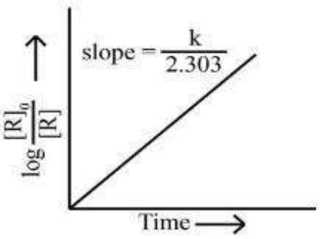
General Instructions:

Read the following instructions carefully and follow them :

- *(i) This question paper contains **33** questions. All questions are compulsory.*
- *(ii) Question paper is divided into FIVE sections-A,B,C,D and E.*
- *(iii) SECTION A -Q.No 1 to 16 are multiple choice type questions. Each question carries 1 mark.*
- *(iv) SECTION B- Q.No 17 to 21 are very short answer type questions. Each question carries 2 marks.*
- *(v) SECTION C- Q.No 22 to 28 consists of 7 are short answer type questions. Each question carries 3 marks.*
- *(vi) SECTION D- Q.No 29 and 30 are case- based questions. Each question carries 4 marks.*
- *(vii) SECTION E- Q.No 31 to 33 are long answer type questions. Each question carries 5 marks.*
- *(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section-A.*
- *(ix) Use of calculators is not allowed.*

SECTION-A

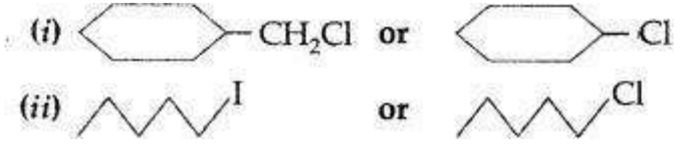
Q No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

1	Number of Faradays (F) required to reduce 1 mole of MnO_4^- ion into Mn^{2+} are (a) 7F (b) 2F (c) 1F (d) 5F	1
2	The half-life of a first order reaction is 69.35 s. The value of rate constant of the reaction is (a) 1.0 s^{-1} (b) 0.1 s^{-1} (c) 0.01 s^{-1} (d) 0.001 s^{-1}	1
3	A plot is shown below between concentration and time t. Which of the given order is indicated by the graph  (a) Zero Order (b) Second Order (c) First Order (d) Fractional Order	1
4	The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment. (a) $3d^7$ (b) $3d^5$ (c) $3d^8$ (d) $3d^2$	1

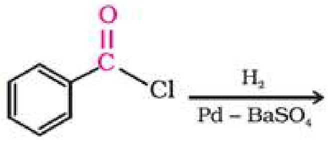
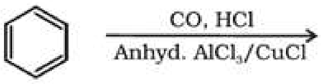
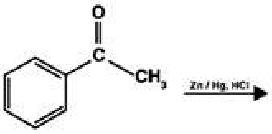
5	Which reagent will you use for the following reaction? $CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$ (a) Cl_2/UV light (b) NaCl + H_2SO_4 (c) Cl_2 gas in presence of Fe in dark (d) Cl_2 gas in dark	1
6	Which of the following pairs of ions have the same electronic configuration? (a) Cu^{2+}, Cr^{2+} (b) Fe^{3+}, Mn^{2+} (c) Co^{3+} ,Ni^{3+} (d) Sc^{3+}, Cr^{3+}	1
7	Phenol is less acidic than: (a) Ethanol (b) o-nitrophenol (c) o-methyl phenol (d) o-methoxyphenol	1
8	A tertiary alcohol is obtained by the reaction of Grignard reagent with: (a) Butanone (b) Propanone (c) Acetone (d) All of the above	1
9	The IUPAC name of CH_3-CH=CH-CHO is: (a) Buten-2-al (b) Butenal (c) But-2-enol (d) But-2-enal	1
10	An organic compound X on treatment with pyridinium chlorochromate in dichloromethane gives compound Y. Compound Y reacts with I_2 and alkali to form triiodo methane. The compound 'X' is: (a)CH_3CH_2OH (b)CH_3CHO (c)CH_3COCH_3 (d)CH_3COOH	1
11	The correct order of the basic strength of methyl substituted amines in aqueous solution is: (a) $CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$ (b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$ (c) $(CH_3)_3N > CH_3NH_2 > (CH_3)_2NH$ (d) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2$	1
12	Which of the following statements are not true about glucose? (a) It is an aldohexose (b) On heating with HI, it forms n-hexane (c) It is present in furanose form (d) It does not give 2,4-DNP test	1
	For Q No. 13 to 16, two statements are given-one labelled as Assertion(A) and the other labelled as Reason(R). Select the most appropriate answer from the options given below: (a) Both A and R are true and R is the correct explanation of A (b) Both A and R are true but R is not the correct explanation of A. (c) A is true but R is false. (d) A is false but R is true.	

13	**Assertion(A)**: Rate constant of a zero-order reaction has the same unit as the rate of a reaction. **Reason(R)**: Rate constant of a zero-order reaction does not depend upon the concentration of the reactant.	1
14	**Assertion(A)**: Tertiary alcohols get converted into an alkene instead of a carbonyl compounds in the presence of heated metallic copper. **Reason(R)**: Tertiary alcohols prefer to undergo dehydrogenation instead of dehydration in the presence of heated copper.	1
15	**Assertion (A)**: For a Daniel cell, Zn(s)/Zn^{2+} (1.0M) // Cu^{2+}(1.0M)/Cu(s) with E^o_{cell}=1.1V, if the external opposing potential is more than1.1V, the electrons flow from Cu to Zn. **Reason(R)**: Cell acts like a Galvanic cell.	1
16	**Assertion(A)**: Benzoic acid does not undergo Friedel Craft's reaction. **Reason(R)**: Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to the carboxyl group.	1

SECTION B

17	Calculate the mole fraction of benzene in a solution containing 30% by mass of it in CCl_4.	2
18	Explain pseudo-order reaction with an example.	2
19	Which one in the following pairs of substances undergoes S_N2 substitution reaction faster and why? 	2
20	(a)Define Glycosidic linkage. (b) Why cannot vitamin C be stored in our body. **OR** (i) What type of linkage is present in nucleic acids? (ii) Give one example each for fibrous protein and globular protein.	2
21	Arrange the following compounds in the increasing order of their property indicated.) CH_3COCH_3, $C_6H_5COCH_3$, CH_3CHO (reactivity towards nucleophilic addition reaction) i) Cl-CH_2-COOH, F-CH_2-COOH, CH_3 -COOH (acidic character)	2

SECTION C

22	When a certain conductivity cell was filled with 0.1 M KCl, it has a resistance of 85 ohms at 25°C. When the same cell was filled with an aqueous solution of 0.052 M unknown electrolyte, the resistance was 96 ohms. Calculate the molar conductivity of the electrolyte at this concentration. Conductivity of 0.1 M KCl = $1.29 \times 10^{-2}\Omega^{-1}\text{cm}^{-1}$	3
23	Write the formula of the following coordination compound: Iron(III)hexacyanoferrate(II). What type of isomerism is exhibited by the complex $[Co(NH_3)_5Cl]SO_4$? Write the hybridisation and number of unpaired electrons in the complex $[CoF_6]^{3-}$. (Atomic Number of Co =27) **OR** (i) What is meant by crystal field splitting energy? (ii) On the basis of crystal field theory, write the electronic configuration of d^4 in terms of t_{2g} and e_g in an octahedral field when (a) $\Delta^0 > P$ (b) $\Delta^0 < P$	3
24	The rate constant of a reaction at 400K and 200K are 0.04 and 0.02 s^{-1} respectively. Calculate the value of activation energy (log2 =0.3010; R = 8.314 $JK^{-1}mol^{-1}$)	3
25	Below, reactants of some organic name reactions are given. Write the structure of the main product in each and also identify the name reaction. **(Any 3)** (a) $CH_3CN + SnCl_2 + HCl \xrightarrow{H_3\overset{+}{O}}$ (b)  (c)  (d)  	3
26	Write mechanism of hydration of ethene to yield ethoxyethane.	3
27	What happens when D-glucose is treated with the following reagents? (i) HI (ii) Bromine water (iii) HNO_3	3
28	Compound ‘A’ with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound ‘A’ only. When another 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 the compounds ‘A’ and ‘B’. (ii) Out of these two compounds, which one will be optically active?	3

SECTION D

29 Read the given passage and answer the questions that follows.

Negative ion or Neutral molecule which bound to the metal ion by secondary valency is called as ligand. In a complex, metal ion acts as Lewis acid and ligand acts as Lewis base. Ligands are classified according to number of electron pair in them. The ligand which can donate one electron pair to the metal atom is called unidentate ligand. The ligand which can donate two electron pairs to the Metal ion is called bidentate ligand. The ligand in which two or more coordination sites are there is called polydentate ligand. Polydentate ligand forms cyclic structure with metal ion and form Chelate.

i) Give an example of unidentate neutral ligand. 1
ii) What are Lewis acids and Lewis bases?. 1
iii) How bidentate and Ambidentate ligands are different? Give example. 2

OR

What are chelate ligands? Give an example.

30 Molar conductivity for weak electrolytes can be obtained from molar conductivities of strong electrolytes at infinite dilution by doing algebraic addition. For example, molar conductivity of weak electrolyte like CH_3COOH can be obtained from molar conductivities at infinite dilution of strong electrolytes like CH_3COONa, HCl and NaCl according to Kohlrauch's law

$\Lambda°mCH_3COOH= [\Lambda°_mCH_3COO^- + \Lambda°_mNa^+] + [\Lambda°_mH^+ + \Lambda°_mCl^-]-[\Lambda°_m Na^+ + \Lambda°_mCl^-]$

(i) What is the expression of $\Lambda°_m$ for an electrolyte A_mB_n? 1
(ii) Define limiting molar conductivity. 1
(iii) Calculate $\Lambda°m$ for AgCl if $\Lambda°m$ ($AgNO_3$) = 133.4, $\Lambda°_m(KCl)=149.9$, $\Lambda°_m(KNO_3)=144.9\ Scm^2mol^{-1}$ 2

OR

Calculate $\Lambda°m$ for HAc if $\Lambda°m$ (HCl) = 425.9, $\Lambda°m(NaCl)=126.4$, $\Lambda°m(NaAc)=91.0\ Scm^2mol^{-1}$

SECTION E

31 a) Complete the following ionic equations: 2
i) $Cr_2O_7{}^{2-} (aq) + I^- (aq) + H^+ (aq) \rightarrow$
ii) $Fe^{2+} (aq) + MnO_4{}^- (aq) + H^+ (aq) \rightarrow$

(b) Explain the following observations: 3
(i) In general, the atomic radii of transition elements decrease with atomic number in a given series.
(ii) The $E°_{M^{2+}/M}$, for copper is positive (+ 0.34 V). It is the only metal in the first series of transition elements showing this type of behaviour.
(iii) The E° value for Mn^{3+}/Mn^{2+} couple is much more positive than for Cr^{3+}/Cr^{2+} or Fe^{3+}/ Fe^{2+} couple.

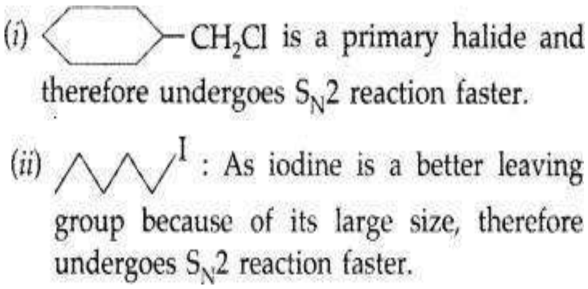
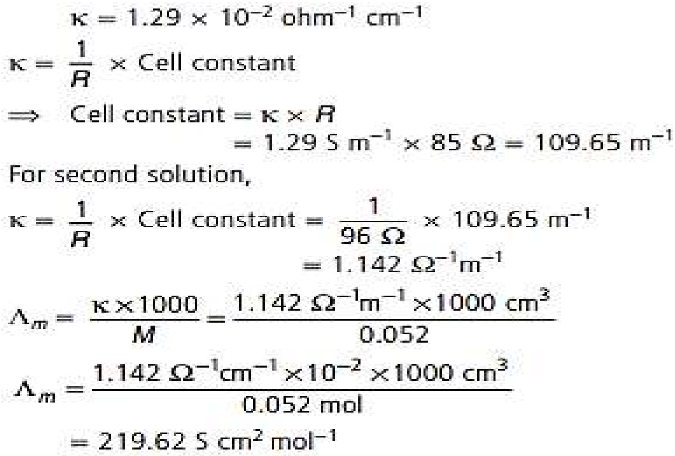
OR

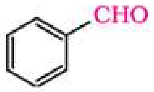
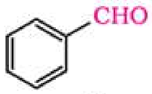
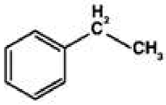
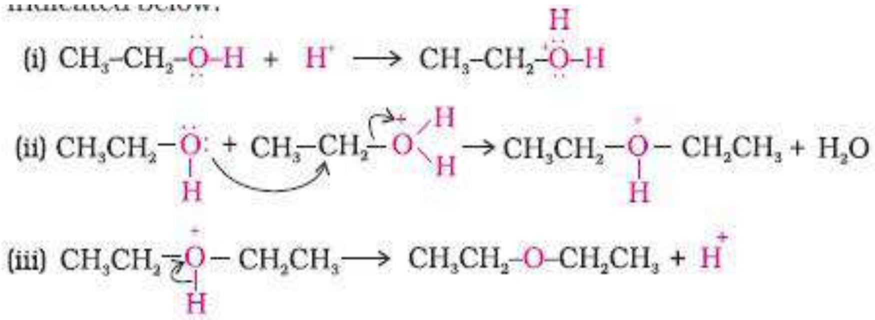
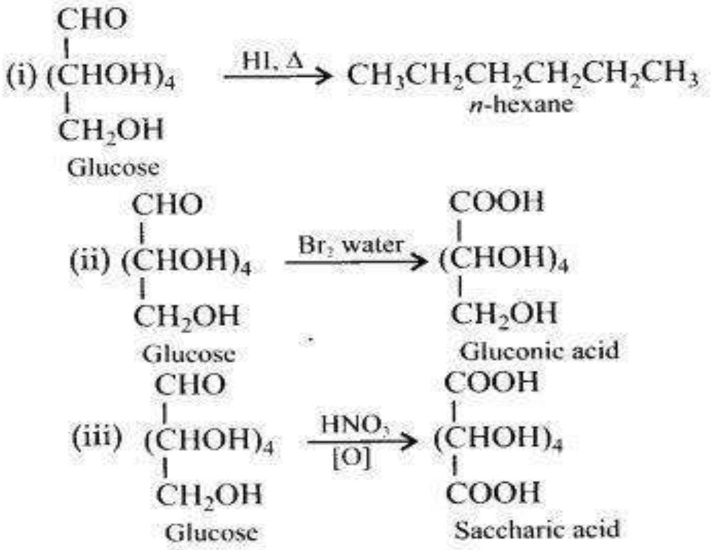
Assign reasons for the following:
a) The enthalpies of atomization of transition elements are high. 1
b) The transition metals and many of their good catalysts. Compounds act as 1
c) $E°M2+/M$ values are not regular for first-row transition metals (3d series). 1
d) Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4, whereas the highest oxide is Mn_2O_7 1
e) Sc^{3+} is colourless in an aqueous solution whereas Ti^{3+} is coloured. 1

32	A colourless substance ‘A’ (C_6H_7N) is sparingly soluble in water and gives a water soluble compound ‘B’ on treating with HCl. On reacting with $CHCl_3$ and alcoholic KOH ‘A’ produces an obnoxious smell due to the formation of compound ‘C’. Reaction of ‘A’ with benzene sulphonyl chloride gives compound ‘D’ which is soluble in alkali. ‘A’ reacts With $NaNO_2$ and HCl, to form compound ‘E’. Identify compounds ‘A’ to ‘E’. **OR** a) Why is benzene diazonium chloride not stored and used immediately after its preparation? b) Explain why $MeNH_2$ is a stronger base than MeOH? c) What is the role of pyridine in the acylation reaction of amines? d) Give one chemical test to distinguish between Aniline and benzylamine e) Give a suitable reaction to convert aniline to bromobenzene, name the reaction also.	3 2 5
33	(i) Define the following terms: (a) Azeotrope (b) Osmotic pressure (c) Colligative properties (ii) Calculate the molarity of 9.8% (w/w) solution of H_2SO_4 if the density of the solution is 1.02 g mL^{-1}. (Molar mass of H_2SO_4 = 98 g mol^{-1}) **OR** (i) On mixing liquid X and liquid Y, the volume of the resulting solution decreases. What type of deviation from Raoult’s law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y? (ii) What happens when we place the blood cell in water (hypotonic solution)? Give reason. (iii) At 25°C the saturated vapor pressure of water is 3.165 kPa (23.75 mm Hg). Find the saturated vapor pressure of a 5% aqueous solution of urea (carbamide) at the same temperature. (Molar mass of urea = 60.05 g mol^{-1})	3 2 2 3

MARKING SCHEME
CHEMISTRY (Theory)
SAMPLE PAPER NO.3

Q.No.	**Value Point/ Expected Answer**	**Marks**
1	(d) 5F	1
2	(c) 0.01 s^{-1}	1
3	(c) First Order	1
4	(b) $3d^5$	1
5	(a) Cl_2/UV light	1
6	(b) Fe^{3+}, Mn^{2+}	1
7	(b) o-nitrophenol	1
8	(d) All of the above	1
9	(d) But-2-enal	1
10	(a)CH_3CH_2OH	1
11	(b) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$	1
12	(c) It is present in furanose form	1
13	a. Both A and R are true and R is the correct explanation of A	1
14	c. A is true but R is false.	1
15	c. A is true but R is false.	1
16	a. Both A and R are true and R is the correct explanation of A	1
17	nC_6H_6=30g/78g=0.385mol $nCCl_4$=70g/154g=0.454mol X C_6H_6= nC6H6/nC6H6 + nCCl4 =0.385 mol /0.385mol + 0.454mol = 0.459	½ ½ 1

18	The reaction which appears to be second order behaves as first order reaction is called pseudo-order reaction. Ex: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6$(Glucose) + $C_6H_{12}O_6$ (Fructose)	1 1
19	 (i) CH_2Cl is a primary halide and therefore undergoes S_N2 reaction faster. (ii) I : As iodine is a better leaving group because of its large size, therefore undergoes S_N2 reaction faster.	1 1
20	(a) The linkage between two monosaccharides through oxygen atom in an oligosaccharide or a polysaccharide is known as glycosidic linkage. (b) As vitamin C is water soluble, therefore, it is readily excreted in urine and hence cannot be stored in the body. OR (i) Phosphodiester linkage. (ii) Fibrous protein: Myosin, keratin, collagen, etc. Globular protein: Insulin, haemoglobin, etc.	1 1 1 ½, ½
21	(i) $C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO$ (ii) $CH_3\text{-}COOH < Cl\text{-}CH_2\text{-}COOH < F\text{-}CH_2\text{-}COOH$	1 1
22	 $\kappa = 1.29 \times 10^{-2}\ \text{ohm}^{-1}\ \text{cm}^{-1}$ $\kappa = \frac{1}{R} \times \text{Cell constant}$ $\Rightarrow \text{Cell constant} = \kappa \times R = 1.29\ \text{S m}^{-1} \times 85\ \Omega = 109.65\ \text{m}^{-1}$ For second solution, $\kappa = \frac{1}{R} \times \text{Cell constant} = \frac{1}{96\ \Omega} \times 109.65\ \text{m}^{-1} = 1.142\ \Omega^{-1}\text{m}^{-1}$ $\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.142\ \Omega^{-1}\text{m}^{-1} \times 1000\ \text{cm}^3}{0.052}$ $\Lambda_m = \frac{1.142\ \Omega^{-1}\text{cm}^{-1} \times 10^{-2} \times 1000\ \text{cm}^3}{0.052\ \text{mol}} = 219.62\ \text{S cm}^2\ \text{mol}^{-1}$	1 1 1
23	$Fe_4[Fe(CN)_6]_3$ Ionisation isomerism. Its ionisation isomer will be $[Co(NH_3)_5(SO_4)]Cl$. Hybridisation – sp^3d^2, number of unpaired electron= 4. **OR** (i) The difference between energies of two sets of d-orbitals t_2g and eg is called crystal field splitting energy (Δ_0). (ii) (a) If $\Delta_0 > P$, the configuration will be t_2g^4, eg^0. Ligands will produce strong field and pairing takes place. (b) If $\Delta_0 < P$, the configuration will be t_2g^3, eg^1. Ligands will produce weak field and no pairing takes place.	1 1 ½, ½ 1 1 1

24	$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$ $T_2 = 400K$; $k_2 = 0.04\ s^{-1}$ $T_1 = 200K$; $k_1 = 0.02\ s^{-1}$ $\log\left(\frac{0.04\ s^{-1}}{0.02\ s^{-1}}\right) = \frac{E_a}{2.303 \times 8.314\ JK^{-1}mol^{-1}}\left(\frac{400K - 200K}{200K \times 400K}\right)$ $\log(2) = \frac{E_a}{2.303 \times 8.314\ JK^{-1}mol^{-1}}\left(\frac{1}{400K}\right)$ $E_a = \log(2) \times 2.303 \times 8.314\ JK^{-1}mol^{-1} \times 400K$ $E_a = 2305\ J\ mol^{-1}$ Ea = 2305 J mol−1	½ 1 1 ½
25	(a) CH_3CHO Stephen reaction (b)  Rosenmund reduction (c)  *Gatterman – Koch reaction* (d)  Clemmensen reduction	1x3
26	indicated below:  (i) $CH_3{-}CH_2{-}\ddot{O}{-}H + H^+ \longrightarrow CH_3{-}CH_2{-}\overset{H}{\overset{+}{\ddot{O}}}{-}H$ (ii) $CH_3CH_2{-}\underset{H}{\ddot{O}}: + CH_3{-}CH_2{-}\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \rightarrow CH_3CH_2{-}\underset{H}{\overset{+}{O}}{-}CH_2CH_3 + H_2O$ (iii) $CH_3CH_2{-}\underset{H}{\overset{+}{O}}{-}CH_2CH_3 \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + H^+$	1x3
27	 (i) $\underset{\text{Glucose}}{\begin{matrix}CHO\\ \vert\\ (CHOH)_4\\ \vert\\ CH_2OH\end{matrix}} \xrightarrow{HI,\ \Delta} \underset{n\text{-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$ (ii) $\underset{\text{Glucose}}{\begin{matrix}CHO\\ \vert\\ (CHOH)_4\\ \vert\\ CH_2OH\end{matrix}} \xrightarrow{Br_2\ water} \underset{\text{Gluconic acid}}{\begin{matrix}COOH\\ \vert\\ (CHOH)_4\\ \vert\\ CH_2OH\end{matrix}}$ (iii) $\underset{\text{Glucose}}{\begin{matrix}CHO\\ \vert\\ (CHOH)_4\\ \vert\\ CH_2OH\end{matrix}} \xrightarrow[{[O]}]{HNO_3} \underset{\text{Saccharic acid}}{\begin{matrix}COOH\\ \vert\\ (CHOH)_4\\ \vert\\ COOH\end{matrix}}$	1 1 1
28	A is 1-Bromo butane. B is 2-Bromo butane. B is optically active.	1 1 1

29	i) Ammine NH_3 ii) Lewis acids are electron pair acceptor whereas Lewis bases are electron pair donor. iii) Bidentate ligand- those which bind to the metal ion through two donor atoms. Eg. Ethane 1-2 diamine $[H_2NCH_2CH_2NH_2]$. Ambidentate ligands – those ligands which have two donor sites but at a time only one atom binds to the metal Eg- NO_2^- **OR** When a ligand attaches to the metal ion in a manner that it forms a ring, then the metal-ligand association is found to be more stable. For example $[Co(en)_3]^{3+}$ is more stable than $[Co(NH_3)_6]^{3+}$.	1 1 1+1 1+1
30	(i) $m\Lambda^\circ An+ + n\Lambda^\circ Bm-$ (ii) Limiting molar conductivity is the molar conductivity at infinite dilution or at zero concentration (iii) $\Lambda^\circ mAgCl = (\Lambda^\circ mAgNO_3 + \Lambda^\circ mKCl) - \Lambda^\circ m\ KNO_3$ $=(133.4+149.9)-144.9$ $= 138.45$ Scm2 mol-1 **OR** $\Lambda^\circ mHAc = (\Lambda^\circ mNaAc + \Lambda^\circ mHCl) - \Lambda^\circ m\ NaCl$ $= (91.0+425.9)-126.4$ $= 390.5$ Scm2 mol-1	1 1 1 ½ ½ 1 ½ ½
31	(a) (i) $5Fe^{2+} (aq) + MnO_4^- (aq) + 8H^+ (aq) \rightarrow Mn^{2+} (aq) + 5Fe^{3+} (aq) + 4H_2O(l)$ (ii) $Cr_2O_7^{\ 2-} (aq) + 6I^- (aq) + 14H^+ (aq) \rightarrow 2Cr^{3+}(aq) + 3I_2 (s) + 7H_2O(l)$ b) (i) Because of increase in effective nuclear charge and weak shielding effect of d electrons, the atomic radii decreases. (ii) It is because Copper has high enthalpy of atomization and low enthalpy of hydration. The high energy required to transform Cu(s) to $Cu^{2+}(aq)$ is not balanced by its hydration enthalpy. (iii)The large positive E° value for $Mn^{3+}\|Mn^{2+}$ shows that Mn^{2+} is much more stable than Mn^{3+} due to stable half-filled configuration ($3d^5$). Therefore the 3rd ionization energy of Mn will be very high and Mn^{3+} is unstable and can be easily reduced to Mn^{2+}. E° value for $Fe^{3+}\|Fe^{2+}$ is positive but small i.e. Fe^{3+} can also be reduced to Fe^{2+} but less easily. Thus Fe^{3+} is more stable than Mn^{3+} OR (a) This is because transition elements have strong metallic bonds as they have large number of unpaired electrons, therefore they have greater interatomic overlap (b)The catalytic activity of transition metals is attributed to the following reasons i) Because of their variable oxidation state, transition metals form unstable intermediate compounds and provide a new path with lower activation	1 1 1 1 1 1 1

	energy for the reaction. ii) In some cases, the transitions metal provides a suitable large surface area with free Valencies on which reactants are adsorbed (c) E°(M^{2+}/M) values are not regular in the first transition series metals because of irregular variation of ionization enthalpies (IE_1 + IE_2) and the sublimation energies. (d) Among transition elements, the bonds formed in +2 and +3 oxidation states are mostly ionic. The compounds formed in higher oxidation states are generally formed by sharing of d-electrons. Therefore, Mn can form MnO_4- which has multiple bonds also, while fluorine cannot form multiple bonds. (e) The absence of unpaired d-electron in Sc^{3+} whereas in Ti^{3+} there is one unpaired electron or Ti^{3+} shows the d-d transition.	1 1 1
32	A= $C_6H_5NH_2$ B=$C_6H_5NH_3^+Cl^-$ C=C_6H_5NC D=N-phenylbenzenesulphonamide E=$C_6H_5N_2^+Cl^-$ **OR** a) Benzene diazonium chloride cannot be stored and is used immediately after its preparation because of its unstable nature. With a slight increase in temperature, it dissociates to give nitrogen gas. b) Nitrogen is less electronegative than oxygen; therefore, lone pairs of electrons on nitrogen are readily available for donation. Hence, $MeNH_2$ is more basic than MeOH. c)Pyridine acts as an acceptor for the acid by-product formed in the reaction. Thus, it removes the side product, i.e. HCl, from the reaction mixture. d)Azo dye Test e) Step 1. Diazotization and step 2.Sandmeyer/Gattermann reaction $C_6H_5N_2Cl \xrightarrow{Cu_2Br_2,HBr} C_6H_5Br + N_2$ $C_6H_5N_2Cl \xrightarrow{Cu,HBr} C_6H_5Br + N_2$	1x5 1x5
33	(i) (a) The binary mixtures of liquids having same composition in liquid and vapour phase and boil at a constant temperature are called azeotropes. (b) The excess of pressure which must be applied to the solution side to prevent the passage of solvent into it through a semipermeable membrane is called osmotic pressure. (c) The properties of solutions which depend only on the number of solute particles in the solution but independent of their nature are called colligative properties.	1 1 1 ½

	(*ii*) Let the mass of solution = 100 g	½
	∴ Mass of $H_2SO_4 = 9.8$ g	
	Number of mole of $H_2SO_4 = \frac{\text{Mass of } H_2SO_4}{\text{Molar Mass}} = \frac{9.8 \text{ g}}{98 \text{ g mol}^{-1}} = 0.1 \text{ mol}$	
	Volume of solution $= \frac{\text{Mass of solution}}{\text{Density of solution}} = \frac{100 \text{ g}}{1.02 \text{ g mL}^{-1}} = \frac{100}{1.02} \text{mL}$	½ ½
	$= \frac{100}{1.02} \text{mL} \times \frac{1}{1000 \text{ mL L}^{-1}} = \frac{1}{10.2} \text{L}$	
	Molarity $= \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$	1 1
	$= \frac{0.1 \text{ mol}}{\frac{1 \text{ L}}{10.2}} = \mathbf{1.02 \text{ mol L}^{-1} \text{ or } 1.02 \text{ M}}$	
	OR	1
	(i) The solution will show negative deviation from Raoult's law. Temperature will rise.	
	(ii) Due to osmosis water enters into the cell and blood cell will swell.	1
	(iii) $W_B = 5 \text{ g}, W_A = 95 \text{ g}, M_B = 60.05 \text{ g mol}^{-1}, M_A = 18 \text{ g mol}^{-1}, p^o_A = 3.165 \text{ kPa}$	½ ½
	Substituting the values in the expression	
	$\frac{p^o_A - p}{p^o_A} = \frac{W_B \times M_A}{M_B \times W_A}$, we get	
	$\frac{3.165 \text{ kPa} - p}{3.165 \text{ kPa}} = \frac{5 \text{ g} \times 18 \text{ g mol}^{-1}}{60.05 \text{ g mol}^{-1} \times 95 \text{ g}} = 0.015$	
	$p = 3.165 \text{ kPa} - 0.015 \times 3.165 \text{ kPa}$	
	$p = \mathbf{3.118 \text{ kPa}}$	