रसायन विज्ञान
Chemistry

कक्षा / Class XII
2025-26

विद्यार्थी सहायक सामग्री
Student Support Material

केन्द्रीय विद्यालय संगठन~Kendriya Vidyalaya Sangathan

संदेश

विद्यालयी शिक्षा में शैक्षिक उत्कृष्टता प्राप्त करना एवं नवाचार द्वारा उच्च - नवीन मानक स्थापित करना केन्द्रीय विद्यालय संगठन की नियमित कार्यप्रणाली का अविभाज्य अंग है। राष्ट्रीय शिक्षा नीति 2020 एवं पी. एम. श्री विद्यालयों के निर्देशों का पालन करते हुए गतिविधि आधारित पठन-पाठन, अनुभवजन्य शिक्षण एवं कौशल विकास को समाहित कर, अपने विद्यालयों को हमने ज्ञान एवं खोज की अद्‌भुत प्रयोगशाला बना दिया है। माध्यमिक स्तर तक पहुँच कर हमारे विद्यार्थी सैद्धांतिक समझ के साथ-साथ, रचनात्मक, विश्लेषणात्मक एवं आलोचनात्मक चिंतन भी विकसित कर लेते हैं। यही कारण है कि वह बोर्ड कक्षाओं के दौरान विभिन्न प्रकार के मूल्यांकनों के लिए सहजता से तैयार रहते हैं। उनकी इस यात्रा में हमारा सतत योगदान एवं सहयोग आवश्यक है - केन्द्रीय विद्यालय संगठन के पांचों आंचलिक शिक्षा एवं प्रशिक्षण संस्थान द्वारा संकलित यह विद्यार्थी सहायक-सामग्री इसी दिशा में एक आवश्यक कदम है । यह सहायक सामाग्री कक्षा 9 से 12 के विद्यार्थियों के लिए सभी महत्वपूर्ण विषयों पर तैयार की गयी है। केन्द्रीय विद्यालय संगठन की विद्यार्थी सहायक- सामग्री अपनी गुणवत्ता एवं परीक्षा संबंधी सामग्री संकलन की विशेषज्ञता के लिए जानी जाती है और शिक्षा से जुड़े विभिन्न मंचों पर इसकी सराहना होती रही है। मुझे विश्वास है कि यह सहायक सामग्री विद्यार्थियों की सहयोगी बनकर निरंतर मार्गदर्शन करते हुए उन्हें सफलता के लक्ष्य तक पहुँचाएगी।

शुभाकांक्षा सहित ।

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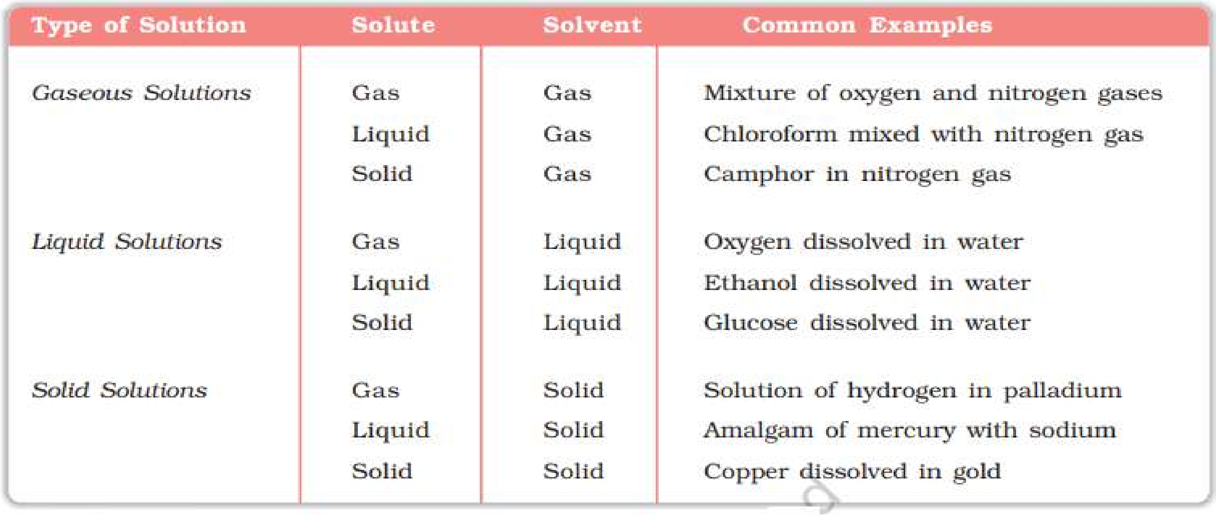
INDEX

CHAPTER - 1 SOLUTIONS

SUMMARY

TYPES OF SOLUTIONS:



Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

CONCENTRATION OF SOLUTIONS

Some basic formulae	**Mole fraction**	**Molarity (**M)
Mass percentage. **w/w%** **For liquid solutions** w/w%=massof component/total mass of solution	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 x10^6/total mass of solution	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

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

$P \alpha X_B$ $P = K_H X_B$ (K_H= Henry's constant)(greater the **K_H**value lower the solubility

APPLICATIONS: 1. Soft drinks are sealed under high pressure to increase solubility of CO_2.

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 is called vapour pressure
- **Raoult's law: -** The partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

$$P_A \alpha X_A \qquad P_B \alpha X_B$$

$$P_A = P_A{}^o X_A P_B{}^o X_A$$

$$P_T = P_A + P_B \text{ (Daltons Law)}$$

Ideal solutions	**Non-Ideal solutions**

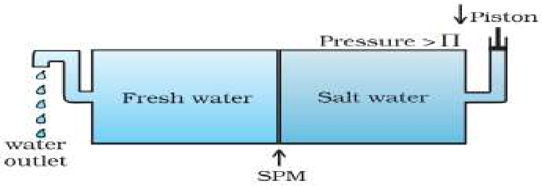
Obeys Raoult's law over the entire range of concentration e.g. Solution of n-hexane and n-heptane	Don't Obey **Raoult's law**
A-A , B-B = A-B interactions	A-A , B-B ≠ A-B interactions
$P_{Total} = P_A + P_B, P_{Total} = P^0_A X_A + P_B{}^0 X_B$	$P_{Total} \neq P_A + P_B, P_{Total} \neq P^0_A X_A + P_B{}^0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

Positive deviation	**Negative deviation**
$P_{Total} > P_A + P_B \ \Delta V_{mix} = +ve, \Delta H_{mix} = +ve$	PTotal< PA+ PB ΔVmix=-veΔHmix=-ve
A – B interaction is weaker than A – A and B – B interactions. EXAMPLE-ethanol+water,acetone+ethanol	A – B interaction is stronger than A – A and B – B interaction Chloroform+acetone,water+HCl
Minimum boiling Azeotrope	Maximum boiling Azeotrope

- **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
- **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**	**Osmotic pressure**
$P^o_A - P_s / P^o_A = X_B$ $X_B = n_B / n_A + n_B$ [for a very dilute solution $n_B << n_A$] $P_A{}^o – P_S / P_A{}^o = n_B / n_A$	**$\Delta T_b = T_b - T_b{}^o$** **$\Delta T_b = K_b$ m** **K_b =** molal elevation or EBULLIOSCOPIC constant. It is the elevation in boiling point of 1 molal solution.	**$\Delta T_f = T_f - T_f{}^0$** **$\Delta T_f = K_f$ m** **K_f=** molal depression or CRYOSCOPIC constant. It is the depression in freezing point of 1 molal solution.	**π=CRT** $\pi = \frac{nRT}{V}$ The excess pressure on solution side which just prevents the flow of solvent molecules is called OSMOTIC PRESSURE.

- **OSMOSIS**-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.**
- **REVERSE OSMOSIS**-The process of movement of solvent through a semipermeable membrane from the solution to the pure solvent by applying pressure more than osmotic pressure on the solution side is called reverse osmosis.



- **Application**-desalination of sea water
- **NOTE:** The **osmotic pressure** method **advantages** over other colligative properties.
- The measurement of osmotic pressure is around the room temperature,
- Gives large measurable value for dilute solution

ISOTONIC SOLUTION	HYPOTONIC SOLUTION	HYPERTONIC SOLUTION
Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. **$\pi_1 = \pi_2$**	solutions having different osmotic pressure at a given temperature, the one with lower osmotic pressure is called **hypotonic** solution	Solution with higher osmotic pressure is called **hypertonic** 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: - **$X_B = i\ P^o_A - P_s/P^o_A$**
- Elevation in boiling point: - **$\Delta T_b = i\ K_b\ m$**
- Depression in freezing point: - **$\Delta T_f = i\ K_f\ m$**
- Osmotic pressure**: - $\pi = iCRT$**

PROPERTY	ASSOCIATION	DISSOCIATION
Colligative property	Lowers	Increases
Molar mass	Greater than theoretical value	lesser
i=1	i < 1	i > 1
α (extent) =degree of dissociation / association	α=i-1/1/n−1 [n = no. of particles associated]	α=i-1/n−1 [n = no. of dissociated particles.]

SECTION -A (1 Mark)

Q1. The value of Henry's Law constant is:

(a) larger for gases with higher solubility (b) larger for gases with lower solubility

(c) Constant for all gases (d) Not related to the solubility of gases

Q2. If a molecule AB undergoes dimerization in Benzene, its Van't Hoff factor is found to be 0.60. The degree of dissociation of AB is

(a) 20% (b) 60% (c) 80% (d) 50%

Q3.Select the property that is not colligative in nature.

(a) Osmotic pressure (b) Lowering of vapour pressure

(c) Depression in freezing point (d) Molal elevation constant

Q4.An unripe mango placed in a concentrated salt solution to prepare pickles shrinks because

(a) It gains water due to osmosis (b) It loses water due to reverse osmosis
(c) It gains water due to reverse osmosis (d) It loses water due to osmosis

Q5. Osmotic pressure of a solution is 0.0821 atm at a temperature of 300 K. The concentration in moles/lit will be:

(a) 0.33 (b) 0.666 (c) 0.0033 (d) 3

Q6.Identify the interaction exists between n-Hexane and n-Octane molecules ?

(a) Ion-dipole interaction (b) London dispersion forces
(c) Hydrogen bonding (d) Dipole-dipole interaction

Q7.Which of the following is not a solid solution?

(a) Brass (b) Bronze
(c) Hydrated salts (d) Aerated drinks

Q8.Out of molality (m), molarity (M), formality (F) and mole fraction (x), those which are independent of temperature are

(a) M, m (b) F, x (c) m, x (d) M, x

Q9.Which has the lowest boiling point at 1 atm pressure?

(a) 0.1 M KCl (b) 0.1 M Urea (c) 0.1 M $CaCl_2$ (d) 0.1 M $AlCl_3$

Q10.The molal elevation constant depends upon

(a) Nature of solute. (b) Nature of the solvent.
(c) Vapour pressure of the solution. (d) Enthalpy change.

Assertion and Reason Questions

(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

Q11.**Assertion (A):** The freezing point of sea water is lower than that of pure water. **Reason (R):** Sea water contains dissolved salts which increase the vapour pressure.

Q12.**Assertion (A):**Azeotropic mixtures cannot be separated by fractional distillation. **Reason(R):**Azeotropes boil at a constant temperature and have the same composition in liquid and vapour phase

Q13.**Assertion(A):** Molality is independent of temperature ,whereas molarity is not.
Reason(R): Molality is based on volume of solution ,while molarity is based on mass of solvent.

Q14.**Assertion(A) :** Osmosis is colligative property.
Reason(R) : Reverse osmosis is used for desalination of water.

Q15**. Assertion (A):** In an ideal solution, $\Delta_{mix}H$ is zero.
Reason (R): In an ideal solution, A–B interactions are lower than A–A and B–B interactions.

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

SECTION - B (2 Marks)

Q1. When resins kept in water. Raisins swell in size Name and explain the phenomenon

Hint : Endosmosis

Q2. Explain the following phenomena

(i) Painful condition known as bends

(ii) Feeling of weakness and discomfort in breathing at High attitude

Hint : Application of Henry's Law

Q3. Explain why on addition of 1 mol of NaCl to 1 lit of water ,the boiling point of water increases ,while the addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point

Hint :NaCl is nonvolatile while methyl alcohol is more volatile than water.

Q4. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetra chloride.

Hint : $nC_6H_6/nC_6H_6+nCCl_4$ Mole fraction=0.458

Q5. a) Ram's father is suffering from high blood pressure , 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?

Hint :a) More salt use will increase ions in the body fluid which increases blood pressure b) B

SECTION- C (3 Marks)

Q1. Account for the following:

a) Cooking is faster in pressure cooker than in cooking pan.

b) RBC shrink when placed in saline water.

C) Fishes are more comfortable in cold water.

Hint :Refer summary

Q2.a) Compare and contrast the properties of ideal and non-ideal solutions.

b) 30 g of urea is dissolved in 846 g of water ,calculate the vapour pressure of water for this solution if vapour pressure of pure water at 298K is 23.8 mm Hg.

Hint ;a) Refer summary

b) Apply formula

$P_O-P_S/P_O=X_B$ (Relative lowering in vapour pressure)

Ps=23.55 mmHg

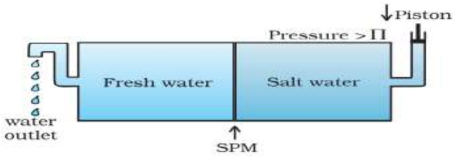
Q3. A 0.01m aqueous solution of $AlCl_3$ freezes at -0.068^oC.calculate the percentage of dissociation.(given Kf for water =1.86K kg/mol).

Hint: $\Delta T_f= i K_f m$

α =i-1/n-1 (n=4)

i=3.65, α =0.8833

Q4. Name the process shown in this figure. How is it different from osmosis? Give one use of the process.



Hint: refer summary

Q5.a) Why the colligative property of an electrolyte solution is always greater than that of non-electrolyte solution**?**

b)Which type of deviation is shown by Carbon tetra chloride and chloroform mixture?

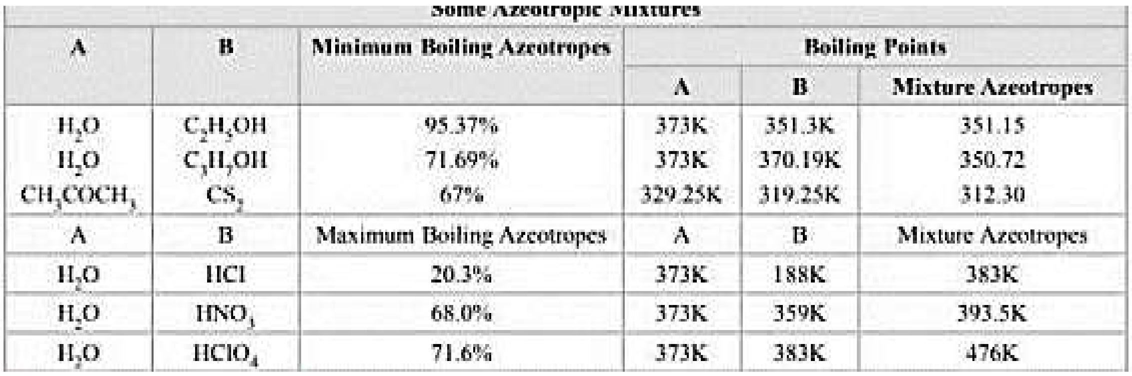
c)What is the unit of eullioscopic constant?

Hint:a) No of ions increases in case of electrolyte.

b) Positive deviation. c) K Kg/mol

SECTION D Case based Study Question(4 Marks)

Q1.Observe the table in which azeotropic mixtures are given along with their boiling points of pure Components and azeotropes and answer the questions thatfollow:



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) Why does H2O and HCl mixture form maximum boiling azeotropes? 1M

(b) What is ment by the termazeotropes? 1M

(c) Negative deviation from Raoult,s law leads to the formation of which type of azetrope? Give an example. 2M

Hint :Refer summary

Q2.**Read the passage carefully and answer the questions that follow:**

Arushi was performing an experiment in her school laboratory to determine the boiling point elevation of a sugar solution. She prepared two solutions by dissolving 34.2 g of sucrose ($C_{12}H_{22}O_{11}$) in 500 g of water and 58.5 g of NaCl in another 500 g of water. She observed that the NaCl solution had a higher boiling point than the sucrose solution. Her teacher explained that this difference was due to the **van’t Hoff factor** and the number of particles into which a solute dissociates in solution.

Sucrose is a non-electrolyte and does not dissociate in water, while NaCl is an electrolyte and dissociates into Na^+ and Cl^- ions.

The elevation in boiling point is a colligative property and is given by:

$\Delta T_b = i\ K_b m$

a) State the van,t Hoff factor (i) for sucrose? 1M

b) Why does the NaCl solution exhibit a higher boiling elevation compared to the sucrose solution,even though both are dissolved in the same amount of water? 1M

c) Calculate the molality of sucrose solution. 2M

Hint : a)i=1 b)NaCl is an electrolyte c) molality=0.2

SECTION - E (5 Marks)

Q1 .a) Describe the effect of temperature and pressure on solubility of solids and gases in liquids.

b) Calculate the elevation in boiling point of a solution of 9.43 g of $MgCl_2$ in 1 kg of water (Given K_b = 0.52Kkg/mol , Molar mass of $MgCl_2$ = 94.3gm/mol)

Hint :a)For solid –solubility increases with increase in temperature(endothermic) ;no effect of pressure For gases-solubility decreases with increase in temperature ;solubility increases with increase in pressure

b) $\Delta T_b = i\ K_b\ m$ i =3 ,ΔT_b=0.156

2. ELECTROCHEMISTRY

SUMMARY

Electrochemistry is a branch of chemistry which deals with inter-conversion of chemical energies and electrical energy

⇨ Before going into details of the chapter , you must know……

<table>
<tr><td colspan="2">Redox reaction: In a redox reaction, both oxidation and reduction reaction takes place simultaneously
Direct redox reaction : Both oxidation and reduction in same vessel.
Indirect redox reaction :oxidation and reduction in different vessels.</td></tr>
<tr><td colspan="2">Conductors: Materials that allow flow of electrons . these are of two types</td></tr>
<tr><td>Electronic or Metallic Conductors
1.Movement of electrons in the metallic lattice, e.g., Cu, Ag, etc
2. Passage of current brings only physical change.
3. No transfer of matter
4. Generally show increase in resistance with increase in temperature.</td><td>Electrolytic or Solution conductors
1. Movement of ions in molten state or in aqueous solution of electrolytes, e.g., NaCl (aq) or NaCl (fused).
2. Chemical and physical change both.
3. Transfer of matter takes place.
4. Generally show decrease in resistance due to decrease in viscosity of medium and degree of hydration of ions.</td></tr>
<tr><td colspan="2">In this chapter we will focus on Electrolytic conduactance and electrochemical cell</td></tr>
<tr><td>ELECTROLYTES:
The substance that in solution or in the molten state, conducts electric current and is simultaneously decomposed. Their extent of dissociation may vary.
Strong electrolytes :
That are 100% decomposed in normal solution.
eg.:All salts (except $CdBr_2$, $HgCl_2$), mineral acids like HCl, H_2SO_4, HNO_3, etc. and bases like NaOH, KOH, etc.
Weak electrolytes : which dissociate only to a small extent in aqueous solution.
eg : All organic acids (except sulphonic acids), inorganic acids like HCN, H_3BO_3, etc. and bases like NH_3, amines, etc.</td><td>ELECTRODE :
To pass the current through an electrolytic conductor, two rods or plates are conducted with the battery. These are called electrodes.
Active Electrodes:
(Basically used in electroplating.)
Actively participate in the electrochemical reaction, either by donating or accepting ions.
eg.Zn, Cu,,Pb and Ag electrodes.
Inert Electrodes:
(basically used in electrolysis, and electrolytic cells)
do not actively participate in the reaction but facilitate the transfer of electrons
eg :Pt, Au, graphite, rhodium etc.</td></tr>
<tr><td>Electrical Conductance
The property of the conductor (metallic as well as electrolytic) which facilitates the flow of</td><td>Specific Conductance or Conductivity
In a conductor if length is 1 cm. And</td></tr>
</table>

electricity through it.
Conductance =1/ Resistance
Unit : mho^{-1}

area is 1 cm^2 , the resistance offered is known as resistivity .R = ρ
The reciprocal of specific resistance or resistivity is known as specific conductance or conductivity (κ)kappa.

$$R=\rho\frac{l}{A}=\frac{1}{k}\frac{l}{A}$$

Where l /A is called cell constant
Unit of (κ) is Siemen Cm^{-1}

Molar Conductance

the conductance of all the ions produced by ionization of 1 g-mole of an electrolyte when present in V ml of solution. It is denoted by Λm.

$$\Lambda_m=\frac{k \text{ x } 1000}{M}$$

Unit : Siemen Cm^{2}mol^{-1}

variation	With temp increase	With conc. decrease
conductivity	Increaseas	decreases
Molar conductivity	increases	increases
conductance	increases	decreases

Kohlrausch' law of independent migration of ions:

Molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions from its individual ions.

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

Molar conductivity, $\Lambda^0_m=v_+\lambda^0_+ + v_-\lambda^0_-$

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

<u>Applications of </u>Kohlrausch's Law :

1. Determining Λ^0 m of a weak electrolyte:
2. Degree of dissocition,
   α=**Λm/Λ^{0}m**
3. Determination of solubility of sparingly soluble salt:

$$\Lambda^0 m = \frac{1000k}{C}$$

where, C is molarity of sol'n and hence solubility

4. Determination of ionic product of water

$$\Lambda^0 m \ (H_2O) = \lambda^0_{H+} + \lambda^0_{OH-}$$

(complete dissocition of water)

$$\Lambda^0 m = \frac{K}{C}$$

Then. $K_W=C^2$

<u>Ionic mobility</u> :For aqueous solution, greater the charge or smaller the size of gaseous ion, greater will be the size of aqueous ion. When such a big ion moves in solution, it experiences greater resistance by the size of solvent particles. This results in a decrease in its conductance as well as ionic mobility. Following are the increasing order of ionic mobilities of some ions:

$Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$; $< F^- < Cl^- < Br^- < I^-$;$< Al^{+3} < Mg^{+2} < Na^+$

Weak electrolytes : These are not completely ionized in polar solvents like water and hence an equilibrium between ions and unionised salt exists

$$AB + \rightleftharpoons A^{+} + B^{-}.$$

We can calculate degree of dissociation(α) and equilibrium constant (K),using expression **$K = c\alpha^2/(1-\alpha)$, if $\alpha << 1$** then use **$K = c\alpha^2$**

Electrode Potential: A metal placed in a solution of its ions obtains either a positive or negative charge with respect to the solution. On account of this, a definite potential is developed between the metal and the solution. This potential difference is called electrode potential.

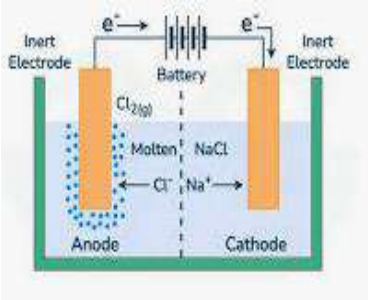
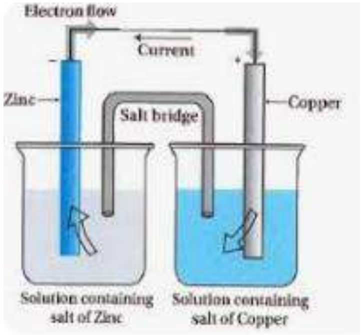
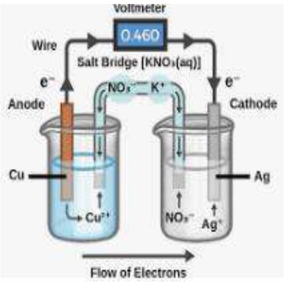
Standard Electrode Potential: The potential difference developed between metal electrode and the solution of its ions of unit molarity (1 M) at 25ºC (298 K).

EMF of a cell: It is the difference in the potential across left and right electrodes due to which electrons flow from anode to cathode.

Standard EMF: The EMF values of an electrode under standard conditions (1 atm, 298 K) and the unit concentrations of its ions

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} \text{ or } E^{\circ}_{cell} = E^{\circ}_{right\ electrode} - E^{\circ}_{left\ electrode}$$

ELECTROCHEMICAL CELLS

ELECTROLYTIC CELLS	DANIEL CELLS	GALVANIC CELLS
Devices in which electrolysis (chemical reaction involving oxidation and reduction) is carried out by using electricity or in which conversion of electrical energy into chemical energy is done. (non spaontaneous redox reaction is carried out) 	A specific type of **voltaic cell** with a copper cathode and zinc anode, using copper sulfate and zinc sulfate solutions, respectively. It is known for its reliable and consistent voltage output. 	A broader term encompassing any electrochemical cell that converts chemical energy to electrical energy through a spontaneous redox reaction. 
Cell reaction : $NaCl + H_2O \rightleftharpoons Na^{+} + OH^{-} + H_2 + Cl_2$ **QUICK COMPARISION** **1. Redox reaction** **Non spontaneous** **2.E^{O}cell is negative** **3.Anode is +ve** **4.Cathode is -ve** **5.flow of electron anode to cathode** **6.Electrolysis, electroplating**	**Cell representation :** **Zn/Zn^{+2} (aq.) II Cu^{+2}(aq.)/Cu** **Redox reaction** **Spontaneous** **E^{O}cell ispositive** **Anode is -ve** **Cathode is +ve** **Anode to cathode**	**Cell representation :** **Cu/Cu^{+2} (aq.)IIAg+/Ag** **Redox reaction** **Spontaneous** **E^{O}cell is positive** **Anode is -ve** **Cathode is +ve** **Anode to cathode**

	Cell	Batteries

Faraday's law of electrolysis

First law:the amount of substance deposited at electrode is proportional to quantity of charge passed through the electrolyte.

W=zit

z is electrochemical equivalent

$$z = \frac{Eq.Wt}{F} = \frac{M}{nF}$$

$$W = \frac{M}{nF} * i * t$$

Second law :the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses,when same quantity of current is passed.

W =Z x Q,

When Q = 96500 coulomb

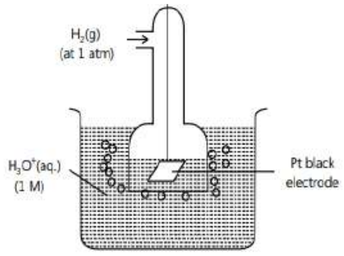
W becomes gm equivalent mass E,

$$Z = \frac{E}{96500} \; ; \; \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Faraday's first law and second

Reference Electrode To determine the cell potential of individual half cell , reference electrode is required. The electrode cell potential of reference electrodes are known.a and on coupling with other electrode, a **voltaic cell** is constituted.

Standard Hydrogen Electrode, SHE or NHE



Electrode : Platinized Platinum
Electrolyte: 1M HCl (freshly prepared)
Temperature : 298 K
Hydrogen gas Pressure : 1 atm or 1 bar

SHE half reaction	Electrode potential
$H_2 \longrightarrow 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \longrightarrow H_2$	0.0 V (Cathode)

Nernst Equation :

Suppose, we reduced the conc. of Zn $^{+2}$ in the Zn/Cu cell from its unit activity value of around 0.5 M to a much smaller value:

Zn/Zn^{+2} (0.001M) II Cu^{+2} /Cu

This will reduce the value of Q for the cell reaction

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

ΔG more negative than ΔG^0 , so
E would be more positive than

$\Delta G^0 = -nFE^o$; $\Delta G = -nFE$

Using $\Delta G = \Delta G^0 + RT\ lnQ$;

$$E = E^\circ - \frac{RT}{nF} lnQ$$

For a general reaction;

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^\circ_{(cell)} - \frac{RT}{nF} lnQ = E^\circ_{(cell)} - \frac{RT}{nF} ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Salt bridge completes the

The overall reaction and ΔGº for each cell is same.
E^0_{cell} and 'n' values are different for each cell.
E^0_{cell} × n is same for each cell.
ΔGº depends on cell reaction and E^0_{cell} depends upon making up of a cell.

up of a cell

law can be combined $W = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times E = \frac{Q}{F} \times \frac{M}{z} = \frac{C \times t}{F} \times \frac{M}{z}$	circuit, maintains electroneutrality and also minimises liquid junction potential.

Preferential Discharge Theory: Electrolysis of solutions containing more than two ions, the ion that requires the least energy (or has the highest reduction potential) to be discharged will be preferentially discharged at the respective electrode.

Cont.

electrolyte	**electrode**	**Cathodic reaction**	**Anodic reaction**	**Remarks if any**
1. Molten NaCl	Pt	$2Na^+ + 2e^- \rightarrow 2Na$	$2Cl^- \rightarrow Cl_2 + 2e^-$	One cation and on anion
2.Molten $PbBr_2$	Pt	$Pb \longrightarrow Pb^{+2} + 2e^-$	$2Br^- + 2e^- \longrightarrow Br_2$	**--do---**
3.NaCl aq. (two competing reactions are possible both at cathode and anode) **The products vary with concentration.**	Pt	**AT pH 7** At cathode : Na+ and water both can be reduced $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-\ E^o = -1.0\ V$ $Na^+(l) + e^- \rightarrow Na(l)\ E^o = -2.71V$ At anode : both water and chloride ion can be oxidised. $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-\ E^o = -1.42\ V$ $2Cl^- \rightarrow Cl_2 + 2e^-\ E = -1.36V$		

A.) **Very dilute aq. NaCl solution**

water with high reduction potential is reduced at cathode

At cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-\ E^o = -1.0\ V$

At anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-\ E^o = +1.4\ V$

In small conc.the electrolysis of water becomes more predominant yielding **oxygen at anode.**

B. **)**High Concentration of Sodium Chloride : **Hydrogen at cathode**

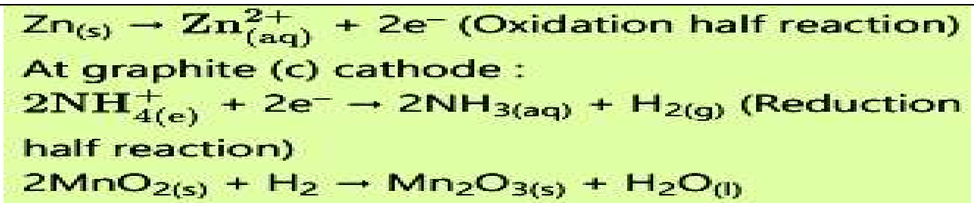
At anode oxidation of water being more positive is more feasible, so the evolution of oxygen gas should happen at the anode. But, the evolution of oxygen from water has an overvoltage of -0.6V, making the voltage for the oxidation of water as -1.4V.So, chloride is, oxidised to **chlorine at the anode**.

BATTERIES : Consist of two or more galvanic cells.these are of two types.

PRIMARY BATTERY

When the reactants have been converted to products, no more electricity is produced.the cell reaction can not be reversed and cell becomes dead.

A.) DRY CELL



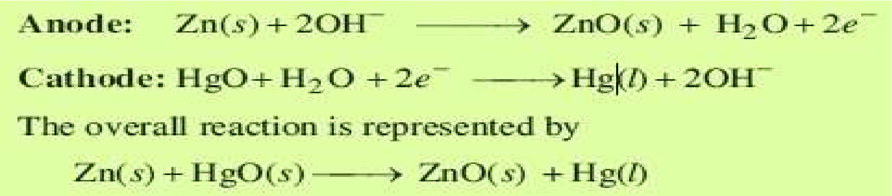
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$ (Oxidation half reaction)

At graphite (c) cathode :

$2NH^+_{4(e)} + 2e^- \rightarrow 2NH_{3(aq)} + H_{2(g)}$ (Reduction half reaction)

$2MnO_{2(s)} + H_2 \rightarrow Mn_2O_{3(s)} + H_2O_{(l)}$

B. **)** MERCURY CELL



Anode: $Zn(s) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$

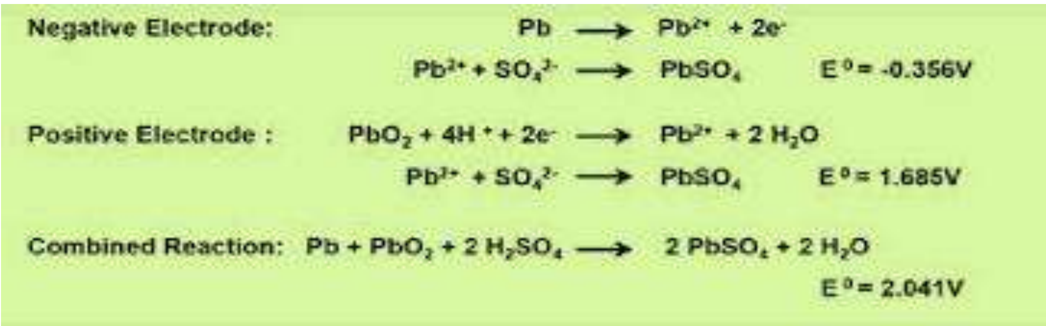
Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

The overall reaction is represented by

$Zn(s) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

SECONDARY BATTERY : The cell reaction can be reversed by passing electricity through the battery(charging).It can be used again and again.

LEAD STORAGE BATTERY :



Negative Electrode: $Pb \longrightarrow Pb^{2+} + 2e^-$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$ $E^0 = -0.356V$

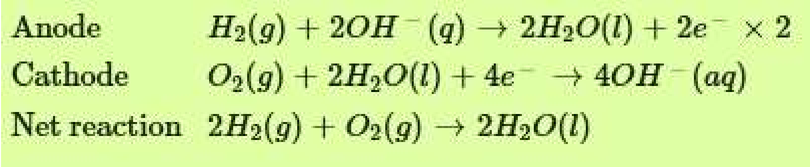
Positive Electrode : $PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$ $E^0 = 1.685V$

Combined Reaction: $Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$

$E^0 = 2.041V$

FUEL CELLS : Electrical cells that are discharged to convert the energy from the combustion of fuels (hydrogen, carbon monoxide, methane, etc.) directly into the electrical energy are called fuel cells.



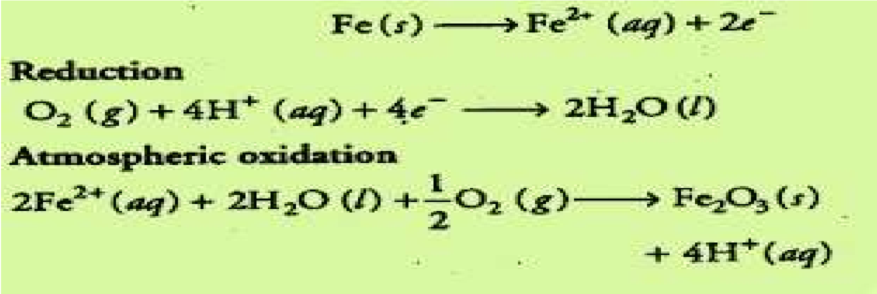
Anode $H_2(g) + 2OH^-(q) \rightarrow 2H_2O(l) + 2e^- \times 2$

Cathode $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Net reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Corrosion of Iron (Rusting)

Rusting of iron which is the most commonly seen example happens when iron comes in contact with air or water. The reaction could be seen as a typical electrochemical cell reaction..



$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$

Reduction

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

Atmospheric oxidation

$2Fe^{2+}(aq) + 2H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow Fe_2O_3(s) + 4H^+(aq)$

PREVENTION OF RUSTING :

BARRIER COATINGS : Paint acts as a coating to protect the metal surface from the electrochemical charge that comes from corrosive compounds.

HOT-DIP GALVANIZATION : The iron in the steel reacts with the zinc to create a tightly bonded alloy coating which serves as protection.

CATHODIC PROTECTION : To prevent corrosion, the active sites on the metal surface are converted to passive sites by providing electrons from another source, typically with galvanic anodes attached on or near the surface. Metals used for anodes include aluminum, magnesium, or zinc.

IMPORTANT LINKS : Representation of electrochemical cell :
https://diksha.gov.in/play/content/do_3129961045697904641131?referrer=utm_source%3Dmobile%26utm_campaign%3Dshare_content

Electrochemistry at a glance :
https://diksha.gov.in/play/content/do_3134757780802928641239?referrer=utm_source%3Dmobile%26utm_campaign%3Dshare_content

QUESTION BANK
SECTION- A (1 MARK)

Q.1) Which device converts chemical energy of a spontaneous redox reaction into electrical energy?
(a) Galvanic cell (b) Electrolytic cell
(c) Daniell cell (d) Both (a) and (c)

Q.2) The difference between the electrode potentials of two electrodes when no current is drawn through the cell is called
(a) Cell potentials (b) Cell emf
(c) Potential difference (d) Cell voltage

Q.3) The most durable metal plating on iron to protect against corrosion is
(a) nickel plating (b) copper plating
(c) tin plating (d) zinc plating

Q.4) The electric charge for electrode decomposition of one gram equivalent of a substance is
(a) one ampere per second (b) 96500 coulombs per second
(c) one ampere for one hour (d) charge on one mole of electrons

Q.5) The ion of least limiting molar conductivity among the following is
(a) SO_4^{2-} (b) H^+ (c) Ca^{2+} (d) $CH\ COO^-$

Q.7) Which of the following batteries cannot be reused?
(a) Lead storage battery (b) Ni-Cd cell
(c) Mercury cell (d) Both (b) and (c)

Q.8) Specific conductance of 0.1 M HNO_3 is 6.3×10^{-2} ohm^{-1} cm^{-1}.The molar conductance of the solution is
(a) 100 ohm^{-1} cm^2 (b) 515 ohm^{-1} cm^2
(c) 630 ohm^{-1} cm^2 (d) 6300 ohm^{-1} cm^2

Q.9) If salt bridge is removed from two half-cells the voltage
(a) drops to zero (b) does not change
(c) increases gradually (d) increases rapidly

Q.10) For the galvanic cell $Zn \mid Zn^{2+}$ (0.1M) $\parallel Cu^{2+}$ (1.0M)$\mid$Cu; the cell potential increase if:
(a) $[Zn^{2+}]$ is increased (b) $[Cu^{2+}]$ is increased
(c) $[Cu^{2+}]$ is decreased (d) surface area of anode is increased

B.)ASSERTION-REASON TYPE QUESTIONS: In the following questions Q.11 to Q.15, each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.

(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion

(c) Assertion is correct, reason is incorrect

(d) Assertion is incorrect, reason is correct.

Q.11 **Assertion** : On increasing dilution, the specific conductance keep on increasing.

Reason : On increasing dilution, degree of ionisation of weak electrolyte increases and molality of ions also increases.

Q.12 **Assertion:** In an electrochemical cell anode and cathode are respectively negative and positive electrodes.

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

Q.13 **Assertion** :Salts like KCl, KNO_3 i.e., inert electrolytes are used in salt bridge.

Reason: An inert electrolyte can easily be filled in the U-tube.

Q.14) **Assertion :** Emf and potential difference are the same for cells.

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

Q.15) **Assertion**: The electrode potential of standard hydrogen electrode is zero.

Reason: There is no potential difference at the electrode – solution interface in this case.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1.d	2.b	3.d	4.b	5.d
6.c	7.c	8.a	9.a	10.b

ASSERTION REASON QUESTIONS

1.d	2.a	3.c	4.d	5.c

SECTION –B (TWO MARKS)

Q.1)Why on dilution the Λ_m of CH_3COOH increases drastically, while that of CH_3COONa increases gradually?

Hint : In the case of CH_3COOH, which is a weak electrolyte, the number of ions increase on dilution.In the case of strong electrolyte such as CH_3COONa, the number of ions remains the same but the interionic attraction decreases.

Q.2)Why does mercury cells give constant voltage?

Hint : Overall cell reaction does not include any ion in the solution whose concentration changes during its lifetime.

Q.3)Consider a cell given below **Cu |Cu^{2+}|| Cl^-/Cl_2,P**t. Write the reactions that occur at anode and cathode..

Hint : Cu is anode as it is getting oxidised. Cl_2 is cathode as it is getting reduced.

Q.4)Why in a concentrated solution, a strong electrolyte shows deviations from Debye-Huckle- Onsagar equation?

Hint :Because interionic forces of attractions are large.

Q.5)Electrolysis of KBr(aq) gives Br_2 at anode but KF(aq) does not give F_2 . Give a reason.

Hint : Oxidation potential of Br^-, H2O, F^- are in the following order. $Br^- > H2O > F^-$ Therefore in the Aqueous Solution of KBr. Br− ions are oxidized to Br_2 in preference to H_2O . On the other hand, in the aqueous solution of KF, H_2O is oxidized in preference to F^{-} . Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

SECTION-C (THREE MARKS)

Q.1)Calculate emf of the following cell at 298K.

$Zn/Zn^{2+}(10^{-4}M)||\ Cu^{2+}(10^{-2}M)/Cu$ (Given $E^0_{Zn2+/Zn} = -0.76$ V,$E^0_{Cu2+/Cu} = +0.34V$)

Hint : Cell reaction is as follows.

$Zn(s)+ Cu^{2}+(aq) \rightarrow Zn^{2}+(aq) + Cu(s)$,Use Nernst equation and put values

n = 2 and T = 298 K (Ans.$E_{cell} = +1.1591V$)

Q.2)What happens when a piece of copper is added to

a. An aqueous solution of $FeSO_4$? b. An aqueous solution of $FeCl_3$?

Hint : a.) No reaction as $E^0_{Cu^{2+}/Cu}$ (−0.34V) > $E^0_{Fe^{2+}/Fe}$ (−0.44V)

b.)copper will dissolve in an aq. solution of $FeCl_3$,as

$E^0_{Fe^{3+}/Fe^{2+}}$(+0.77V)>$E^0_{Cu^{2+}/Cu}$ (−0.34V)

Q.3)The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2mol^{-1}. Calculate the conductivity of this solution.

Hint : $K = \Lambda m \times C/1000 = 138.9 \times 1.5/1000 = 0.20835\ S\ cm^{-1}$

Q.4)How many grams of chlorine can be produced by the electrolysis of molten NaCl with a current of 1.02 A for 15 min?

Hint : use formula ;

$$w = \frac{\text{m.wt of Cl x i x t in sec}}{\text{n x F}}$$

Ans:0.331 gm.

Q.5) Why is it necessary to platinize the electrodes of a conductivity cell before it is used for conductance measurement?

Hint : platinization increases the surface area of the electrode and lead to better conduction measurement.

SECTION –D CASE BASED/SITUATION BASED QUESTIONS

PASSAGE 1

Read the passage given below and answer the following questions:

"Replacing fossil fuels with sustainable, environmentally benign, and affordable energy sources and carriers is amongst the most pressing challenges for future socio-economic development. To that goal, hydrogen is presumed to be the most promising energy carrier.

Electrocatalytic water splitting, if driven by green electricity, would provide hydrogen with a minimal CO_2 footprint. The viability of water electrolysis hinges on the availability of durable, earth-abundant electrocatalyst materials and the overall process efficiency.

This review spans the fundamentals of electrocatalytically initiated water splitting to the latest scientific findings from university and institutional research, also covering specifications and special features of current industrial processes.

Recently developed strategies for the optimization and discovery of active and durable materials for electrodes increasingly harness first-principles calculations and machine learning. Additionally, a techno-economic analysis of water electrolysis is included to assess the extent to which large-scale implementation of water splitting can help combat climate change."

(Source: Adapted from "Water electrolysis: from textbook knowledge to the latest scientific strategies and industrial developments," Chemical Society Reviews, 2022, published by the Royal Society of Chemistry.)

Q.1)What is the primary goal of electrocatalytic water splitting as described in the passage, and why is hydrogen considered a promising energy carrier in this context?

Hint :To produce hydrogen with a minimal CO_2 footprint by using green electricity. Hydrogen is considered a promising energy carrier because it can replace fossil fuels.

Q.2)Why might the use of earth-abundant materials be critical for the large-scale implementation of this technology ?

Hint :because they are more readily available and cost-effective compared to rare or expensive materials.

Q.3)Water electrolysis system using Nickel Oxide as an electrocatalyst has an efficiency of 75%, If 1000 kWh of green electricity is supplied to the system, calculate the energy available for hydrogen production?

Ans. Efficiency = 75% = 0.75

Energy Available = Input Energy × Efficiency

Energy Available = 1000 kWh × 0.75 = 750 kWh

OR

Q.3)Calculate the total cost of operating three water electrolysis systems, each using a different electrocatalyst material, for 5,000 hours. Assume the cost of operation is $0.10 per kWh of energy, and each system consumes 200 kW of power continuously?

Ans. Energy Used = Power Consumption × Operating Time

= 200 kW × 5,000 hours = 1,000,000 kWh

Operating Cost = Energy Used × Cost per kWh

Operating Cost = 1,000,000 kWh × $0.10/kWh

= $100,000 (same for all, as cost depends on input energy.

PASSAGE 2

Read the passage given below and answer the following questions:

"Corrosion, the spontaneous deterioration of metals through chemical or electrochemical interaction with their environment, poses a significant challenge to industrial and societal infrastructure. This natural process often converts refined metals into more stable forms, such as oxides, hydroxides, or sulfides, driven by thermodynamic favorability.

Electrochemical corrosion, the most prevalent type, occurs in the presence of an electrolyte, where anodic oxidation releases electrons from the metal, and cathodic reactions, such as oxygen reduction or hydrogen evolution, consume them. The rate of the rate of corrosion depends on factors like the nature of the metal, the presence of impurities, the electrolyte's pH, temperature, and oxygen availability.

Recent advances leverage computational tools, including first-principles calculations and machine learning, to predict corrosion behavior and design corrosion-resistant materials. Protective strategies, such as coatings, cathodic protection, and inhibitors, are critical to mitigating corrosion, which costs the global economy approximately $2.5 trillion annually, underscoring the need for innovative solutions to enhance durability and sustainability."

(Source: Adapted from "Corrosion Science and Technology: Advances in Understanding and Mitigation," Chemical Reviews, 2021, published by the American Chemical Society.)

Q.1) What are the two primary types of reactions involved in electrochemical corrosion?

Hint :anodic oxidation and cathodic reactions

Q.2) Name two forms that metals can turn into during corrosion, as mentioned in the passage. [Hint : oxides and hydroxides]S

Q.3)If you notice a car's metal body rusting near the ocean. Based on the passage, what factor might be speeding up the corrosion?

OR

Q.3)steel bridge component has a corrosion rate of 0.8 mm/year, as noted in the sample database. If the component is 10 mm thick and exposed to corrosion for 5 years without protection, calculate the thickness lost and the remaining thickness.

Hint : Thickness Lost = Corrosion Rate × Exposure Time

Thickness Lost = 0.8 mm/year × 5 years = 4.0 mm

Remaining thickness = 6.0 mm.

Extended Learning :

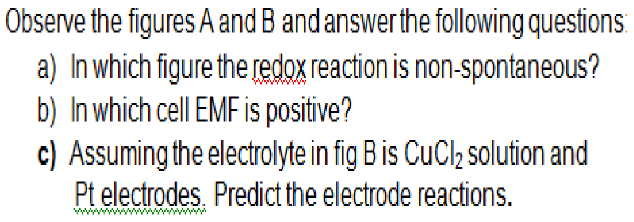
The passage states corrosion costs the global economy $2.5 trillion annually. Assume a small country's share of this cost is 1.5% of the total, and they implement protective strategies (e.g., coatings) that reduce corrosion damage by 30%. So, what may be the country's initial corrosion cost and the cost savings after applying these strategies.

Now see

Global Cost = $2,500,000,000,000 ($2.5 trillion)
Country's Share = 1.5% = 0.015
Initial Cost = Global Cost × Country's Share
Initial Cost = $2,500,000,000,000 × 0.015 = $37,500,000,000 ($37.5 billion)
Reduction Percentage = 30% = 0.30
Cost Savings = Initial Cost × Reduction Percentage
Cost Savings = $37,500,000,000 × 0.30 = $11,250,000,000 ($11.25 billion)
Initial Corrosion Cost: $37.5 billion

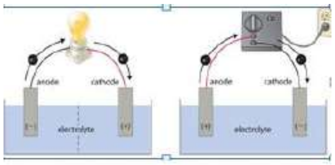
SECTION-E (5 MARKS)

Q.1) a.)



Observe the figures A and B and answer the following questions:

a) In which figure the redox reaction is non-spontaneous?
b) In which cell EMF is positive?
c) Assuming the electrolyte in fig B is $CuCl_2$ solution and Pt electrodes. Predict the electrode reactions.



b)A solution of magnesium sulfate ($MgSO_4$) has a conductivity of 0.00635 S cm^{-1} at 25°C when its concentration is 0.01 M. Calculate the molar conductivity. If the solution is diluted to 0.005 M and the conductivity drops to 0.00350 S cm^{-1}, what is the new molar conductivity?

Hint : b.)$\Lambda m = (\kappa \times 1000) / c$

$\Lambda m = (0.00635 \text{ S cm}^{-1} \times 1000) / 0.01 \text{ mol L}^{-1}$

$= 635 \text{ S cm}^{2} \text{ mol}^{-1}$

Initial molar conductivity = 635 S cm^{2} mol^{-1}

Molar Conductivity After Dilution

$\Lambda m = (0.00350 \text{ S cm}^{-1} \times 1000) / 0.005 \text{ mol L}^{-1}$

$= 700 \text{ S cm}^{2} \text{ mol}^{-1}$

Chapter- 3 Chemical Kinetics

Summary

- **Rate of a Chemical Reaction**: It is the change in concentration of a reactant or product per unit time.

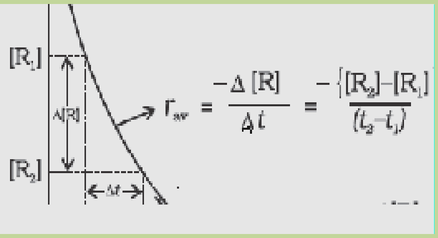
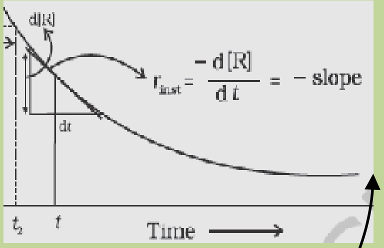
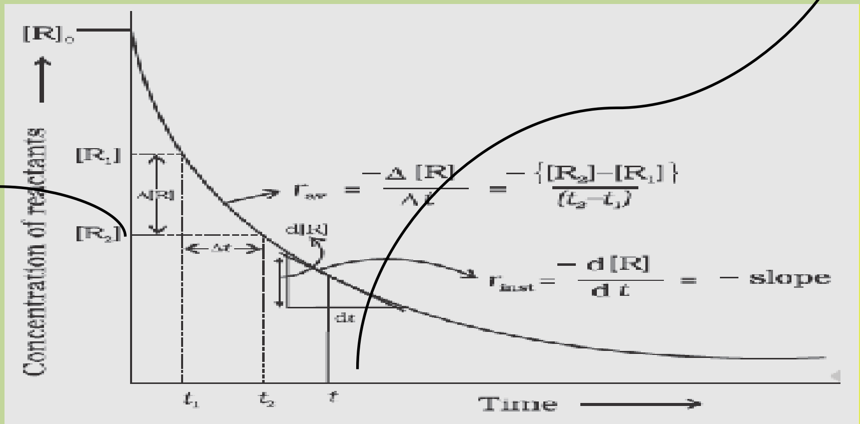
Expression for rate of reaction:

Consider a reaction,

$$R \rightarrow P$$

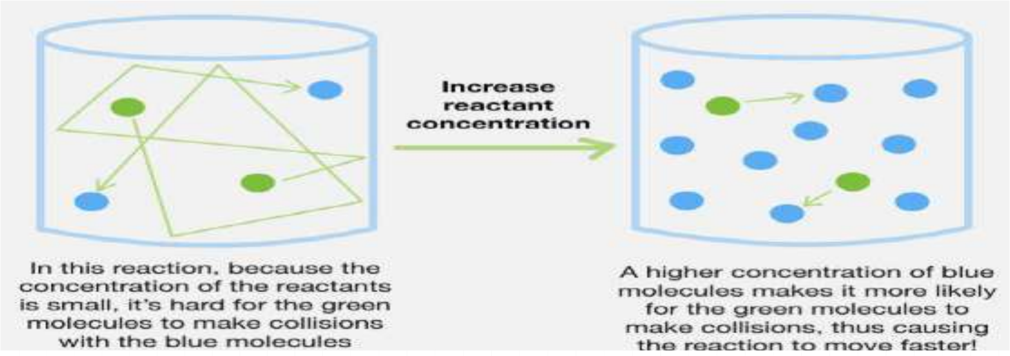
Units of rate of a reaction: mol $L^{-1}s^{-1}$

$$\frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

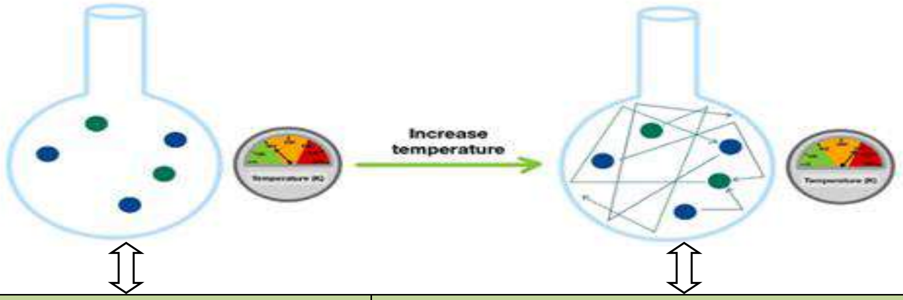
Average Rate	**Instantaneous Rate**
It is the change in concentration of reactants in a given interval of time.	Rate of a chemical reaction at a particular moment of time, is known as instantaneous rate of reaction.
	
	

- **Factors Influencing Rate of a reaction:**

(i) Effect of concentration of reactants (pressure in case of gases).



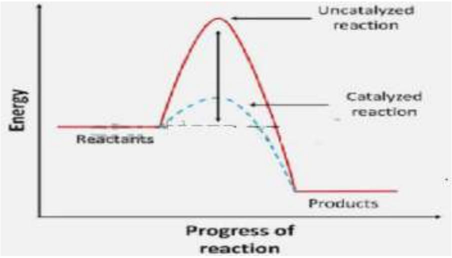
(ii) Effect of temperature



The molecules in this reaction Moving very slowly, which makes it hard for collisions to occur. This iscausing the reaction to proceed at a very slow rate	Increasing the temperature causes the K.E. of the molecules to increase thus causing the molecules tomove faster which causing collisions tooccur more frequently. More collision meansthe rate increases

(iii) Effect of catalyst

(a) A catalyst does not alter Gibbs energy.
(b) It catalyses the spontaneous reactions but does not catalyse non-spontaneous reactions.
(c) It is also found that a catalyst does not change the equilibrium constant ofa reaction rather, it helps in attaining the equilibrium faster.



- **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.

Zero order reaction (n = 0) = mol L^{-1} s^{-1}

Rate = $k\,[A]^x\,[B]^y$

Second order reaction (n = 2) = mol^{-1} L s^{-1}

Units of rate constant

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

x+ y = n ; n = order of reaction.

$(concentration)^{1-n}$ $time^{-1}$

On considering S.I.unit of concentration as **mol L^{-1}** and time as **seconds**, the unit of

$k = (mol\ L^{-1})^{1-n}\ s^{-1}$

first order reaction (n = 1)

= s^{-1}

- **Order of a Reaction**: The sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero-order reaction means that the rate of reaction is independent of the concentration of reactants.

When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called complex reactions.

The reactions taking place in one step are called elementary reactions.

Molecularity of a reaction

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

The slowest step in a reaction called the rate determining step.

The integrated rate equations

Zero order reaction

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

First order reaction

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

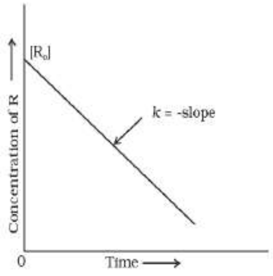
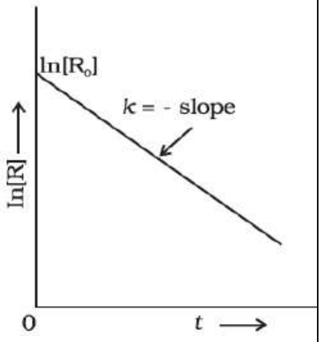
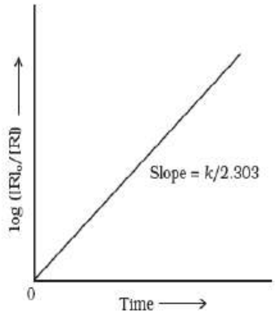
Where

$[R]_0$ = initial concentration of reactant,

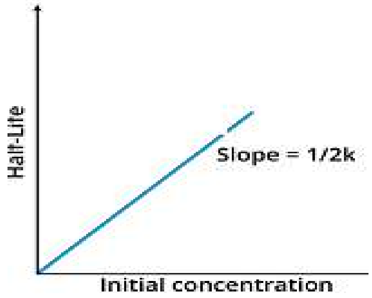
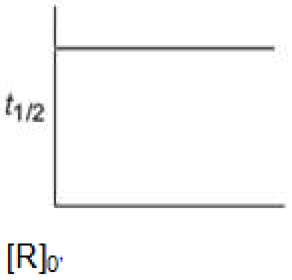
$[R]$ = the final concentration at time 't' ,

t = time taken

- **Important Graph plots for zero order and first order reaction-**

	Graph -1 (zero order reaction)	Graph -2 (First order reaction)	Graph -3 (First order reaction)
Line equation	$[R] = -kt + [R]_0$	$\ln[R] = -kt + \ln[R]_0$	$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$
Figure			
Plot	[R] vs time	In[R] vs time	Log $\frac{[R]0}{[R]}$ vs time
Slope	–k	-k	k/2.303
Intercept	$[R]_0$	In $[R]_0$	0

- **Half life period:** The half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $t_{1/2}$.
- The *half life period* for a zero order reaction is directly proportional to the initial concentration of the reactants and inversely proportional to the rate constant.
- For a first order reaction, half-life period isconstant, i.e., it is independent of initial concentration of the reactingspecies.
- **Graph plots for half life period of reaction-**

	Graph -1 for zero order reaction	Graph-2 for First order of reaction
Line equation	$t_{1/2} = \frac{[R]0}{2k}$	
Figure		
Plot between	$t_{1/2}$ vs $[R]_0$	$t_{1/2}$ vs $[R]_0$
Slope	$\frac{1}{2k}$	No slope (independent to initial concentration of reactant)
Intercept	0	

- **pseudo first order reactions**.The concentration of water does not get altered much during the course of the reaction. So, the reaction behaves as first order reaction.Such reactions are called **pseudo first order reactions**.
  Inversion of cane sugar is pseudo first order reaction.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\text{Rate} = k\,[C_{12}H_{22}O_{11}]$$

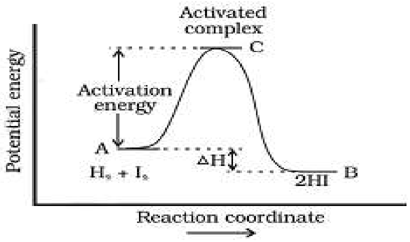
- **Activation Energy**: The energy required to form this intermediate, called activated complex(C), is known as activation energy (*E*a).
- According to Kinetic theory of Molecular gases, the average kinetic energy of reacting gaseous molecules is directly proportional to absolute temperature.

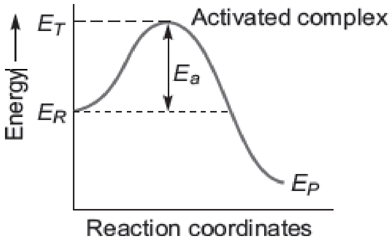
$$K.E \propto T$$

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

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

- **Threshold energy(E_T)**:The minimum amount of energy whichthe reactant must possess in order to convert into products is known as**threshold energy**.





- **Important formula to relate activation energy , temperature and rate constant-**

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

Where: k_1 and k_2 are the values of rate constants attemperatures T_1 and T_2 respectively

E_a= Activation energy, R= Gas constant

- **Graph:-**

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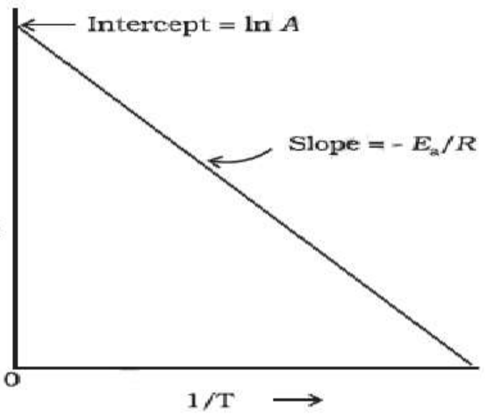
<tr><td rowspan="3">
</td><td>**Plot between ln k vs 1/T** ,</td></tr>
<tr><td>Straight line equation
$$\ln k = -\frac{E_a}{RT} + \ln A$$</td></tr>
<tr><td>slope = -$\frac{Ea}{R}$and intercept = ln$A$</td></tr>
</table>

- **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.
- **Collision frequency**: The number of collisions persecond per unit volume of the reaction mixture is known ascollision frequency (Z).
- **Effective collisions**:To facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as effective collisions.

****

QUESTION BANK

Section – A (1 Mark)

Q.1"For the reaction 2A + B → A_2B, the order with respect to each reactant is 1 .what will be the effect on the reaction rate if the concentration of reactant A is doubled and the concentration of reactant B is decreased by half?"

(a) increase 2 times
(b) increase 4 times
(c) decrease 2 times
(d) remain the same

Q.2The value of rate constant for a reaction is 2.96×10^{-30} s^{-1} . What is the order of the reaction?

(a) 1 (b) 3 (c) 2 (d)Zero

Q.3 The role of a catalyst is to change :

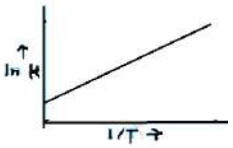
(a) equilibrium constant (b) Δ_rG (c) Δ_rH (d) E_a

Q.4 "If the rate of the reaction $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$ is $r = k[H_2O_2]$, what is the reaction order?"

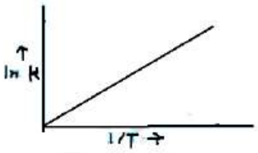
(a) second order (b)first order (c) third order (d) zero order

Q.5 According to Arrhenius equation rate constant k is equal to A $e^{-Ea/RT}$. Which of the following options represents the graph of ln k vs 1/T ?

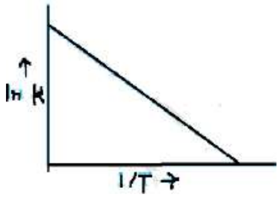
(a)



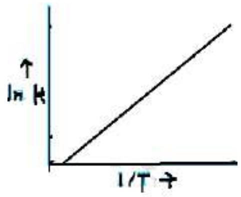
(b)



(c)



(d)



Q.6 In the graph plotted between In [R] and t for a first order reaction, the intercept on y-axis is

(a) -k (b) [R] (c) ln $[R]_0$ (d) k/2.303

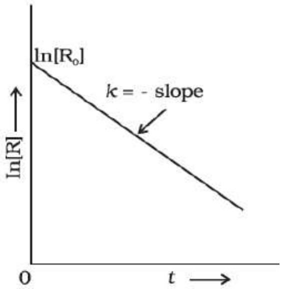
Q.7A reaction follows first-order kinetics and has a half-life of 69.3 seconds. What is the rate constant (k) for this reaction?

(a) 1.0 s^{-1} (b)0.01 s^{-1} (c) 0.1 s^{-1} (d) 0.001 s^{-1}

Q.8If the rate of reaction is proportional to the concentration of A and the square of the concentration of B, what is the total order of the reaction?

(a) 6 (b) 5 (c) 2 (d) 3

Q.9 To what order of a reaction does the following graph belong to?



(a) Zero order reaction (b) First order reaction

(c) Second order reaction (d) Third order reaction

Q.10 In pseudo unimolecular reactions:

(a) Both reactants are present in low concentrations,

(b) Both reactants are present in the same concentrations,

(c) One reactant is present in excess,

(d) One reactant is non-reactive.

ASSERTION AND REASON TYPE QUESTIONS

For the Questions given below, 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

Q.11**Assertion(A):** The overall order of a complex reaction is the same as the molecularity of its slowest step.

Reason(R): The rate-determining step governs the speed of the entire reaction.

Q.12 **Assertion (A):** Activation complex for the forward reaction will have lower energy than that for the backward reaction in an exothermic reaction.

Reason (R): Reactants have greater energy than products for an exothermic reaction.

Q.13**Assertion(A):** Increase in concentration of reactant will not change the rate for a zero-order reaction.

Reason(R): Rate constant for a zero-order reaction is a constant for a particular initial concentration.

Q.14**Assertion(A):** Every collision between reacting molecules results in the formation of products.

Reason(R): Product formation occurs only when colliding molecules have the proper orientation and enough energy.

Q.15 Assertion(A): For a certain reaction, a large fraction of molecules have energy more than the threshold energy, still the rate of reaction is very slow.

Reason(R): The colliding molecules must not be properly oriented for effective collisions.

Answer Keys :

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

Section – B (Short answer Questions) 2 marks each

Q.1 sA chemical reaction reduces the amount of a substance following first-order kinetics, with $k = 60\ s^{-1}$. How long will it take for the substance to shrink to 1/16 of what it was?

(Hint: Put the values in formula $k = \frac{2.303}{t}\log\frac{[R]o}{[R]}$, Answer: 0.0460 Seconds)

Q.2.How will you compare Order and Molecularity.

(Hint: Refer to the summary of the chapter.)

Q.3 Can the activation energy of a reaction be zero. Justify your answer.

(Hint: All the collisions can not be 100% effective collisions)

Q.4 The conversion of X to Y is a second- order reaction. Compare the rate of reaction when the concentration of X is increased from its initial value to three times that amount.

(Hint: rate will increase by nine times)

Q.5From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants:

(a) $3NO_{(g)} \longrightarrow N_2O_{(g)} + NO_{2(g)}$ rate = $k[NO]^2$

(b) $C_2H_5Cl_{(g)} \longrightarrow C_2H_{4(g)} + HCl_{(g)}$ rate = $k[C_2H_5Cl]$

(Hint: (a) II order reaction and unit - $Mol^{-1}\ L\ s^{-1}$; (b) I order reaction and unit- s^{-1})

Section – C (3 marks)

Q.1 A chemical reaction has rate constants of 0.02 s^{-1} at 500 K and 0.07 s^{-1} at 700 K. Using this data, determine the activation energy and the frequency factor (A) using the Arrhenius equation.

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

(Hint: Put the value of E_a by this formula

And A by this formula $\log k = \log A - \frac{Ea}{2.303RT}$)

Q.2. In a graph In[reactant] was plotted vs. time, it gave a straight line, predict the order of the reaction also give the expression of its half life and rate costant.

[Hint: 1st order, $t_{1/2}=0.693/k$, rate constant $k= 2.303/t \text{ Log } [R_0]/[R]$

Q3 . For the reaction A + B → C, you find that the rate = k[A]^2. What does this imply about the mechanism of the reaction?

[Hint: 2nd order w.r.t.A, B do not participate in rate determining step(large excess)]

Q4. Account for the following:

(a) Reactions with higher molecularity are rare.

(b) A zero-order reaction show a linear concentration vs. time graph

(c) Adsorption of gases becomes faster on powdered charcoal

[Hint: (a)- Chances of effective collision decreases, (b)- Rate is independent of initial concentration, (c)- Large surface area]

Q5 .If half life period of A in a first order reaction reaction is 2 minutes , How long will it take [A] to reach 25% of its initial concentration

[Hint: Use formula of $t_{1/2}$ K for 1st order,Ans- t_{75} = 4 min.]

Section – D (CBQ) 04 marks

A group of Class 12 students performed an experiment to study the rate of decomposition of hydrogen peroxide (H_2O_2) in the presence of a potassium iodide (KI) catalyst. They observed that the reaction was faster at higher temperatures. The balanced reaction is:

$$2H_2O_{2(aq)} \xrightarrow{KI} 2H_2O_{(l)} + O_{2(g)}$$

They measured the time taken to collect a certain volume of oxygen at different temperatures and found that the reaction rate increased with temperature. Their teacher explained that the reaction follows first-order kinetics and the rate constant k can be calculated using the integrated rate equation:

$K = (2.303/t) \log[R]^0/[R]$

The class was also introduced to the Arrhenius equation:

$k=Ae^{-Ea/RT}$

which shows how the rate constant changes with temperature and activation energy.

(a) What role does potassium iodide (KI) play in the reaction?

(b) Predict the order and unit of rate constant for the above reaction

(c) How does temperature affect the rate of a chemical reaction? If the rate constant at two temperatures is known, how can you calculate the activation energy?

Hint: (a) Catalyst

(b)Definition ,first order

(c) As the temperature increases rate of reaction increases.

[LogK_2/K_1 = Ea / 2.303R[1/T_1 -1/T]

LONG ANSWER TYPE QUESTIONS [5 MARKS]

Q 1(a). Radioactive decay follows first order kinetics. The rate constant for the decomposition of a hydrocarbon is 2·418 x 10-5 s-1 at 546 K. If the energy of activation is 179·9 kJ mol-1, what will be the value of pre-exponential factor.

According to Arrhenius equation,

[Hint: $\log K = \log A - \frac{E_a}{2 \cdot 303RT}$ so value of pre-exponential

$A = \text{Antilog } 12{\cdot}5916 = \mathbf{3{\cdot}9 \times 10^{12}\ s^{-1}}$.

(b).The initial rate of a reaction A+B→CA + B is studied at various initial concentrations.

The data obtained is:1.

[A] (mol/L)	[B] (mol/L)	Initial Rate (mol L^{-1} s^{-1})
0.1	0.1	0.02
0.2	0.1	0.04
0.2	0.2	0.08

Determine the order of the reaction with respect to A and B. Write the rate law and the value of rate constant (k).

Hint:(b).order: w.r.t. A= 1 , w.r.t. B = 1

rate law R = k [A] [B]

K= 2 lit / mol sec

Q 2. (a).Describe the concept of pseudo first order reaction and support your explanation with an example.

(b). For a zero order reaction ,the rate constant k is 0.005 mol/L sec.If the initial concentration of the reactant is 0.2 mol/L then calculate :

(i) The time required for the reactant to be reduced to 0.05 mol/L.

(ii). The half- life of the reaction.

[Hint: (a)Refer summary]

(b)t = A^0-A / k

t = 30 sec

$t_{1/2}$ = [A] /2k =20 sec

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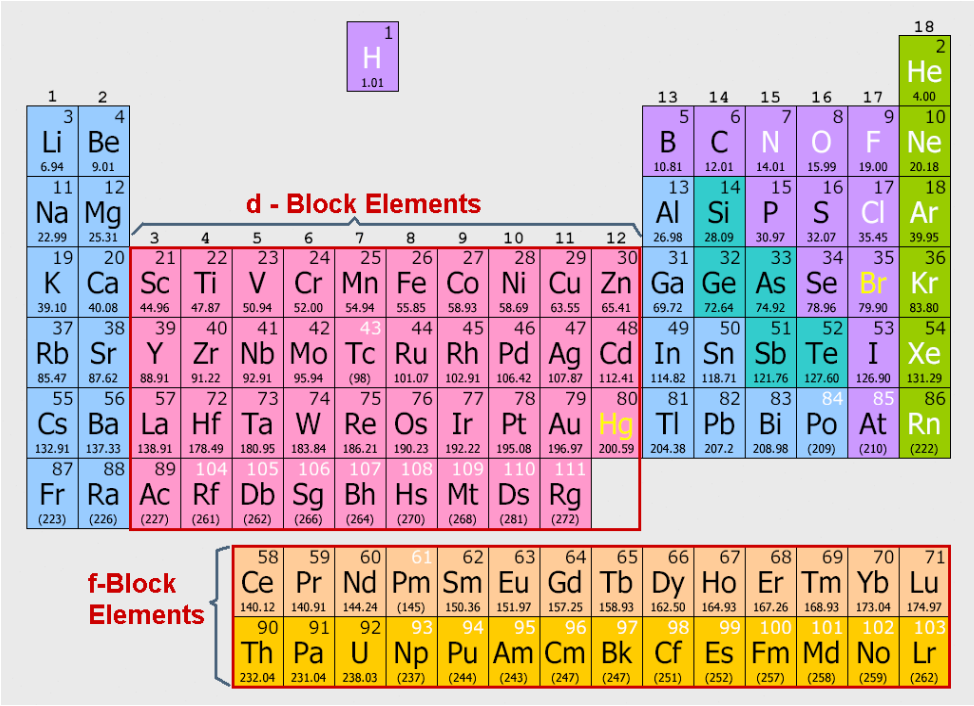
CHAPTER-8 d & f-BLOCK ELEMENTS

SUMMARY



General introduction-

- The TRANSITION ELEMENTS are those elements which have partially filled d-sub shell in their elementary form or in their commonly occurring oxidation states.
- Zn, Cd and Hg not regarded as transition elements because they do not have partially filled d- subshell

ELECTRONIC CONFIGURATION - (n-1) d^{1-10} ns^{1-2}

There are four transition series in d-Block of elements –

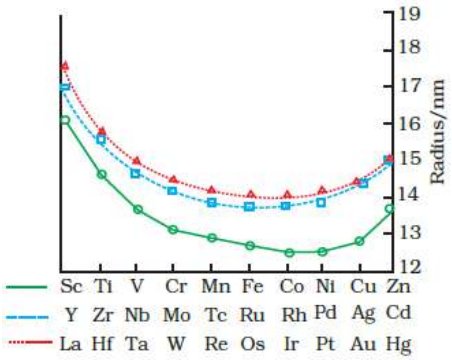
GENERAL CHARACTERISTICS OF d- BLOCK ELEMENTS

- Metals with high tensile strength, ductility, malleability, thermal and electrical conductivity.
- Solids except Mercury with high Melting and Boiling Points.

1. Atomic Radii

- The atomic radii decrease with increase in atomic number.
- In the middle of the series atomic radii become almost constant.
- At the end of the series the atomic radii show a small increase.
- On moving down the atomic radii increase due to increase in number of shells.

- However the atomic radii of second and third transition series are almost same. due to ‘LANTHANOID CONTRACTION’.



2. Metallic Character and Enthalpy of Atomisation

- Metallic character is due to low ionisation energies.
- These are hard metals with high enthalpies of atomisation. This is due to strong bonding due to overlap of unpaired electrons of different atoms.
- Values of enthalpies of atomisation increase with increase in number of unpaired electrons.

3. Densities

- All transition metals have high density due to small size and high atomic mass.
- Densities increase in a series due to increase in atomic mass and decrease in atomic size.

4. Melting and Boiling Points

- In general transition metals have high melting and boiling points. This is due to strong metallic bonds.
- The melting points in a series rise to a maximum value in middle and then decrease. This can be explained on basis of number of unpaired electrons.

5. Ionisation Enthalpies and Electrode Potentials

- IE_1 of d-block elements is higher than s-block elements but lower than p-block elements.
- In a series ionisation enthalpies generally increase from left to right due to increase in nuclear charge.
- The stability of a particular oxidation of an element depends on total value of all of its ionisation enthalpies. Lower is the total of ionisation enthalpies for a particular oxidation state, more is the stability of that oxidation state.
- The stability of a particular oxidation in aqueous solution depends on values of electrode potentials. Higher is the value of oxidation potential of a metal more is stability of its particular oxidation state in aqueous solution.
- The oxidation potential of a metal involves the following process –

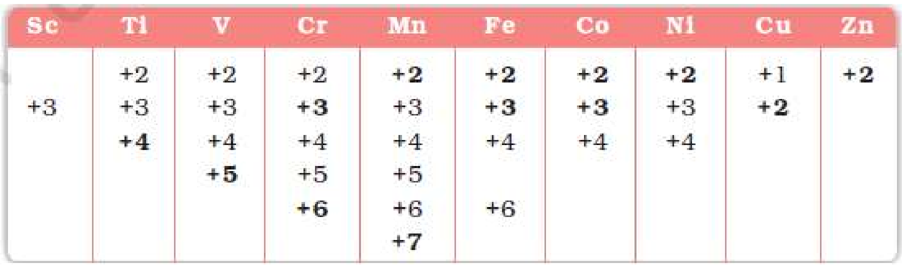
$$M(s) \rightarrow M^{+}(aq) + e^{-}$$

6. Oxidation States

- Most of the transition elements show variable oxidation states.
- The variable oxidation is due to the participation of (n-1)d electrons beside ns electrons. This is due to the fact that ns and (n-1)d electron differ very less in energy and (n-1)d electron can also participate in bond formation beside ns electrons.
- The highest oxidation states are found in their fluorides and oxides

- Except Sc, the most common oxidation state for first transition state is +2.

- The elements with highest oxidation state lies in or near middle of the series.
- For all elements the lowest oxidation state is equal to number of ns electrons while the highest oxidation state is equal to sum of ns and (n-1)d electrons only for first five elements.
- In +2 and +3 oxidation states the bonds are mostly ionic while in higher oxidation states these are essentially covalent.
- Within the group highest oxidation state increase down the group.



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

7. Formation of coloured ions

- Most of the compounds of transition elements are coloured in solid/solution form.
- This can be explained on basis of presence of incomplete (n-1)d sub-shell/presence of unpaired electrons/d-d transition.

8. Magnetic Properties

- Most of the compounds of transition elements are paramagnetic in nature.
- This can be explained on basis of presence of unpaired electrons in (n-1)d sub-shell.
- Higher is the number of unpaired electrons in a substance, the greater is its paramagnetic character.
- $\mu = \sqrt{n(n+2)}$, where n is the number of unpaired electrons and μ is the magnetic
moment in units of Bohr magneton (BM).

9. Formation of Complexes

- Transition elements form a large number of coordination complexes. This tendency of transition elements is due to-
  1. Small size of atoms and ions of transition metals.
  2. High nuclear charge.
  3. Availability of vacant d-orbitals of suitable energy to accept lone pair of electrons from
other groups.

`For example- $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$, $[Zn(OH)_4]^{2-}$

10. Formation of Interstitial Compounds

- Transition elements form large number of interstitial compounds with H, B, C, and N.
- This is because the small atoms of these elements get trapped in vacant spaces of the lattice of the metal.
- Interstitial compounds are generally non-stoichiometric e.g. $TiH_{1.7}$, $VH_{0.56}$, etc.

11. Catalytic Properties

Many transition elements and their compounds act as catalysts in various chemical reactions.The transition elements have ability to form reaction intermediates due to variable oxidation states. The formation of reaction intermediates leads the reaction to a path of lower activation energy increasing the rate.In some cases transition metals provide adsorption surface to reactants and increase their concentrations.

12. Alloy Formation

- Transition metals form a large number of alloys e.g. steel, bronze, brass, etc.
- This is because the transition elements are quite similar in size and their atoms can easily accommodate themselves in each other's lattice.

13. Preparation of Potassium dichromate ($K_2Cr_2O_7$): It is prepared by fusion of chromate ore ($FeCr_2O_4$) with sodium carbonate in excess of air.

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

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

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

- **Effect of pH on chromate and dichromate ions: The chromates and dichromates are inter-convertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.**

  $$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$
  $$Cr_2O_7^{2-} + 2OH^- \rightarrow 2CrO_4^{2-} + H_2O$$

- **Potassium dichromate acts as a strong oxidizing agent in acidic medium:**

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

  Thus, acidified potassium dichromate will oxidise iodides to iodine, sulphides to sulphur, tin(II) to tin(IV) and iron(II) salts to iron(III). The half-reactions are noted below:

  $6\,I^- \rightarrow 3I_2 + 6\,e^-$; $\quad 3\,Sn^{2+} \rightarrow 3Sn^{4+} + 6\,e^-$

  $3\,H_2S \rightarrow 6H^+ + 3S + 6e^-$; $\quad 6\,Fe^{2+} \rightarrow 6Fe^{3+} + 6\,e^-$

14. Preparation of Potassium permanganate ($KMnO_4$):

a) Potassium permanganate is prepared by fusion of MnO4 with alkali metal hydroxide (KOH) in presence of O2 or oxidising agent like KNO_3. It produces dark green K_2MnO_4 which undergoes oxidation as well as reduction in neutral or acidic solution to give permanganate.

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$
$$4H^+ + 3MnO_4^{2-} \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

b) Commercially, it is prepared by the alkaline oxidative fusion of MnO2 followed by the electrolytic oxidation of manganate (VI).

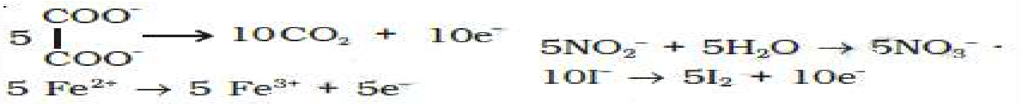
$$\underset{Green}{MnO_4^{2-}} \xrightarrow{electrolytic\ \text{oxidation in alkaline medium}} MnO_4^-(Purple)$$

c) In laboratory, Mn²+ salt can be oxidized by peroxodisulphate ion to permanganate ion.

Potassium permanganate acts as a strong oxidizing agent in acidic medium, neutral or faintly basic medium:

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

Acidified permanganate solution oxidises oxalates to carbon dioxide, iron(II) to iron(III), nitrites to nitrates and iodides to free iodine. The half-reactions of reductants are:



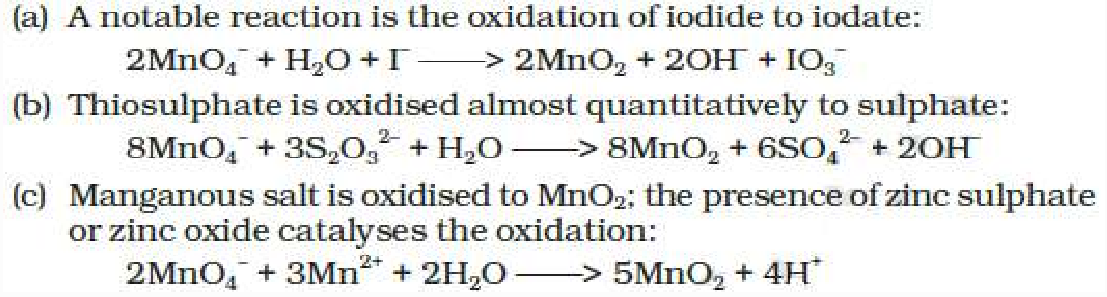
$5\,\begin{matrix}COO^-\\|\\COO^-\end{matrix} \longrightarrow 10CO_2 + 10e^-$

$5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^-$

$5NO_2^- + 5H_2O \rightarrow 5NO_3^-$ -

$10I^- \rightarrow 5I_2 + 10e^-$

In neutral or faintly basic medium: $MnO_4^- + 3e^- + 2H_2O \rightarrow MnO_2 + 4OH^-$



(a) A notable reaction is the oxidation of iodide to iodate:

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(b) Thiosulphate is oxidised almost quantitatively to sulphate:

$$8MnO_4^- + 3S_2O_3^{2-} + H_2O \longrightarrow 8MnO_2 + 6SO_4^{2-} + 2OH^-$$

(c) Manganous salt is oxidised to MnO_2; the presence of zinc sulphate or zinc oxide catalyses the oxidation:

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

15. Properties of the lanthanoids:

- General electronic configuration is [Xe] $4f^{1-14}\,5d^{0-1}\,6s^2$.
- The metals are silvery-white in colour, malleable, ductile, having low tensile strength and are good conductors of heat and electricity.
- They have relatively high density and possess high melting points.
- The lanthanides exhibit a principal oxidation state of + 3. However, some elements also exhibit + 2 (Eu^{2+}) and + 4 (Ce^{4+}) oxidation states.
- Many of the lanthanide ions are coloured due to the electronic transition between different 4 f-levels.
- The majority of the lanthanide ions exhibit paramagnetism due to the presence of unpaired electrons. The lanthanoid ions that do not exhibit paramagnetism are those with either no 4f-electrons, e. g., La^{3+} and Ce^{4+} or with a completed 4f-level, e.g., Yb^{2+} and La^{3+}..
- The lanthanoid compounds are generally predominantly ionic.

lanthanoid contraction

- Steady decrease in the atomic and ionic (Ln^{3+}) radii with the increase in atomic number of the lanthanoid elements is called lanthanoid contraction.

Cause of lanthanoid contraction

- This is because the additional electron goes to 4*f*-subshell which have poor shielding effect.

Consequences of Lanthanoid Contraction

- There is decrease in basic strength of hydroxides from La to Lu.
- Lanthanoid contraction causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series.
- a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

Properties of actinoids:

- General electronic configuration is [Rn] $5f^{1-14}\,6d^{0-1}\,7s^2$.
- The elements are all silvery-white metals.
- The melting points of the actinoids are moderately high.
- The ionic size of the actinoids decreases gradually along the series.
- The actinoids have the ability to exhibit several oxidation states. However, +4 oxidation state is preferred in actinides.

- Some actinoid elements can exist in + 6 oxidation state, e.g., uranium, neptunium and plutonium.
- Many actinoid elements are radioactive. The elements beyond uranium are man-made.
- The actinides have a much greater tendency to form complexes than lanthanides.
- Actinoid contraction is greater from element to element than lanthanoid contraction resulting from poor shielding by 5*f* electrons.

Mischmetall : It is a well-known alloy which consists of a lanthanoid metal $(\sim 95\%)$ and iron $(\sim 5\%)$and traces of S, C, Ca and Al.

QUESTIONS AND ANSWERS

Section A (1 MARK)

1. For a catalyst which condition is not essential?
(a) Variable valency (b) High ionisation energy
(c) Empty orbitals (d) Free valency on the surface

2. Which element is having lowest melting and boiling point?
(a) Ti (b) Cu (c) Zn (d) Mn

3. Density of which of the following element is highest:
(a) Pt (b) Hg (c) Mn (d) Cu

4. The adsorption of hydrogen by platinum black is called:
(a) Hydrogenation (b) Reduction (c) Occlusion (d) Hydration

5. To which of the following series the transition element from Z = 39 to Z = 48 belong:
(a) 3d series (b) 4d series (c) 5d series (d) 6d series

6. Permanent magnets are generally made of alloys of:
(a) Co (b) Zn (c) Mn (d) Pb

7. The reaction of O_2 and CO with haemoglobin gives:
(a) Only oxygen-haeme complex (c) Both but oxygen-haeme-complex is more stable
(b) Only CO-haeme complex (d) Both but CO-haeme-complex is more stable

8. Which of the following statement is not correct:
(a) Fe, Ni, Co form interstetial compound
(b) $CuSO_4 + Ca(OH)_2$ is called Bordeaux mixture
(c) Verdigris is basic copper acetate $[Cu(COOCH_3)_2Cu(OH)_2]$
(d) 24 carat gold is an alloy of Au and Cu

9. Chromium forms most stable compound in the following oxidation state:
(a) Cr (I) (b) Cr(II) (c) Cr (III) (d) Cr (IV)

10. Not more than one oxidation state is shown by:
(a) Mn (b) Cr (c) Fe (d) Sc

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

Section B (Assertion-Reason questions)

ASSERTION & REASON QUESTIONS

These questions contains Assertion and Reason

(a) Assertion is True, Reason is True; Reason is a correct explanation for Assertion
(b) Assertion is True, Reason is True; but Reason is NOT a correct explanation for Assertion
(c) Assertion is True, Reason is False. (d) Assertion is False, Reason is True.

1. **Assertion:** 1st ionisation potential of mercury is greater than cadmium.
Reason: Hg has stable electronic configuration ($5d^{10}$ $6s^2$).

2. **Assertion:** Cu^+ is more stable than Cu^{+2}.
Reason: $\Delta_i H$ is greater than 16 eV

3. **Assertion:** AgI is coloured while AgF is colourless.
Reason: Unpaired electron is present in AgI

4. **Assertion:** Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.
Reason: Change in colour is due to the complexation of alcohol with $K_2Cr_2O_7$.

5. **Assertion:** K_2CrO_4 has yellow colour due to charge transfer.
Reason: CrO_4^{2-} ion is tetrahedral in shape.

Ques	1	2	3	4	5
Ans	B	D	C	C	B

Section- C (2 Marks questions)

1. Why Sm^{2+}, Eu^{2+}, and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidizing agent?

(Hint: The most stable oxidation state of lanthanoids is +3. Hence +2 oxidation state tend to change +3 state by loss of electron whereas those in +4 oxidation state tend to change to +3 oxidation state by gain of electron.)

2. E^o of Cu is + 0.34V while that of Zn is – 0.76V. Explain.

(Hint: High ionisation enthalpy to transform Cu(s) to Cu^{2+} (aq) is not balanced by its hydration enthalpy. However, in case of Zn after removal of electrons from 4s-orbital, stable $3d^{10}$ configuration is acquired.)

3. On what ground can you say that scandium (Z = 21) is a transition element but zinc (Z = 30) is not?

(Hint. Scandium (Z = 21), atom has incompletely filled d-orbitals ($3d^1$) in its ground state, On the other hand zinc (Z = 30) atom has completely filled d-orbitals ($3d^{10}$) in its ground state as well as most common oxidation state of +2.)

4. Which element of first transition series is a strong oxidising agent in +3 oxidation state and why?

(Hint: Mn, because change of Mn^{3+} to Mn^{2+} give stable half filled (d^5) electronic Configuration).

5. Most of the transition metal ions exhibit characteristic colours in aqueous solutions. Explain

(Hint: d-d transition/presence of unpaired electrons)

Section - D (3 Marks questions)

1. Give reasons for the following features of transition metal chemistry.
   (a) There is a general increase in density from titanium (Z = 22) to copper (Z = 29)
   (b) Transition metals are well known to form complex compounds
   (c) The second and third members in each group of the transition elements have very similar atomic radii

(Hint: (a) Atomic volume decreases but at the same time, atomic mass increases.
(b) Small size and high charge on cation and presence of vacant d-orbitals.
(c) Due to lanthanoid contraction.)

2. Demonstrate your understanding of the lanthanoid contraction by explaining it, analyzing the causes behind it, and evaluating its impact on the chemical properties of elements that follow the lanthanoids in the periodic table.

(Hint: Steady decrease is the size of lanthanoids with increase in atomic number across the period is known as Lanthanoid contraction. It is because the electrons of 4f orbitals offer imperfect/poor shielding effect in the same sub-shell.
Consequence: 1) Due to this 5d series elements have nearly same radii as that of 4d series.
2) Basic Strength decreases from $La(OH)_3$ to $Lu(OH)_3$.
3) Lanthanoid contraction makes separation of lanthanoids possible.)

3. Assign reasons for the following:
(i) The enthalpies of atomisation of transition elements are high.
(ii) The transition metals and many of their compounds act as good catalysts.
(iii) Scandium (Z= 21) does not exhibit variable oxidation states and yet it is regarded as a transition element.

(Hint: (i) strong metallic bonds due to large number of unpaired electrons.
(ii) Because of their variable oxidation states suitable larger surface area.
(iii) Partially filled *d* orbitals in the ground state ($3d^1\ 4s^2$) of scandium .)

4. Explain why Cu^+ ion is not stable in aqueous solutions? Give another example of a disproportionation reaction in aqueous solution.

Hint: Cu^+ ion undergoes disproportionation.

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

$$3\ Mn^{VI}O_4^{2-} + 4H+ \rightarrow 2\ Mn^{VII}O_4^{-} + Mn^{IV}O_2 + 2H_2O$$ (or any other)

5. Compare the chemistry of the actinoids with that of lanthanoids with reference to:
(i) Electronic configuration (ii) Oxidation states and (iii) Chemical reactivity.

Ans. (i) For lanthanoids is $[Xe]^{54}\ 4f^{0-14}\ 5d^{0-1}\ 6s^2$ and that for actinoids is $[Rn]^{86}\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$.

(ii) The principal oxidation state of lanthanoids is (+3). However, some also exhibit oxidation states of + 2 and + 4. Actinoids exhibit a greater range of oxidation states. Again, (+3) is the principal oxidation state for actinoids.

(Hint: In the lanthanoid series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided.)

Section - D (Case Based questions)

1. Read the passage given below and answer the following questions:

The lanthanoids, also known as rare earth elements, are a series of elements in the f-block of the periodic table, from atomic number 58 (Cerium) to 71 (Lutetium). These elements are characterized by the filling of 4f orbitals. Lanthanoids exhibit similar chemical properties due to their similar electronic configurations and are known for their high melting points and ability to form colored compounds. The lanthanoid contraction, caused by the poor shielding effect of 4f electrons, results in a gradual decrease in atomic and ionic radii across the series. These elements are widely used in industries, such as in the production of alloys, catalysts, and phosphors for electronic displays.

(i) Why do lanthanoids show similar chemical properties? (1 Mark)

(ii) How does the poor shielding of the 4f electrons effect Lanthanoids? (1 Mark)

(iii) Explain how lanthanoid contraction affects the atomic radii of the third transition series compared to the second transition series. (2 Marks)

(Hint: (i) Their similar outer electronic configurations and lanthanoid contraction results in minimal differences in the size of the lanthanoid ions.

(i) Lanthanoid contraction.

(ii) Similar atomic radii of both transition series.)

2. Read the passage given below and answer the following questions:

The d-block elements exhibit unique magnetic properties due to the presence of unpaired electrons in their d-orbitals. For instance, iron (Fe, [Ar] $3d^6$ $4s^2$) can form compounds like $FeSO_4$, where Fe^{2+} has a $3d^6$ configuration. The magnetic behavior of such compounds depends on whether the electrons are paired or unpaired. Paramagnetic substances are attracted to magnetic fields due to unpaired electrons, while diamagnetic substances, with all electrons paired, are weakly repelled. The magnetic moment is calculated using the formula $\sqrt{[n(n+2)]}$ BM, where n is the number of unpaired electrons.

(i) Write the electronic configuration of Fe^{2+} ion? (1 Mark)

(ii) What is meant by paramagnetic behaviour? (1 Mark)

(iii) Calculate the spin-only magnetic moment of Fe^{2+} ion and explain whether it is paramagnetic or diamagnetic. (2 Marks)

(Hint: (i) The electronic configuration of Fe^{2+} ion is [Ar] $3d^6$.

(ii) Paramagnetic behaviour refers to the property of a substance to be attracted to an external magnetic field due to the presence of unpaired electrons in its orbitals.

(iii) For Fe^{2+} ([Ar] $3d^6$), use n=4 in the formula , $\mu=\sqrt{[n(n+2)]}$ BM)

Section - E (5 Marks questions)

1. (a) When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallised from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.

(b) Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with: (i) Iodide and (ii) H_2S

Hint: (a) A = $FeCr_2O_4$, B = Na_2CrO_4, C = $Na_2Cr_2O_7.2H_2O$, D = $K_2Cr_2O_7$

(b) (i) $Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

(ii) $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O$

2. When an oxide of manganese (A) is fused with KOH in the presence of an oxidising agent and dissolved in water, it gives a dark green solution of compound (B). Compound (B) disproportionates in neutral or acidic solution to give purple compound (C). An alkaline solution of compound (C) oxidises potassium iodide solution to a compound (D) and compound (A) is also formed. Identify compounds A to D and also explain the reactions involved. (Hint: A = MnO_2 (B) K_2MnO_4 (C) $KMnO_4$ (D) KIO_3

Chapter 5: CO-ORDINATION COMPOUNDS

Summary –

- **Coordination Compounds**

  Compounds in which a central metal atom or ion is linked to a number of non metal ions or neutral molecules by coordinate bonds

- **Type of addition compounds-**

1. Double Salt	2.Complex compound
Dissociate into simple ions completely when dissolved in water.	Do not dissociate into simple ions in water
e.g. Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ Potash Alum $K_2SO_4Al_2SO_4.24H_2O$	e.g. $K_4[Fe(CN)_6]$.Complex ion $[Fe(CN)_6]^{4-}$ does not dissociate into Fe^{2+} and CN^- ions.

- **IMPORTANT TERMINOLOGY OF COMPLEX COMPOUND.**

(i) Coordination entity: It constitutes the central metal ion or atom bonded to a fixed number of ions or molecules represented within a square bracket.

(ii) Central atom/ion: 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.

iii) **Ligands**: Ligands are the neutral or negative ions donate lone pairs to the central metal ion via coordinate bonds, acting as Lewis bases. Its may be classified as-

Monodentate/ Unidentate:	Ligands which Contain only one donar atom Ex-Cl^- ;H_2O; NH_3 ; NO_2^-.
Didentate	Ligands which Contain two donor atoms. Ex-$C_2O_4^{2-}$(ox); $NH_2CH_2CH_2NH_2$(en)
Polydentate	which Contain two or more donor atoms present in a single ligand. Ex-$(EDTA)^{4-}$
Chelating ligands	Di-or polydentate ligands that uses two or more donor atoms to bind to a single metal ion to form ring-like complexes.(Ox); (edta)
Ambidentate ligand	A ligand that can ligate through two different atoms, one at a time. Ex-NO_2^-; SCN^- ,CN^-

Coordination number: The no.of ligand donor atoms to which the metal is directly bonded through coordinate bond. It determine the geometry of coordination complex.

Counter ions: The ionisable groups written outside the square bracket. Ex- K^+ in $K_4[Fe(CN)_6]$ OR 3 Cl^- in $[Co(NH_3)_6]Cl_3$

Coordination Polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central metal atom/ion. They are commonly Octahedral, Square-planar or Tetrahedral.

Oxidation number: The charge that the central atom would carry if all the ligands are removed along with their pairs of electrons shared with the central atom.

Homoleptic complexes: Complexes in which only one kind of Ligand . Ex-$[Co(NH_3)_6]^{3+}$

Heteroleptic complexes: Complexes in which more than one kind of Ligand Ex-$[Co(NH_3)_4 Cl_2]^+$

- **Key Points of Werner's theory of coordination theory-**

  Developed by Alfred Werner in 1893.in coordination compounds metals show two types of valencies-Primary and Secondary.

  IUPAC NOMENCLATURE- The following rules are used when naming complex.

(i) The cation is named first in both positively and negatively charged Complex.

(ii) The ligands are named in an alphabetical order before the name of the central metal.

(iii) Names of the anionic ligands end in –o.

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of the individual ligands in the coordination entity. When the names of the ligands include a numerical prefix, then the terms, *bis*, *tris*, *tetrakis* are used.

(v) Oxidation state of the metal in cation, anion or neutral coordination entity is indicated by Roman numeral in parenthesis.

(vi) If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix – ate. For example, Co in a complex anion, $\{Co(SCN)_4\}^{-2}$ is called cobaltate.

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**
- Two or more substances having the same molecular formula but different spatial arrangements are called isomers and the phenomenon is called isomerism.
- Coordination compounds show two main types of isomerism-

A) Structural Isomerism B) Stereoisomerism

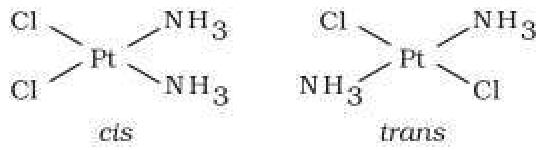
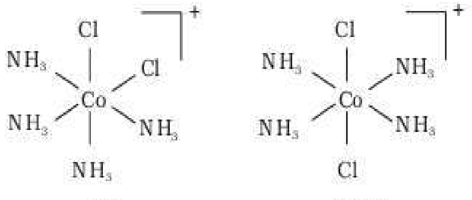
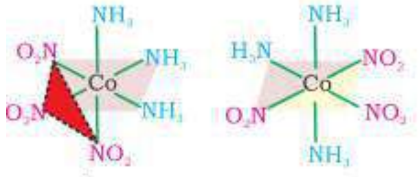
A) Summary of Structural Isomerism:

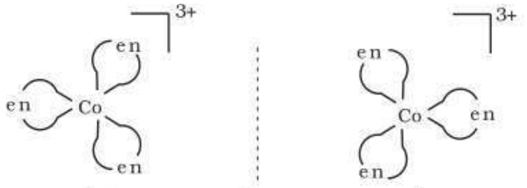
Sr.No.	Type	Description
1	Ionisation Isomerism	Exchange of counter-ions between the coordination sphere and ionizing sphere. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
2	Linkage Isomerism	Ligand binds through different atoms (e.g., NO_2 binds through nitrogen or oxygen). $[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$
3	Coordination Isomerism	Distribution of ligands between two metal centers differs. [Co(NH3)6][Cr(CN)6] and [Cr(NH3)6][Co(CN)6]
4	Solvation 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 $[Cr(H_2O)_5Cl]Cl_2.H_2O$

B) Summary of Stereo Isomerism: Stereoisomers have the same chemical formula and chemical bonds but theyhave different spatial arrangement.They are of two kinds

A. Geometrical isomerism B.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*
	$[Ma_3b_3]$ $[Co(NH_3)_3(NO_2)_3]$	 *fac–* *mer–*

Optical Isomerism: Optical isomers are mirror images that cannot be superimposed on one another and are called as enantiomers.
Optical isomers of $[Co(en)_3]^{+3}$  *dextro* mirror *laevo*

Bonding in Coordination Compounds (Valence Bond Theory) : Key Points of VBT

1. The central metal atom/ion provides empty hybrid orbitals (equilivalent energy orbitals) to accept lone pairs from ligands, forming coordinate bonds.

2. **Hybridization and Geometry of the complex-**

Coordination number	Type of hybridisation	Acquired geometry
4	**sp^3**	Tetrahedral
4	**dsp^2**	Square planar
6	**sp^3d^2**	Octahedral
6	**d^2sp^3**	Octahedral

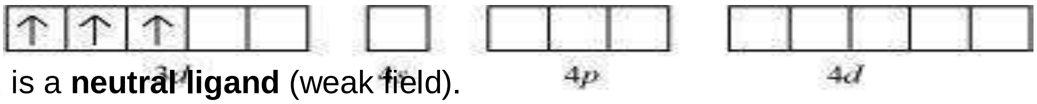
3. **Magnetic Behavior**: VBT to explain paramagnetic (unpaired electrons) or diamagnetic (all paired electrons) nature.

4. **Spectro chemical series:** The arrangement of common ligands in the increasing order of their crystal-field splitting energy (CFSE) values.

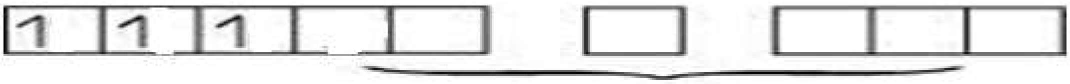
$I^- < Br^- <$ S2− $< SCN^- <$ Cl-⁻ $<$ N3- $< F^- < OH^- < C_2O_4^{2-} \sim H_2O < NCS^- \sim H^- < CN^- < NH_3 <$ en $\sim SO_3^{2-} < NO_2 <$phen$<$ CO

Examples: **1. $[Cr(NH_3)_6]^{3+}$**

Atomic no. of Cr = 24 → Cr^{3+} = 21 electrons → $3d^3$



NH_3 is a **neutral ligand** (weak field).



Hybridization: **d²sp³** ; Geometry: **Octahedral;** Magnetic: **Paramagnetic** (due to 3 unpaired electrons)

Some more example:-

Sr.No.	**Complex**	**Oxidation State**	**Type of Ligand**	**Hybridization**	**Geometry**	**Magnetic Nature**
1	$[Cr(NH_3)_6]^{3+}$	+3	Weak	d^2sp^3	Octahedral	Paramagnetic
2	$[Ni(CN)_4]^{2-}$	+2	Strong	dsp^2	Square planar	Diamagnetic
3	$[Fe(CN)_6]^{4-}$	+2	Strong	d^2sp^3	Octahedral	Diamagnetic
4	$[FeF_6]^{3-}$	+3	Weak	sp^3d^2	Octahedral	Paramagnetic

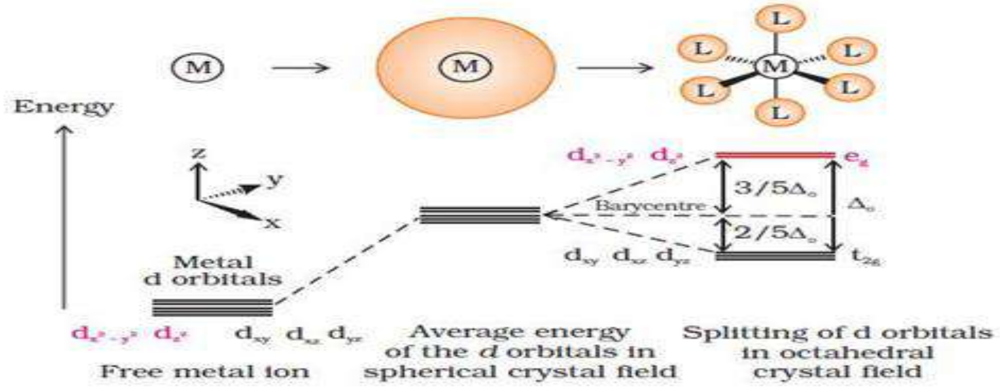
Crystal Field Theory - Key Points of CFT

1. Electrostatic Model: CFT treats ligands as point charges (or dipoles in the case of neutral ligands like NH_3 or H_2O). The interaction between these ligands and the metal's *d*-orbitals causes splitting of energy levels.

2. Degeneracy of *d*-orbitals is Lifted: In a free metal ion, the five *d*-orbitals are degenerate (have the same energy). In a complex, due to the ligand field, these orbitals split into groups with different energies.

3. Geometry-Dependent Splitting:

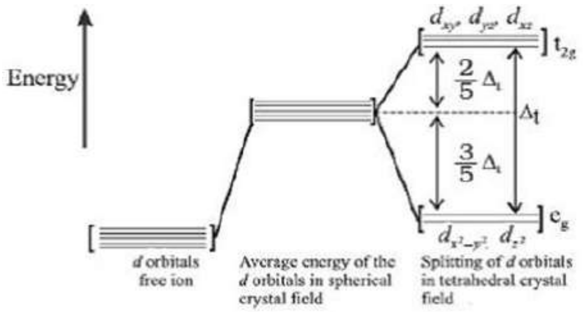
4. Octahedral field (common for 6 ligands): The *d*-orbitals split into two sets:
Lower energy: t_2g → (d_{xy}, d_{xz}, d_{yz}), Higher energy: eg→ $(d_{z2}, dx^2{-}y^2)$,
Energy difference = **Δ_0 (octahedral splitting energy)**



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

Weak field ligands	Strong field ligands
Δo < P	Δo > P
Form high spin complexes	Form low spin complexes

5. Tetrahedral field (4 ligands): Lower energy: eg→ $(dz^2, dx^2{-}y^2)$, Higher energy: t_2g → (dxy,dxz,dyz), Energy difference = **Δt (Tetrahedral splitting energy)**



Why Coordination Compounds are Colored-

1. d–d Transitions: In transition metal complexes, the d-orbitals split in the presence of ligands (crystal field splitting). Electrons can be excited from a lower-energy d orbital to a higher one using visible light.

2. Charge Transfer Transitions:Electrons are transferred between the metal and ligands. These transitions also absorb light in the visible region, producing color.

3. Ligand Field Effect: Different ligands cause varying d-orbital splitting (Δ). Strong-field ligands like CN^- cause more splitting than weak ones like H_2O, affecting the colour of complexes. For example, $[Ti(H_2O)_6]^{3+}$ is violet because Ti^{3+} ($3d^1$) absorbs blue-green light, promoting the electron from t_2g to e_g level($t_2g^1eg^0 \rightarrow t_2g^0\ eg^1$). Without ligands, no crystal field splitting occurs, so the substance remains colourless.

Note: (i) For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour.

(ii) Zn^{2+}, Cd^{2+}, Sc^{3+}, etc.: These are **colorless** in solution because they have **no d–d transitions** (either d^0 or d^{10} configuration).

BONDING IN METAL CARBONYLS: *In metal carbonyls, the M–C bond has both σ and π character. The σ bond forms by donation of a lone pair from CO to the metal vacant d orbital, and the π bond forms by back-donation from the metal's d-orbital to the CO* π^* antibonding orbital. This two-way interaction creates a synergic effect, strengthening the M–CO bond.

QUESTION BANK

SECTION –A (1 MARK EACH)

1. One mole of the complex compound $Co(NH_3)_5Cl_3$, gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl (s). The structure of the complex is

(a) $[Co(NH_3)_3Cl_3]. 2NH_3$ (b) $[Co(NH_3)_4Cl_2]\ Cl . NH_3$

(c) $[Co(NH_3)_4Cl]\ Cl_2. NH_3$ (d) $[Co(NH_3)_5Cl]\ Cl_2$

2. In the coordination compound, K4[Ni(CN)4], the oxidation state of nickel is

(a) 0 (b) +1 (c) +2 (d) –1

3. $[EDTA]^{4-}$ is a :

(a) monodentate ligand (b) bidentate ligand

(c) quadridentate ligand (d) hexadentate ligand

4. Which one of the following is not a ligand ?

(a) PH_3 (b) NO^+ (c) Na^+ (d) F^-

5. Some salts although containing two different metallic elements give test for only one of them in solution. Such salts are

(a) complex (b) double salts (c) normal salts (d) None of these

6. Choose the correct statement.

(a) Coordination number has nothing to do with the number of groups or molecules attached to the central atom

(b) Coordination number is the number of coordinate bonds formed between the central metal atom and its ligands.

(c) Werner’s coordination theory postulates only one type of valency

(d) All the above are correct

7. As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is :

(a) Tetraaquadiaminecobalt (III) chloride (b) Tetraaquadiamminecobalt (III) chloride

(c) Diaminetetraaquacoblat (II) chloride (d) Diamminetetraaquacobalt (III) chloride

8.Which of the following will give maximum number of isomers?

(a) $[Ni(C_2O_4)(en)_2]^{2-}$ (b) $[Ni(en)(NH_3)_4]^{2+}$ (c) $[Cr(SCN)_2(NH_3)_4]^{+}$ (d) $[Co(NH_3)_4Cl_2]^{+}$

9.Which of the following statements is correct ? (Atomic number of Ni = 28)

(a) $Ni(CO)_4$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic

(b) $Ni(CO)_4$and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic

(c) $Ni(CO)_4$and $[NiCl_4]^{2-}$are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic

(d) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic

10.$[Sc(H_2O)_6]^{3+}$ ion is :

(a) colourless and diamagnetic (b) coloured and octahedral

(c) colourless and paramagnetic (d) coloured and paramagnetic

ASSERTION- REASON TYPE QUESTIONS (1 MARK EACH)

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

a) Both A and R are true and R is correct explanation of A.

b) Both A and R are true but R is not correct explanation of A.

c) A is true but R is false. d) A is False but R is true.

11. Assertion(A): NF_3 is a weaker ligand than $N(CH_3)_3$.

Reason (R): NF_3 ionizes to give F^- ions in aqueous solution.

12. Assertion(A): $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

Reason(R) : $[Fe(CN)_6]^{3-}$ has +3 oxidation state while $[Fe(CN)_6]^{4-}$ has +2 oxidation state.

13. Assertion (A): $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

Reason (R): *d-d* transition is not possible in $[Sc(H_2O)_6]^{3+}$.

14.Assertion (A): Optical isomerism is not shown by square planar complexes .

Reason (R): Square planar complexes do not possess chiral structures.

15.Assertion(A): The coordination number of Pt in $[Pt(NH_3)_2Cl_2]$ is 4.

Reason (R): Pt can form only two bonds in this complex.

ANSWERS KEY :

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	d	a	d	c	a	b	d	c	c	A	c	b	a	a	C

SECTION –B (TWO MARKS EACH)

1. A cationic complex has two isomers A & B. Each has one Co^{3+}, five NH_3, one Br and one SO_4^{2-}. A gives a white precipitate with $BaCl_2$ solution while B gives a yellow precipitate with $AgNO_3$ solution.

(a) What are the possible structures of the complexes A and B ?

(b) Will the two complexes have same colour ?

(HINT: (a) $[Co(NH_3)_5\ Br]\ SO_4$ and $[CO\ (NH_3)_5\ SO_4]$; (b) No

2. A, B and C are three complexes of Chromioum with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have Cl and H_2O molecules as the ligands. Complex A does not react with conc. H_2SO_4. Complexes B and C lose 6.75% and 13.5% of their original weight respectively on heating with conc. H_2SO_4. Identify A, B and C

(HINT- Data suggests that the complexes are hydrate isomers. As complex A does not lose any molecule of H_2O on heating which shows that no water molecule of H_2O is outside the co-ordination sphere. A = $[Cr\ (H_2O]_6]Cl_3$. As B loses 6.75% actual loss in wt. = × 266.5 = 18 amu, B = $[Cr\ (H_2O)_5\ Cl]\ Cl_2\ .\ H_2O$ As C loses 13.5% of wt. on heating which is twice the loss in the first case. C isomer exists as a dihydrate :
$[Cr\ (H_2O)_4\ Cl_2]\ Cl\ .\ 2\ H_2O$.)

3. How t_{2g} and e_g orbitals are formed in an octahedral complex?

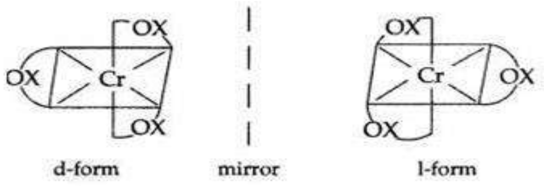
(HINT-In an octahedral complex, the metal ion is at the center and ligands at the corners. The $d_{x^2-y^2}$ and d_{z^2} orbitals point along the axes (toward ligands), causing greater repulsion and higher energy. The other d orbitals lie between the axes, facing less repulsion and have lower energy.)

4. A solution of $[Ni\ (H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

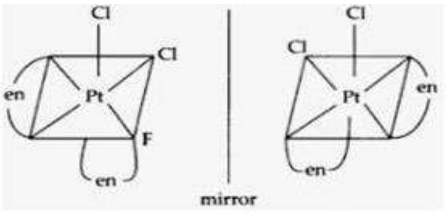
HINT- -In $[Ni(H_2O)_6]^{2+,}$ $H_2\ddot{O}$ is a weak field ligand. Therefore, there are unpaired electrons in $Ni^{2+.}$In this complex, the d electrons from the lower energy level can be excited to the higher energy level i.e., the possibility of d−d transition is present. Hence, $Ni(H_2O)_6]^{2+}$is coloured. In $[Ni(CN)_4]^{2-,}$ the electrons are all paired as CN- is a strong field ligand. Therefore, d-d transition is not possible in$[Ni(CN)_4]^{2-.}$ Hence, it is colourless. As there are no unpaired electrons, it is diamagnetic.

5. Draw the structures of optical isomers of each of the following complex ions:
$[Cr(C_2O_4)_3]^{3-,}$ $[PtCl_2(en)_2]^{2+}$

HINT-



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



Optical isomers of $[PtCl_2(en)_2]^{2+}$

SECTION - C (3 MARKS EACH)

1. A student prepared three co-ordination complexes containing chromium having the following characteristics:

Sr. No.	Formula	colour	Cl- ions present in solution per formula unit
(A)	$CrCl_3.6H_2O$	violet	3
(B)	$CrCl_3.6H_2O$	Light green	2
(C)	$CrCl_3.6H_2O$	Dark green	1

(a) Write the structures of the three complexes.

(b) Give IUPAC name of the complex

HINT- According to Werner's Coordination theory.

2. On the basis of valence bond theory explain geometry, nature of hybridisation, magnetic property & optical isomerism of $[Co(OX)_3]^{3-}$ and $[CoF_6\}^{3-}$

HINT- According to Valance bond theory.

3. Calculate the magnetic moment of the following complexes;

(i) $[Cr(NH_3)_6]^{3+}$ (ii) $[CoF_6]^{3-}$ (iii) $[Fe(CN)_6]^{3-}$

HINT- Use formula **$\mu=\sqrt{n(n+2)}$ BM**

4. What will be the correct order for the wavelengths of absorption in the Visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

HINT-: Stronger field → larger Δo → absorbs higher energy (shorter wavelength)
Weaker field → smaller Δo → absorbs lower energy (longer wavelength)
ligand strength increases roughly in this order: $H_2O<NH_3<NO_2^-$
Hence, order of the wave length of absorption is as follows

$$[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Ni(NO_2)_6]^{4-}$$

5. (a) On the basis of crystal field theory, write the electronic configuration of d^6 in terms of t_2g and eg in an octahedral field when $\Delta_0 < P$.and $\Delta_0 > P$

b. Low spin configuration are rarely observed in tetrahedral coordination entity formation. Explain.

HINT-1.a)

Weak field ligands	Strong field ligands
$\Delta o < P$	$\Delta o > P$
t_2g^4,eg^2	t_2g^6,eg^0

b). The orbital splitting energies, $\mathbf{\Delta_t}$ are not sufficiently large for forcing pairing of electrons in the tetrahedral coordination entity formation.

SECTION –D Case Study Based question (Four marks)

1.Read the passage carefully and answer the questions that follows.

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

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

HINT- (i) 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) $[Cr(H_2O)_6]Cl_3$

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

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 (Δo) 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 Δo 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)

HINT: (i) Magnetic moment= $\sqrt{n\times(n+2)}$; Answer: $\mu=\sqrt{24}$ BM

(ii) As per the summary (iii) As per the summary

OR

(iii) a) Paramagnetic. b) Diamagnetic

SECTION -E (5 MARKS):

1**.** Explain Crystal Field Theory (CFT) in detail. Discuss the crystal field splitting in octahedral and tetrahedral complexes. How does CFT explain the magnetic properties and color of coordination compounds? Support your answer with suitable examples.

HINT: As per the summary

2.A) (i) Write the IUPAC name of the following complexes:

(a) $[Cr(H_2O)_6]Cl_3$ (b) $[Pt(NH_3)_2Cl_4]$ (c) $[Fe(CN)_6]^{3-}$

(ii) Give the formula for the following complexes:

(a) Tetraamminecopper(II) sulphate (b) Potassium trioxalatochromate(III)

(c) Hexaamminecobalt(III) chloride

B).Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:

(i) $[Fe(CN)_6]^{4-}$ (ii) $[FeF_6]^{3-}$

HINT-A) (i) (a) Hexaaquachromium (III) chloride. (b) Diamminetetra-chloroplatinum (II) (c) Hexacyanoferrate(II) ion

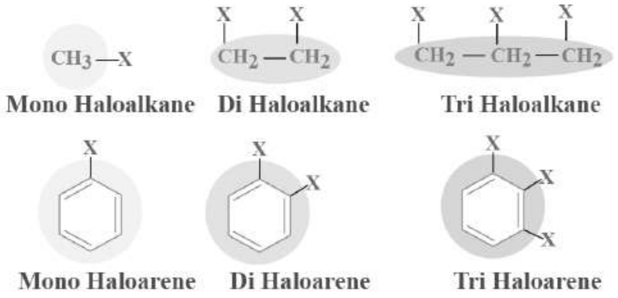
ii) (a) $[Cu(NH_3)_4]SO_4$ (b) $K_3[Cr(C_2O_4)_3]$ (c)$[Co(NH_3)_6]Cl_3$

B) (i). $[Fe(CN)_6]^{4-}$ CN^- is a strong field ligand, hence pairing of 3d orbital takes place ; d^2sp^3

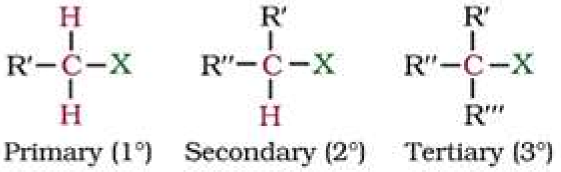
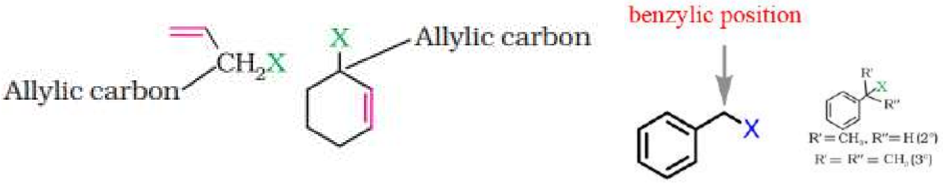
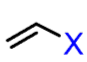
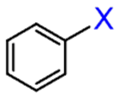
(ii) $[FeF_6]^{3-}$, F^- is a weak field ligand hence pairing doesn't occur; Answer: sp^3d^2

HALOALKANES AND HALOARENES
SUMMARY

- When one or more hydrogen atoms in a hydrocarbon—either aliphatic or aromatic—are replaced by halogen atoms, the resulting compounds are known as alkyl halides (haloalkanes) and aryl halides (haloarenes), respectively.
- **CLASSIFICATION OF HALOALKANE AND HALOARENE**
- Based on the number of Halogen Atoms



- Based on the type of carbon atom to which the halogen is attached

Halogen attached to sp^3 carbon	 Primary (1°) Secondary (2°) Tertiary (3°)
	
Halogen attached to sp^2 carbon	 vinyl halide  aryl halide

- **Nature of C-X bond**: Carbon-halogen bond of alkyl halide is polar in nature because chlorine is more electronegative in nature. The carbon atom has a partial positive charge and halogen atom has a partial negative charge.

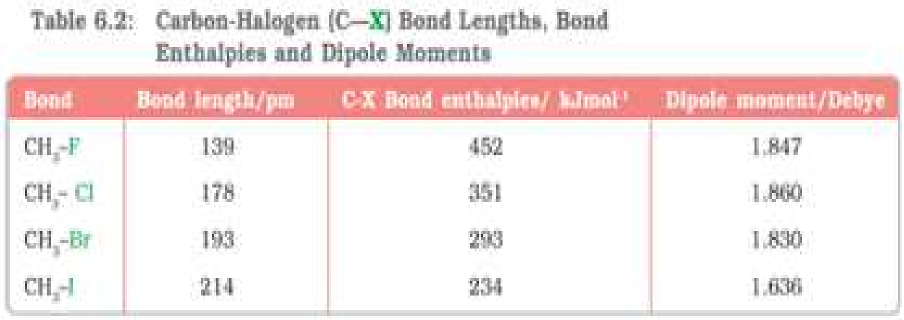


Table 6.2: Carbon-Halogen (C—X) Bond Lengths, Bond Enthalpies and Dipole Moments

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol^{-1}	Dipole moment/Debye
CH$_3$-F	139	452	1.847
CH$_3$- Cl	178	351	1.860
CH$_3$-Br	193	293	1.830
CH$_3$-I	214	234	1.636

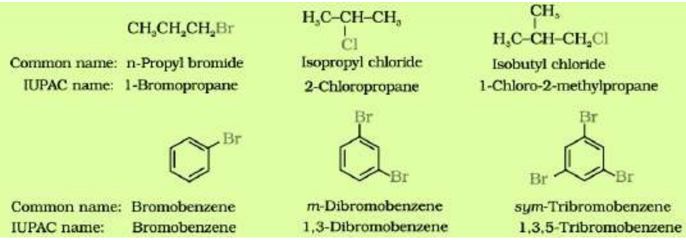
important Trends

Bond Polarity

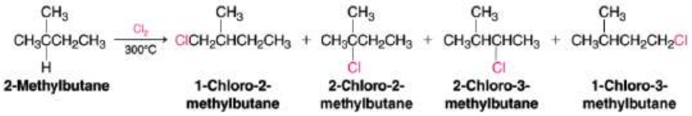
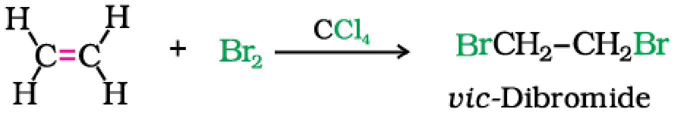
➢ Nomenclature:

Rules

(I) Identify the longest carbon chain and number it to get the lowest set of locants
(II) Follow alphabetical order for substituents (halogens and alkyl groups)
(III) Use prefixes like di-, tri- as needed.
(IV) Halogen is indicated as a prefix (fluoro-, chloro-, bromo-, iodo-) to the name of the parent

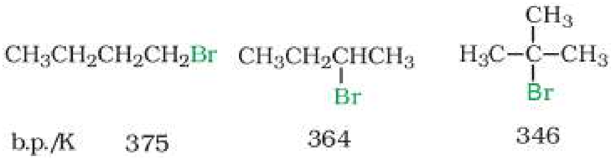


➢ Methods of Preparation for Haloalkane:

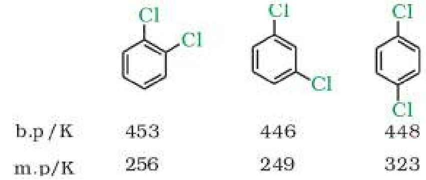
1. From Alcohol	$R{-}OH + HCl \xrightarrow{ZnCl_2} R{-}Cl + H_2O$ $R{-}OH + NaBr + H_2SO_4 \longrightarrow R{-}Br + NaHSO_4 + H_2O$ $3R{-}OH + PX_3 \longrightarrow 3R{-}X + H_3PO_3 \quad (X = Cl, Br)$ $R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$ $R{-}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R{-}X$ $R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$	Important Point: (i) Thionyl chloride($SOCl_2$) is preferred because the other two side products are escapable gases. Hence the reaction gives pure alkyl halides. (ii) The order of reactivity of alcohols with a given haloacid(HCl) is 3°>2°>1°.
2. From Hydrocarbons	$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$ 	(i) Reaction follows free radical substitution reaction. (ii) if a molecule has different types of carbon atoms (primary, secondary, tertiary), different products will be formed.
	$CH_3CH = CH_2 + H{-}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$	(i) Alkene reacts with hydrogen halide (ii) Major and minor product is given by Markovnikov's rule.
		In this reaction, brown color of bromine water disappears, indicating the presence of unsaturation (C=C or C≡C).
3. Halogen Exchange	$R{-}X + NaI \xrightarrow{\text{dry acetone}} R{-}I + NaX$ $X=Cl, Br$	(i) Name reaction: Finkelstein Reaction (ii) NaCl or NaBr formed as side product is precipitated in dry acetone and facilitates the forward reaction.
	$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$ Other metallic halide AgF, Hg_2F_2, CoF_2 or SbF_3	(i) Name reaction: Swarts Reaction

➢ **Physical Properties**

- Haloalkanes have higher boiling points than alkanes due to stronger intermolecular forces of attraction, including dipole-dipole and dispersion forces.
- For the same alkyl group, boiling points of alkyl halides decrease as RI > RBr > RCl > RF due to stronger van der Waals forces with heavier halogens.
- The boiling points of isomeric haloalkanes decrease with increase in branching. Example is given below:



- Melting and boiling point order for dihalobenzene is given below:

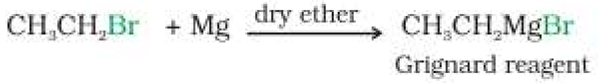
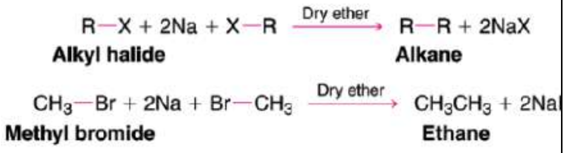


Note: Para-isomers have higher melting points than ortho- and meta-isomers due to their symmetrical structure, allowing better crystal lattice packing.

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

➢ **CHEMICAL PROPERTIES**

1. Reaction with Metal:

(a) Haloalkanes react with magnesium in dry ether to form RMgX, a compound known as a Grignard reagent. The reaction is given below:  $CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$ Note: Traces of moisture must be avoided as Grignard reagents are highly reactive due to their nucleophilic nature and react with proton sources like water, alcohols, or amines to form hydrocarbons. Hence, the reaction is carried out in <u>dry</u> ether.  $R{-}MgCl + H{-}\ddot{O}{-}H \longrightarrow R{-}H + Mg(OH)Cl$	(b) Wurtz reaction: This reaction produces symmetrical alkanes with twice the number of carbon atoms as in the original alkyl halide. The reaction is given below:  $\underset{\text{Alkyl halide}}{R{-}X} + 2Na + X{-}R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R{-}R} + 2NaX$ $\underset{\text{Methyl bromide}}{CH_3{-}Br} + 2Na + Br{-}CH_3 \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3CH_3} + 2NaI$

2. Nucleophilic substitution reaction:

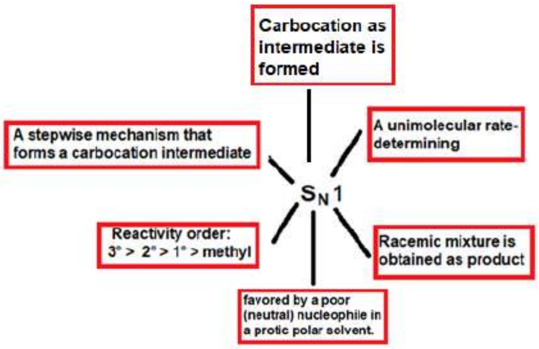
- General definition: The reaction in which a strong nucleophile replaces the already existing weak nucleophile in a molecule is called nucleophilic substitution reaction.

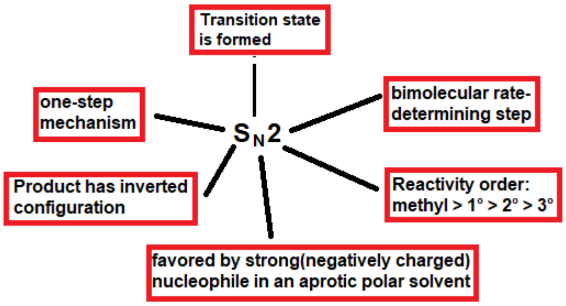

$RCH_2CH_2X + Y^- \xrightarrow[\text{a substitution reaction}]{} RCH_2CH_2Y + X^-$

- Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. The example is given below:

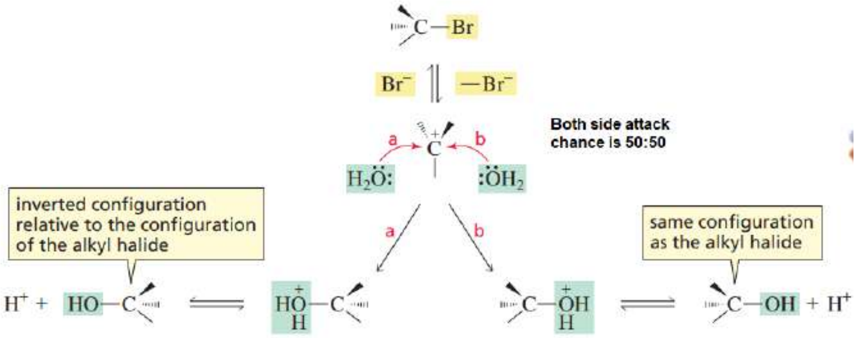
  R-X + AgCN → R-NC ; R-X + KCN → R-CN

- **Substitution nucleophilic unimolecular (S_N1) and Substitution nucleophilic bimolecular (S_N2)**

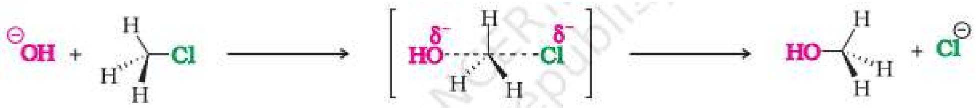




- **Mechanism:**



= S_N1



= S_N2

Note: (i) Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles.

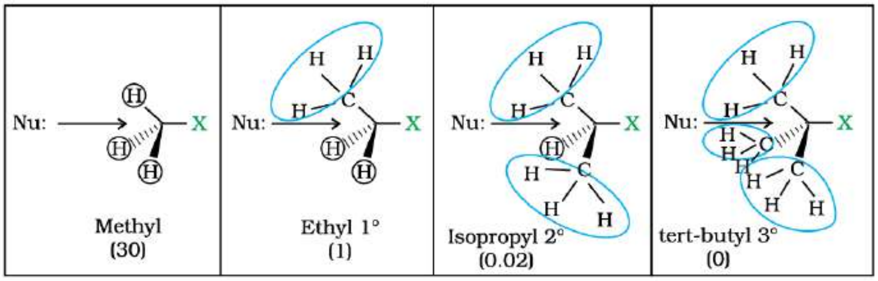
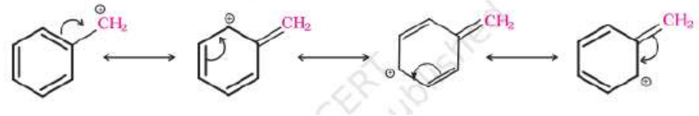


Fig.10.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

(ii) In S_N1 rate of reaction depends on the stability of carbocation. Allylic and benzylic halides are highly reactive in S_N1 reactions due to resonance-stabilized carbocations.



(ii) For a given alkyl group, the reactivity of the alkyl halide R-X, follows the same order in both the mechanisms R–I> R–Br>R–Cl>>R–F

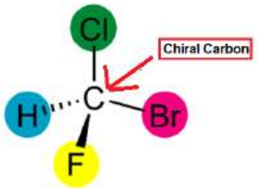
STEREOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION REACTIONS

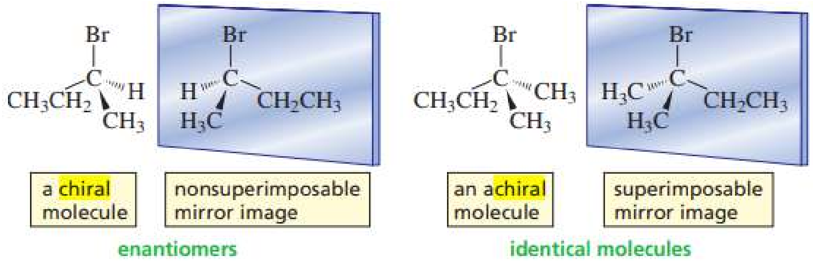
- Some important Terms

  (i) A tetrahedral carbon bonded to four different substituents is called a chiral carbon/chiral center/ asymmetric carbon/stereocentre.

The objects or molecule which are non-superimposable on their mirror image are said to be chiral and property is known as chirality. Optically active	The objects or molecule which superimposable on their mirror images are called achiral. Optically inactive

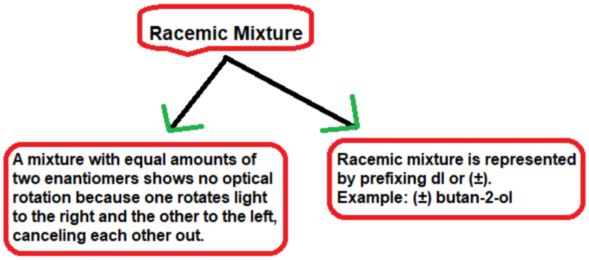
(ii) Nonsuperimposable mirror-image molecules are called **enantiomers.**





(a) Enantiomers rotate the plane polarized light in opposite direction hence it is known as optical isomers.	(b) Enantiomers possess identical physical properties namely, melting point, boiling point, refractive index, etc.	(c) They only differ with respect to the rotation of plane polarised light. (i) If rotates plane-polarized light to the right (clockwise) is called **dextrorotatory (d-form)** and marked with a **(+)** sign. (ii) If it rotates light to the left (anticlockwise), it is **laevorotatory (l-form)** and marked with a **(–)** sign.

(iii)



Racemic Mixture

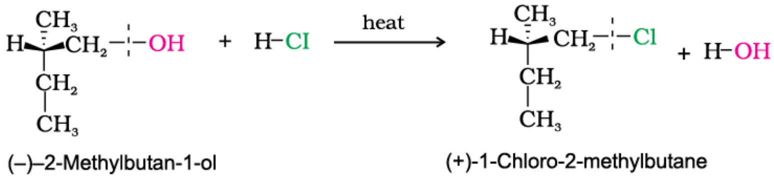
A mixture with equal amounts of two enantiomers shows no optical rotation because one rotates light to the right and the other to the left, canceling each other out.

Racemic mixture is represented by prefixing dl or (±). Example: (±) butan-2-ol

The process of conversion of enantiomer into a racemic mixture is known as racemisation.

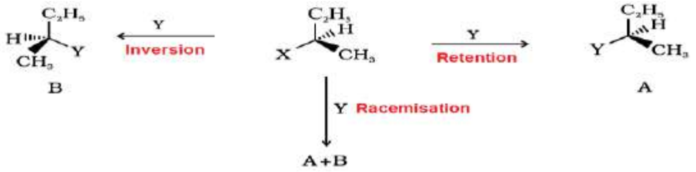
INVERSION, RETENTION AND RACEMISATION

- Inversion: (a) A process in which the relative configuration of an atom in a molecule changed. (b) Inversion takes place in S_N2.
- Retention: It is the process in which configuration of substrate and product remains the same.



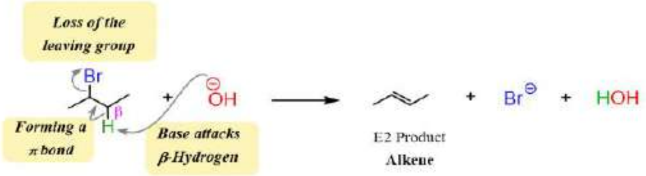
(I) Here, + and - indicate different optical activity.
(II) Configuration at a symmetric centre in the reactant and product is same

- Racemisation: (a) The process in which optically active compounds are converted into optically inactive compounds with zero optical activity.
  (b) Racemisation takes place in S_N1.

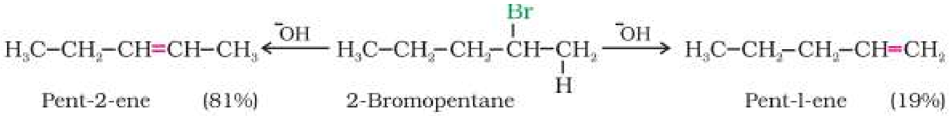


3. Elimination reaction/Dehydrohalogenation/ β-elimination

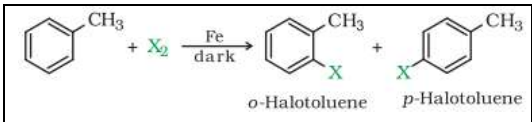
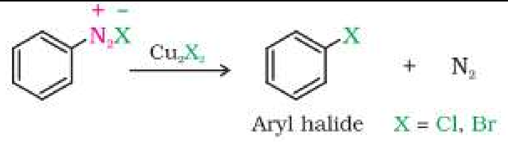
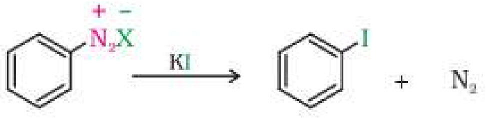
- Elimination of hydrogen atom from β -carbon and a halogen atom from the α-carbon atom simultaneously takes place.
- The strong base like alcoholic KOH is used in this reaction.
- Mechanism:



Note: If more than one α-hydrogen is available, multiple alkenes may form. The major product is predicted by Saytzeff’s rule. The example is given below:

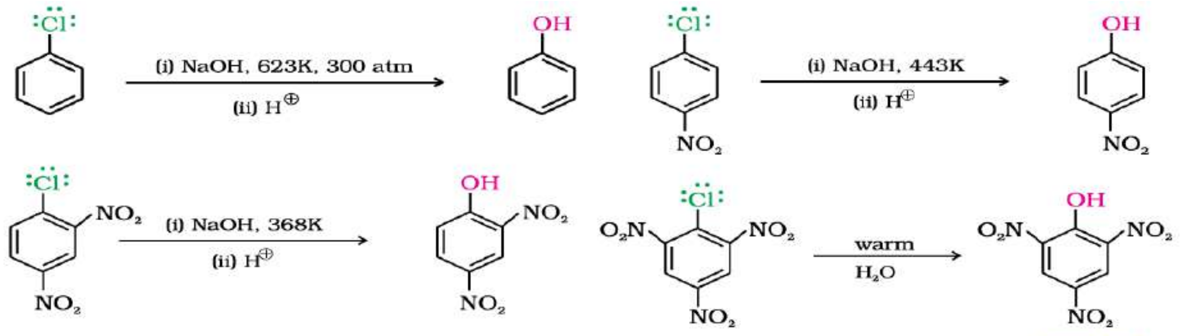


PREPARATION OF HALOARENE:

 Electrophilic substitution reaction	(i) The given reaction is an example of an electrophilic aromatic substitution reaction, where X_2 can be Cl_2 or Br_2.
	(ii) The ortho and para isomers can be easily separated due to large difference in their melting points.
 For Chloro or bromobenzene	(i) Name Reaction: Sandmeyer’s reaction  For iodobenzene

CHEMICAL PROPERTIES OF HALOARENE:

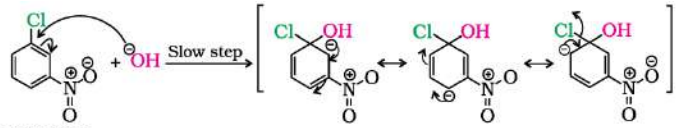
1. When chlorobenzene reacts with aqueous NaOH at high temperature and pressure, a substitution reaction occurs, forming phenol.
Introducing NO_2 groups at the ortho and para positions makes the reaction condition milder and increases the reactivity towards substitution reactions. The reactions are given below:



Picric Acid

Note: The effect is not observed when the NO_2 group is attached at the meta position because in meta-nitrobenzene, none of the resonance structures place a negative charge on the carbon with the $–NO_2$ group.

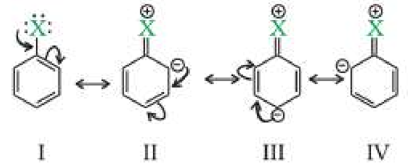
So, the nitro group at the meta position doesn't help stabilize the negative charge, and it doesn't increase the reactivity of the ring. The reaction in given below:



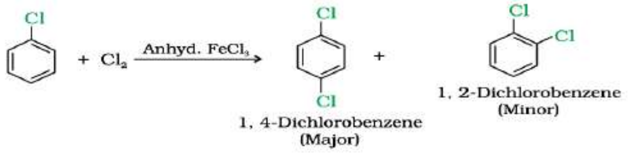
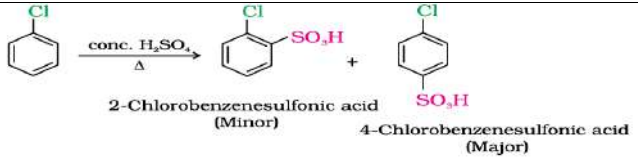
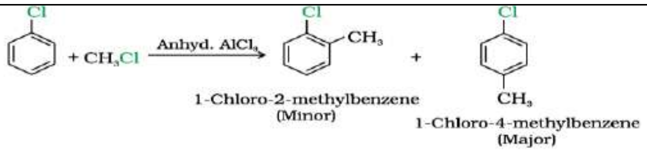
m-isomer

2. <u>Electrophilic substitution reactions:</u>

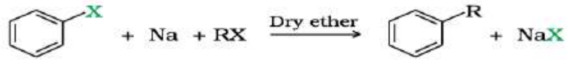
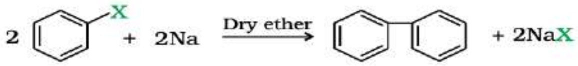
(a) Haloarenes undergo electrophilic substitution. The halogen is slightly deactivating due to –I effect but directs new groups to the ortho and para positions due to resonance, which increases electron density at these sites.



(b) The major product is the para-substituted compound, as it is favored over the ortho product.

(a) Halogenation	
(b) Nitration	
(c) Sulphonation	
(d) Friedel-Crafts reaction	

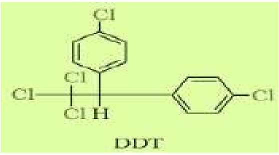
3. Reactions with Metals

(a) Wurtz-Fittig reaction	
(b) Fitting reaction	

- **Polyhalogen Compounds**

(a) Dichloromethane (Methylene chloride)	Used as a solvent(in drug industry), paint remover, propellant in aerosols Harms the central nervous system, Skin contact causes intense burning and mild redness. Eye contact can burn the cornea.
(b) Trichloromethane (Chloroform)	The main use of chloroform today is to produce the refrigerant Freon R-22. Chloroform slowly oxidizes in air and light to form poisonous phosgene gas(carbonyl chloride). It is stored in dark, tightly sealed bottles to keep air out. $2CHCl_3 + O_2 \xrightarrow{light} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$
(c) Triiodomethane (Iodoform)	Iodoform was once used as an antiseptic, but its effects come from releasing free iodine, not iodoform itself, and its unpleasant smell has led to its replacement by other iodine-based formulations.
(d) Tetrachloromethane (Carbon tetrachloride)	Use in the manufacture of refrigerants and propellants for aerosol cans, feedstock in the synthesis of chlorofluorocarbons. used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. It cause dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells.
(e) Freons	Chlorofluorocarbon compounds of methane and ethane. Eg: Freon 12 (CCl_2F_2) Extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases. It is manufactured from tetrachloromethane by Swarts reaction. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.
(f) p,p'Dichlorodiphenyltrichloroethane (DDT)	DDT is chemically stable and fat soluble. It is not metabolized very rapidly by animals; it is deposited and is stored in the fatty tissues. Being non-biodegradable its residues accumulate in environment and are toxic to mammals etc.

Structure of DDT is given below:



QUESTION BANK
SECTION – A (1 MARK)

1. Which of the following is the most preferred method for preparing pure alkyl chlorides from alcohols?

(a) R-OH + HCl $\xrightarrow{ZnCl_2}$ R-Cl + H_2O (b) R−OH + $PCl_5 \rightarrow$ R−Cl + $POCl_3$ + HCl

(c) R−OH + $SOCl_2 \rightarrow$ R−Cl + SO_2 + HCl (d) None of these

2. Ferons are among the most commonly used haloalkanes in industries. The reaction through which they are manufactured from tetrachloromethane is known as

(a) Finkelstein reaction (b) Sandmeyer's reaction

(c) Swarts reaction (d) Wurtz-Fittig reaction

3. Choose the incorrect statement regarding S_N2 reactions:

(a) As nucleophile concentration rises, reaction rate increases.

(b) Both the attack of the nucleophile and the departure of the leaving group occur simultaneously.

(c) Inversion of configuration occurs on asymmetric centers

(d) The S_N2 mechanism is predominant in tertiary alkyl halides.

4. Given below are two statements:

Statement 1: The process of conversion of enantiomer into a racemic mixture is known as racemization.

Statement 2: 1-chlorobutane has a higher boiling point than 2-chlorobutane.

(a) Statement 1 is **true** and statement 2 is **false**

(b) Statement 1 is **false** and statement 2 is **true**.

(c) Both statement 1 and statement 2 are **false**.

(d) Both statement 1 and statement 2 are **true**.

5. Match Column I (Compounds) with Column II (Uses), and mark the appropriate option:

Column I (Compounds)	**Column II (Uses)**
(A) Carbon tetrachloride	(i) Paint remover
(B) Methylene chloride	(ii) Refrigerators and air conditioners
(C) DDT	(iii) Fire extinguisher
(D) Freons	(iv) Non-biodegradable insecticide

(a) (A)=(ii), (B)=(iii), (C)=(i), (D)=(iv) (b) (A)=(iv), (B)=(iii), (C)=(ii), (D)=(i)

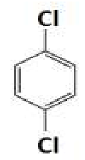
(c) (A)=(i), (B)=(ii), (C)=(iii), (D)=(iv) (d) (A)=(iii), (B)=(i), (C)=(iv), (D)=(ii)

6. What is the correct order of dipole moments from highest to lowest among the following?

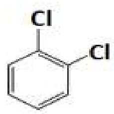
(a) $CH_3Cl > CH_3Br > CH_3F$ (b) $CH_3Cl > CH_3F > CH_3Br$

(c) $CH_3Br > CH_3Cl > CH_3F$ (d) $CH_3Br > CH_3F > CH_3Cl$

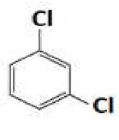
7. The correct order of melting point for the given compounds is:



A



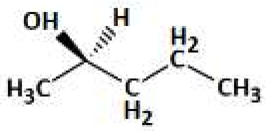
B

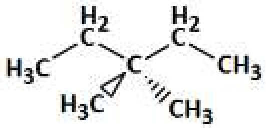


C

(a) A > B > C (b) A > C > B (c) B > A > C (d) C > A > B

8. Consider the following compounds:

I. 

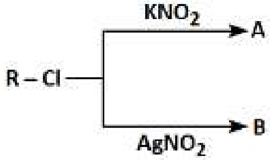
II. 

Identify the correct statement related to these compounds.

(a) I and II are chiral. (b) I and II are achiral.

(c) I is chiral and II is achiral. (d) I is achiral and II is chiral.

9. Consider the following reactions:

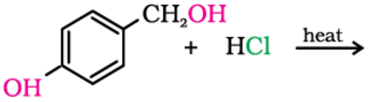


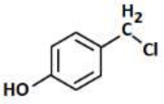
The relation between A and B are:

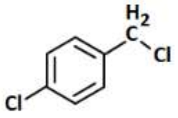
(a) Enantiomers (b) Functional group isomers

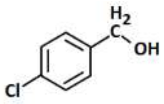
(c) Position isomers (d) Identical compounds

10. Examine the given reaction and predict the structure of the major monohalo product.



(a) 

(b) 

(c) 

(d) None of the these

ASSERTION REASON TYPE QUESTIONS (1 MARKS)

These questions are based on Assertion-Reason and write the correct option from the following four options given:

(a) Both A and R are correct and R is the correct explanation of A.

(b) Both A and R are correct but R is not the correct explanation of A.

(c) A is correct and R is not correct. (d) A is not correct but R is correct

11. **Assertion (A):**  undergoes S_N2 reaction faster than 

Reason(R): Iodine is a better leaving group because of its larger size.

12. Assertion (A): Aryl halides and vinyl halides are less reactive than alkyl halides and are not easily hydrolyzed.

Reason (R): The cleavage bond in aryl halides acquires a double bond character due to resonance, which makes its cleavage difficult.

13. Assertion (A): Grignard's reagent reaction occurs in aqueous medium.

Reason (R): In the presence of water, Grignard's reagent gets destroyed.

14. **Assertion (A):** AgCN gives alkyl isocyanides (R–NC) as the major product in nucleophilic substitution reactions with alkyl chloride.

Reason (R): AgCN is predominantly covalent, allowing the nitrogen atom to act as the nucleophile.

15. **Assertion (A):** The S_N2 reaction of (–)-2-bromooctane with sodium hydroxide gives (+)-octan-2-ol with inversion of configuration.

Reason(R): S_N2 reactions proceed through a carbocation intermediate which allows for the inversion of configuration.

Answer Key

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

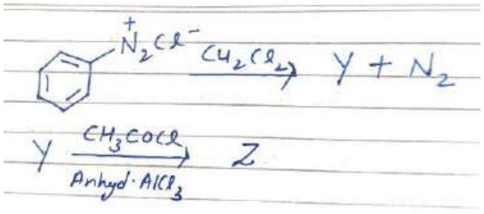
SECTION - B (2MARKS)

1. Carry out the following conversions in not more than two steps:
(i) Benzyl alcohol to phenylethanenitrile

2. You are working in a school chemistry laboratory where you synthesize butan-2-ol. After the reaction, you obtain a mixture of two optical isomers: dextro and laevo butan-2-ol. Your lab instructor suggests using **fractional distillation** to separate the two products.Will **fractional distillation** be the best method to separate these two compounds? Justify your answer.
(Hint: dextro and laevo-rotatory isomers are enantiomers they have the same boiling point.)

3. Chlorobenzene and benzyl chloride are both aromatic halo compounds, but they react differently with alcoholic silver nitrate solution. Explain how you can distinguish between the two using this reagent.
(Hint: Due to resonance aryl halide is less reactive towards nucleophilic substitution reaction.)

4. Identify the compound Y and Z in the following reaction.



(Hint: Second reaction is Friedel-crafts acylation of aryl halides)

5. Apply your understanding of solubility and intermolecular forces to explain why alkyl halides are insoluble in water despite having polar bonds.
(Hint: Unable to form hydrogen bonds with water molecules)

SECTION – C (3 MARKS)

1.(a) Indicate the products of the following reactions and point out the mechanism as S_N1, or S_N2.
(i) $(CH_3)_3CBr + CH_3OH$, heat; (b) $CH_3CHBrCH_3 + NaOCH_3$
(b) On substitution of one H by Cl in the isomers of C_4H_{10}. (i) Which isomer gives a tertiary alkyl halide?

2. (a) Out of $C_6H_5CH_2Cl$ and $C_6H_5CHCl\ C_6H_5$ which is more easily hydrolysed by aqueous KOH?
(Hint: With aqueous KOH reaction follow S_N1; Stability of carbocation)
(b) Give reasons: (i) C-Cl bond length in chlorobenzene is shorter than C-Cl bond length is CH_3-Cl.

(Hint: Due to resonance chlorobenzene acquires partial double bond character while in methyl chloride, C-Cl bond has pure single bond character.)

3. Apply your understanding of resonance and electron-withdrawing groups to explain why p-nitrochlorobenzene undergoes nucleophilic substitution faster than chlorobenzene. Support your answer with appropriate resonating structures.

(Hint: In this reaction a carbanion intermediate is formed which is stabilized by –R effect (resonance) as well as –I effect of NO_2 group.)

4. Prop-1-ene undergoes electrophilic addition reaction in the presence of HBr.

(i) Write the **names of all products** formed in the reaction.

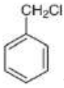
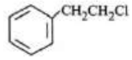
(ii) Identify the **major product** and explain **why it is formed in greater amount.**

5. (a) Study the reaction below and answer the questions that follow:

$CH_3CH_2Cl + NaI \rightarrow CH_3CH_2I + NaCl$

(i) Suggest a way to increase the rate of the forward reaction in the given process.

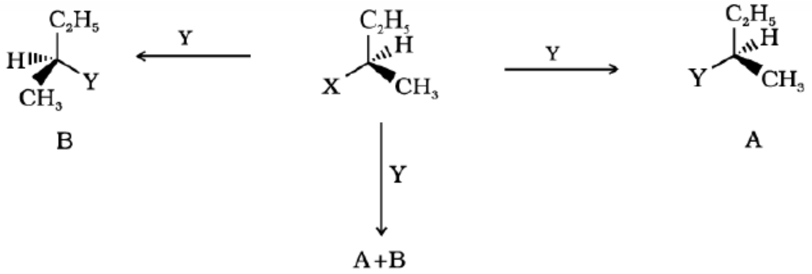
(ii) If ethyl fluoride is to be prepared, which reaction should be used?

(b) Out of  and , which is an example of benzyl halide.

SECTION – D CASE BASED QUESTIONS (4 MARKS)

1. **Read the passage given below and answer the following questions:**

When a chemical reaction occurs at an **asymmetric carbon atom**, the spatial configuration around that carbon may change depending on the mechanism of the reaction. In the replacement of a group **X** by another group **Y**, three outcomes are possible. The image is given below:

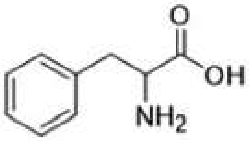


(i) In the given reaction, if compound B is the only product formed, what type of configuration change has occurred?

(a) Retention of configuration (b) Inversion of configuration

(c) Racemisation (d) No change in configuration

(ii) Observe the compound shown in the image given below and determine how many **chiral centers** are present in the molecule



(iii) If compounds A and B are present in equal proportions, will the resulting mixture be optically active or optically inactive? **Explain your answer.**

2. Read the passage given below and answer the following questions:

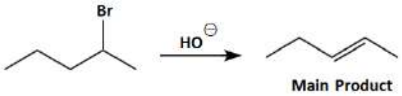
When a **haloalkane** containing a **β-hydrogen atom** is heated with alcoholic potassium hydroxide (KOH), it undergoes **β-elimination**, where a hydrogen atom is removed from the β-carbon and a halogen atom is removed from the α-carbon. This results in the formation of an **alkene**. Elimination reactions follow the order of reactivity: **Tertiary (3°) > Secondary (2°) > Primary (1°)**.

If more than one β-hydrogen is available, multiple alkenes may be formed. In such cases, the **major product** follows **Zaitsev's Rule**, which states that:

"In dehydrohalogenation reactions, the preferred product is the alkene with the greater number of alkyl groups attached to the doubly bonded carbon atoms."

For example, in the elimination of 2-bromopentane, the major product is **pent-2-ene**, which is more substituted and thus more stable.

(i) Select the correct statement by considering the following reaction:



(a). Hydroxide ion is a base. (b). Hydroxide ion is a nucleophile.

(c). It is a nucleophilic addition reaction. (d). It is a nucleophilic substitution reaction.

(Hint: hydrogen atom is removed from the β-carbon by base)

(ii) Predict the major product formed when 2-chloro-2-methylpropane is heated with alcoholic potassium hydroxide.

(Hint: Follow the mechanism of elimination reaction given in summary)

(iii) Out of 2-bromopentane, 2-bromo-2-methylbutane and 1-bromopentane, which compound is most reactive towards elimination reaction and why ?

(Hint: Elimination reaction order $3^{o} > 2^{o} > 1^{o}$)

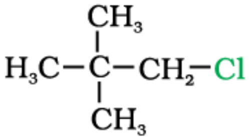
SECTION –E (5 MARKS)

1. (a) Starting with ethane, how could the following compounds be prepared?

(i). Propane nitrile; (ii). Ethyl benzene

(Hint: Halogenation, followed by nucleophilic substitution; Halogenation, followed by friedel-craft alkylation)

(b) Provide the IUPAC name of the given compound



$$H_3C-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}-CH_2-Cl$$

2. (a) A common lab solvent can cause liver and kidney damage with prolonged exposure. When exposed to air and light, it slowly forms a highly toxic gas. To prevent this, it is stored in sealed, dark-coloured bottles.

(i) Name the poisonous gas formed.

(ii) Write the chemical reaction involved in its formation.

(Hint: Gas is phosgene; formula is $COCl_2$)

(b) A student is asked to prepare an aromatic–alkyl hydrocarbon in the lab. They use a mixture of an aryl halide and an alkyl halide, along with metallic sodium in dry ether. The reaction produces a compound used in fuels and perfumes.

(i) Name the reaction taking place in this case.

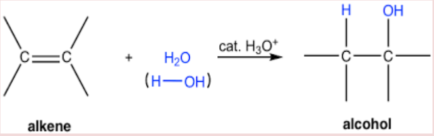
(ii) Write the balanced chemical equation for the reaction between bromobenzene and methyl bromide.

Hint: (wurtz-fittig reaction)

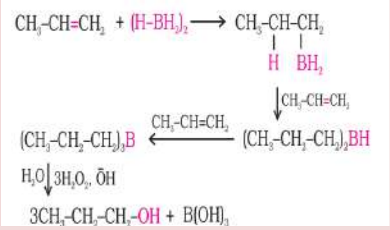
7.ALCOHOLS, PHENOLS AND ETHERS SUMMARY

PREPARATION OF ALCOHOLS

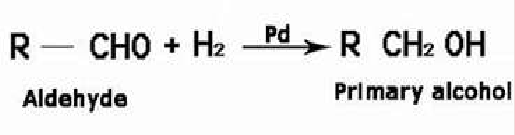
I)FROM ALKENE (BY ACID CATALYSED HYDRATION)



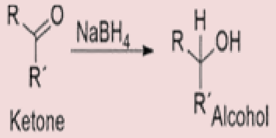
II)FROM ALKENE (BY HYDROBORATION–OXIDATION:)



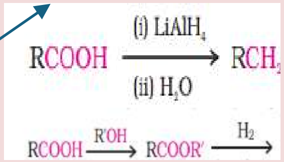
III) FROM CARBONYL COMPOUNDS(FROM ALDEHYDES)



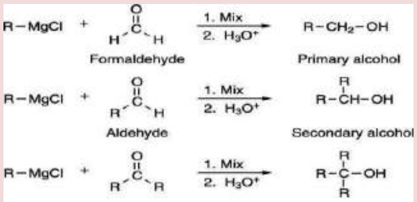
IV)FROM CARBONYL COMPOUNDS(FROM KETONES)



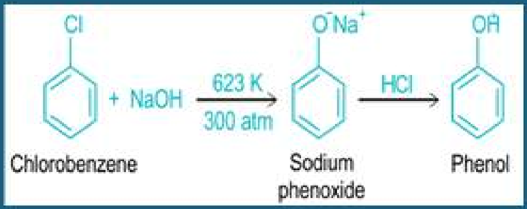
v)FROM CARBONYL COMPOUNDS(FROM CARBOXYLIC ACIDS AND ESTERS:



VI) FROM GRIGNARD REAGENTS



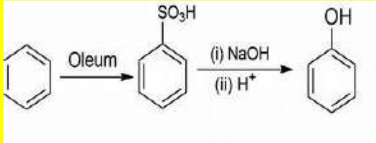
i)From haloarenes



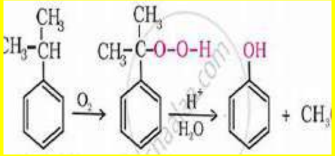
PREPARATION

OF PHENOLS

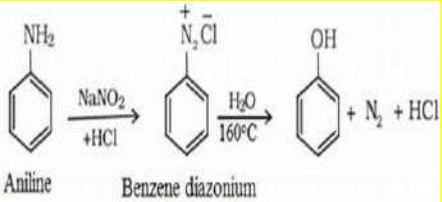
ii) From benzenesulphonic acid



iv)Fromcumene



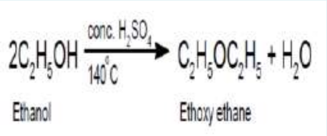
iii)Fromdiazonium salts



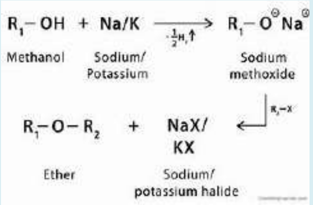
PREPARATION

OF ETHERS

i)By dehydration of alcohols



ii) Williamson synthesis



PHYSICAL PROPERTIES OF ALCOHOL ,PHENOL AND ETHERS-(KINDLY GO THROUGH THE DIKSHA LINK GIVEN)-
https://diksha.gov.in/play/content/do_31347577181469900811590

CHEMICAL REACTIONS OF ALCOHOL AND PHENOLS

I)Reactions involving cleavage of O – H Bond

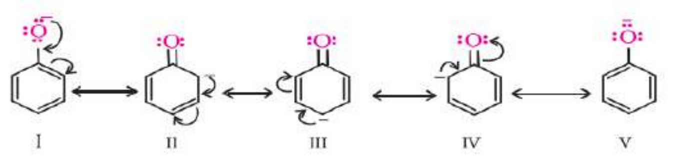
(a) Acidity of alcohols and phenols:

- $2R-OH + 2Na \rightarrow 2R-ONa + H_2$
- $2C_6H_5-OH + 2Na \rightarrow 2\,C_6H_5-ONa + H_2$

➢ 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°

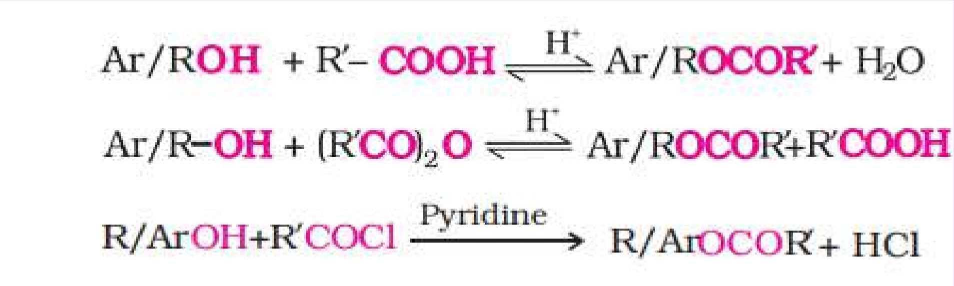
➢ Phenol is more acidic than alcohols due to stabilization of phenoxide ion through resonance



➢ Presence of electron withdrawing groups increases the acidity of phenol by stabilizing phenoxide ion

➢ presence of electron releasing groups decreases the acidity of phenol by destabilizing phenoxide ion.

(b)Esterification

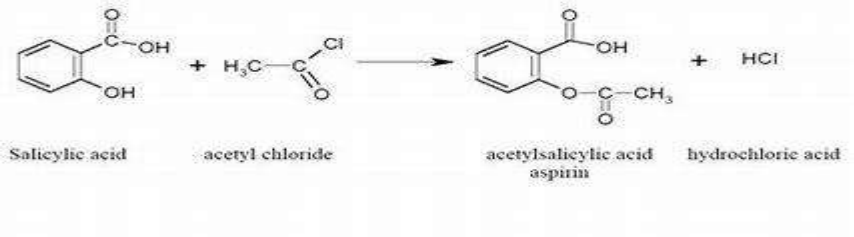


$$Ar/ROH + R'-COOH \underset{}{\overset{H^+}{\rightleftharpoons}} Ar/ROCOR' + H_2O$$

$$Ar/R-OH + (R'CO)_2O \overset{H^+}{\rightleftharpoons} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

Acetylation of salicylic acid produces aspirin.



CHEMICAL REACTIONS OF ALCOHOL AND PHENOLS(ii)Reactions involving cleavage of carbon – oxygen (C–O) bond in Alcohols

(a) Reaction with hydrogen halides:

Alcohols react with hydrogen halides to form alkyl halides.

ROH + HX →R–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.

(b)Reaction with phosphorus trihalides:

$$CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

(C)Dehydration:

The relative ease of dehydration of alcohol is Tertiary > Secondary >

(d)Oxidation- it involves loss of dihydrogen from an alcohol molecule

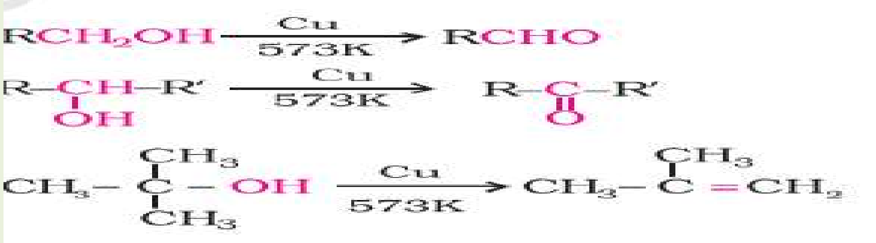
Primary alcohol → Aldehyde → Carboxylic acid

Primary alcohol → Carboxylic acid (strong oxidizing agent, acidified $KMnO4$)

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + [O] \xrightarrow{CrO_3} \underset{\text{Ethanal}}{CH_3CHO} + H_2O$$

$$\underset{\text{Ethanol}}{CH_2OH} + 2[O] \xrightarrow{\text{Alkaline } KMnO_4} \underset{\text{Ethonic a}}{CH_3COOH}$$

When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place.

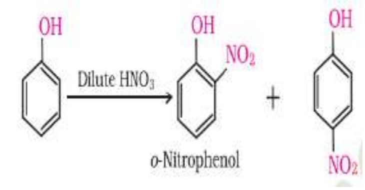
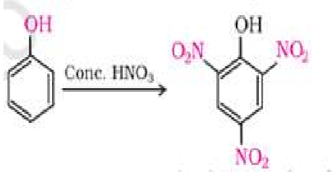
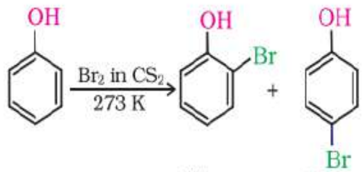
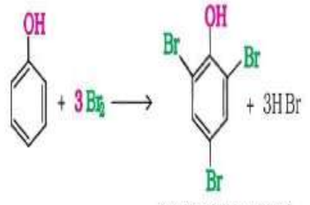
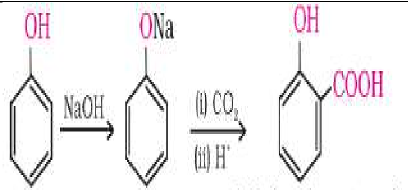
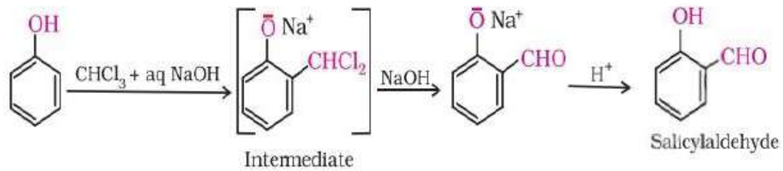
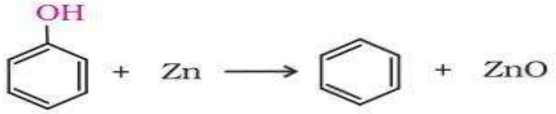


$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

$$R-\underset{OH}{CH}-R' \xrightarrow[573K]{Cu} R-\underset{O}{\overset{\|}{C}}-R'$$

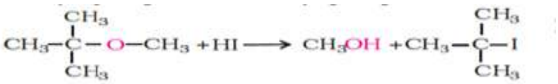
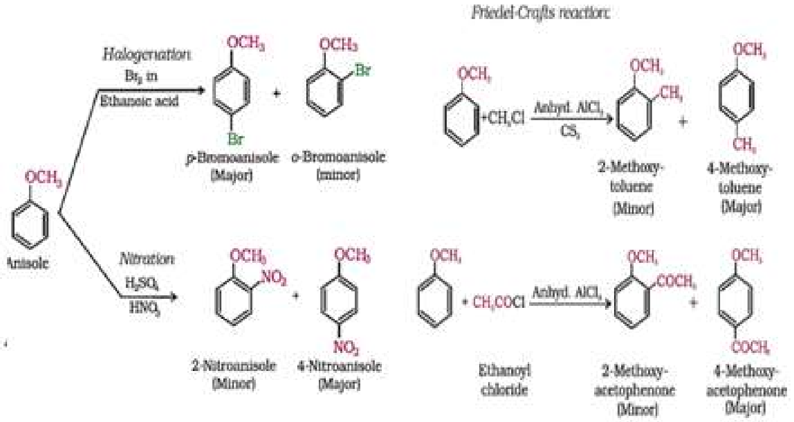
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[573K]{Cu} CH_3-\overset{CH_3}{C}=CH_2$$

CHEMICAL REACTIONS OF PHENOL

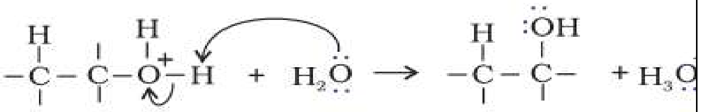
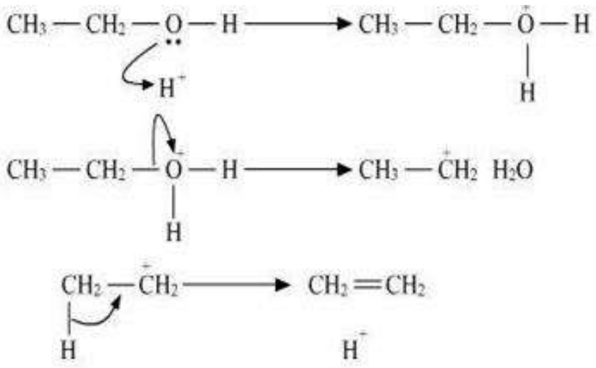
CHEMICAL REACTIONS OF PHENOLS **(a)Electrophilic aromatic substitution on aromatic ring of Phenol**	**i)Nitration**  o-Nitrophenol  2,4,6-Trinitrophenol (Picric acid) - The ortho and para isomers can be separated by steam distillation. - o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is
	ii)Halogenation (Bromination).  Minor Major  2,4,6-Tribromophenol -When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature, mono-bromophenols are formed. -When phenol is treated with bromine water, 2,4,6-
(b)Kolbe's reaction	 2-Hydroxybenzoic acid (Salicylic acid) -Phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution. Hence, it undergoes electrophilic substitution with carbon dioxide,
(C) Reimer-Tiemann reaction	 Intermediate Salicylaldehyde
(d)Reaction of phenol with zinc dust	

(e) Oxidation	 Oxidation of phenol with chromicacid /$Na_2Cr_2O_7$ produces a conjugated diketoneknown as benzoquinone.

CHEMICAL REACTIONS OF ETHERS

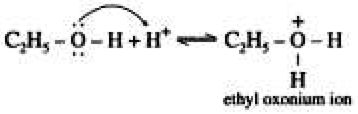
(a) Reactions involving Cleavage of C–O bond in ethers	• Reactions involving Cleavage of C–O bond in ethers $R\text{-}O\text{-}R + HX \longrightarrow RX + R\text{-}OH$ $R\text{-}OH + HX \longrightarrow R\text{-}X + H_2O$ • When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide (SN2 reaction). $CH_3-\ddot{\underset{..}{O}}-CH_2CH_3 + H\text{-}I \longrightarrow CH_3\text{-}I + CH_3CH_2\text{-}OH$ • when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide (SN1reaction)  $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_3 + HI \longrightarrow CH_3OH + CH_3-\overset{CH_3}{\underset{CH_3}{C}}-I$
(b) Electrophilic substitution-alkoxy group (-OR) is ortho, para directing	

MECHANISM OF REACTIONS-

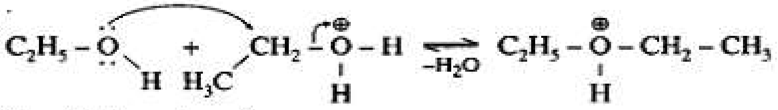
I)**Preparation of Alcohols (From alkenes)- By acid catalysed hydration** Protonation of alkene to form carbocation by electrophilic attack of H_3O^+  Nucleophilic attack of water on carbocation.  Deprotonation to form an alcohol. 	II) **Dehydration of Alcohols** 

III) FORMATION OF ETHER

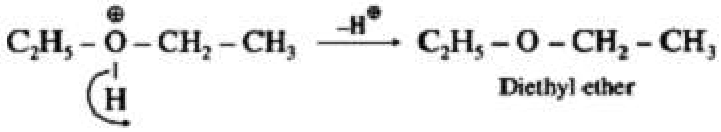
Step 1 Protonation



Step 2 S_N2 mechanism



Step 3 Deprotonation



QUESTION BANK

SECTION - A (1 MARK)

Q1.One mole of ethyl acetate on treatment with an excess of $LiAlH_4$ in dry ether and subsequent acidification produces

(a) 1 mole acetic acid + 1 mole ethyl alcohol

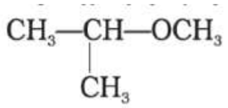
(b) 1 mole ethyl alcohol + 1 mole methyl alcohol

(c) 2 moles of ethyl alcohol (d) 1 mole of 2-butanol

Q2.Which of the following reagents can not be used to oxidise primary alcohols to aldehydes ?

(a) CrO_3 in anhydrous medium (b) $KMnO_4$ in acidic medium
(c) Pyridiniumchlorochromate (d) Heat in the presence of Cu at 573 K

Q3.IUPAC name of the following compound



$CH_3-CH(CH_3)-OCH_3$

(a) 1-methoxy-1-methylethane (b) 2-methoxypropane
(c) 2-methoxy-2-methylethane (d) isopropylmethylethe

Q4.Which of the following is the proper method to prepare n-hexane from n-propyl alcohol ?

$$\mathbf{CH_3CH_2CH_2OH \xrightarrow{(X)} CH_3CH_2CH_2Br \xrightarrow{(Y)} CH_3(CH_2)_4CH_3}$$

(a) (X) → HBr, (Y) → HCN (b) (X) → HBr, (Y) → Na, ether
(c) (X) + Br_2, (Y) → CH_3CN (d) (X) → Br_2, (Y) → $KMnO_4$

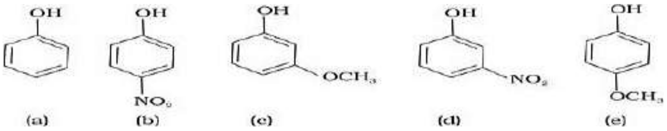
Q5.1-Propanol and 2-propanol can be best distinguished by
(a) Oxidation with $KMnO_4$ followed by reaction with Fehling solution?
(b) Oxidation with acidic dichromate followed by reaction with Fehling solution.
(c) Oxidation by heating with copper followed by reaction with Fehling solution.
(d) Oxidation with cone. H_2SO_4 followed by reaction with Fehling solution.

Q6.The product of acid catalysed hydration of 2-phenylpropene is
(a) 3-Phenyl-2-propanol (b) 1-Phenyl-2-propanol
(c) 2-phenyl-2-propanol (d) 2-phenyl-1-propanol.

Q7.Which of the following is true?
(a) Lower alcohols are liquid at room temperature and the higher ones are solid
(b) Lower alcohols and higher alcohols, both are liquid at room temperature
(c) Higher alcohols are liquid at room temperature and the lower ones are solid
(d) Both lower and higher alcohols are solid at room temperature

Q8. 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
(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol
(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol
(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

Q9. Mark the correct order of decreasing acid strength of the following compounds.



(a) e> d >b > a > c (b) b > d > a > c > e
(c) d> e >c > b > a (d) e > d > c > b > a

Q10.Tert-butyl methyl ether on heating with 1M HI gives
(a) $CH_3I + (CH_3)_3COH$ (b) $CH_3OH + (CH_3)_3I$ (c) $CH_3I + (CH_3)_3OH$ (d) None of these

In these questions (Q11-Q15), 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.

Q11. Assertion : Among n-butane, ethoxyethane,1-propanol and 2-propanol, the increasing order of boiling points is,1-butanol < 1-propanol <ethoxyethane< n-butane.
Reason: Boiling point increases with increase in molecular mass.

Q12. Assertion : Williamson's synthesis method cannot be used for preparing diphenyl ether.
Reason : Aryl halides do not undergo nucleophilic substitution easily.

Q13. Assertion: Bromination of phenol does not require the presence of Lewis acid.
Reason: -OH group attached to benzene ring has highly activating effect

Q.14. Assertion: Ethanol is a weaker acid than phenol.
Reason: Ethanol reacts with Na and phenol reacts with Na and NaOH

Q15. Assertion: Phenol is more reactive than benzene towards electrophilic substitution reaction.
Reason: In the case of phenol, the intermediate carbocation is more resonance stabilized.

Answer key-

Question no.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Answer	(c)	(b)	(b)	(b)	(c)	(c)	(a)	(a)	(b)	(a)	(d)	(a)	(a)	(b)	(a)

EXTRA QUESTIONS FOR PRACTICE –
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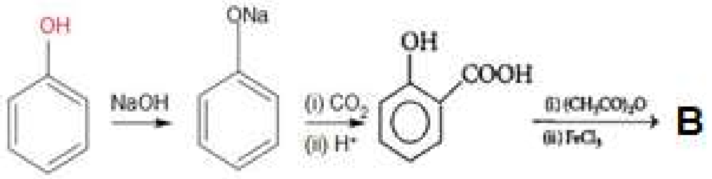
VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

Q1.Arrange each set of compounds in the decreasing order of property indicated
a) Ethanol, isopropanol, tertiary butyl alcohol (reactivity towards Lucas reagent)
Hint- reactivity order -Tertiary > secondary > primary
b) Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-Methyl phenol (acidic strength)
Hint-electron releasing and electron withdrawing groups.

Q2 Give the structures and IUPAC names of the products expected from the following reaction

a) 

b) 

Hint-a) oxidation reaction b) formation of Asprin .

Q3 a) In the process of wine making, ripened grapes are crushed so that sugar and enzyme should come in contact with each other and fermentation should start. What will happen if anaerobic conditions are not maintained during this process?

Hint -oxidation of alcohol.

b) 2,4,6-trinitrophenol gives sodium bicarbonate test. why?

Hint-presence of three nitro group showing electron withdrawing effect.

Q4 Give one chemical test each to distinguish between the following pairs of compounds: (i) Phenol and Benzoic acid (ii) Methanol and ethanol.

Hint-i)Ferric Chloride Test ii) Iodoform Test

Q5 Alcohol reacts with sodium metal whereas ether do not.

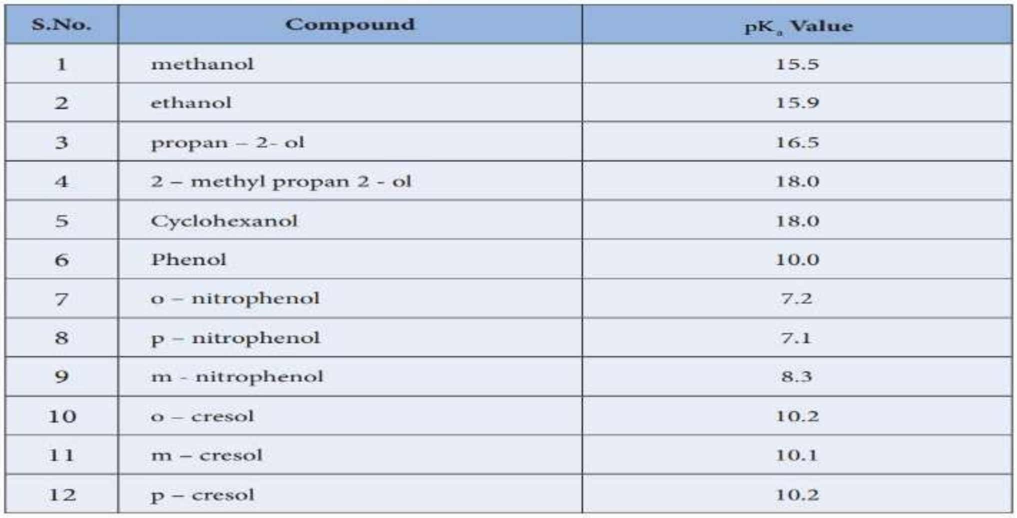
Hint-presence of active hydrogen.

b) Write the equations involved in the following reaction- Reimer - Tiemann reaction.

Hint-refer chemical reactions of phenol (name reaction)

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

Q1 Study the table and answer the questions based on table.



S.No.	Compound	pK_a Value
1	methanol	15.5
2	ethanol	15.9
3	propan – 2- ol	16.5
4	2 – methyl propan 2 - ol	18.0
5	Cyclohexanol	18.0
6	Phenol	10.0
7	o – nitrophenol	7.2
8	p – nitrophenol	7.1
9	m - nitrophenol	8.3
10	o – cresol	10.2
11	m – cresol	10.1
12	p – cresol	10.2

(a) What is relationship between pKa and acidic character?

Hint-A lower pKa value indicates a stronger acid

(b) from the table given above identify ,out of cresols and phenols which one is a weaker acid?

Hint-electron-donating effects of the methyl group

(c) Why is o-fluoro phenol weakest acid than p and m-fluoro phenol?

Hint-hydrogen bonding

Q2.Account for the following: -

(a) PCl_5 reacts with ethanol to form chloroethane. However, with phenol, it does not give chlorobenzene but gives triphenyl phosphate. Explain.

Hint- S_N2 mechanism,partial double bond character of the O-H bond.

(b) While separating a mixture of ortho and paranitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Hint- inter and Intra molecular hydrogen bonding

(c) Why in the Reimer-Tiemann reaction the major product is ortho-substituted?

Hint- intermolecular hydrogen bonding

Q3 A compound A ($C_4H_{10}O$) is optically active, on mild oxidation it gives compound B but on vigorous oxidation it gives compound c The compound 'C' along with 'D' are also formed from 'B' by reacting with iodine in the presence of alkali. Deduce the structures of 'A','B','C' and 'D'.

Hint-A-alcohol ,B-ketone, C-carboxylic acid ,D-refer iodoform reaction .

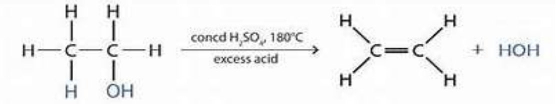
Q4 [X] and [Y] are functional isomers of each other with molecular formula C_3H_8O.
(i) Draw the isomers.
(ii) Which compound will have a lower boiling point and why?
Hint- i) alcohol and ether.   ii) hydrogen bonding

Q5 a) Show how the following alcohols are prepared by reaction with a suitable Grignard reagent on methanal .
i) 2-methylpropan-1-ol   ii) CH_3CH_2OH.
Hint-method of preparation of alcohol using Grignard reagent .
b) You are given a benzene, cone. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents
Hint-preparation of phenol.

CASE STUDY BASED QUESTIONS (4 MARKS)

Read the passage carefully and answer the questions.

Q1.Dehydration of alcohols can lead to the formation of either alkenes or ethers. This dehydration can be carried out either with protonic acids such as cone. H_2SO_4, H_3PO_4 or catalysts such as anhydrous $ZnCl_2$ or Al_2O_3.When primary alcohols are heated with cone. H_2SO_4 at 433-443 K, they undergo intramolecular dehydration to form alkenes. Secondary and tertiary alcohols undergo dehydration under milder conditions. The ease of dehydration of alcohols follows the order: 3° > 2° > 1°. The dehydration of alcohols always occurs in accordance with the Saytzeffs rule. Primary alcohols when heated with protic acid at 413 K, gives dialkyl ether.



$$2C_2H_5OH \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

i) The dehydration of alcohol belongs to which category of reactions?
(a) Substitution reaction (b) Elimination reaction (c) Addition reaction (d) Both (a) and (b)
Ans – (b) Elimination reaction
ii) Why is tertiary alcohol dehydration the easiest way to dehydrate?
Hint – tertiary carbocations are more stable
iii) During the dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is:
(a) Formation of carbocation   (b) Protonation of alcohol
(c) Formation of carbanion   (d) Elimination of water.
Ans- (b) Protonation of alcohol
iv) Why do more substituted alkenes are more stable?
Hint- Refer Saytzeffs rule.

Q2. A forensic lab received three unknown organic liquid samples labeled X, Y, and Z from a crime scene. The chemist is tasked with identifying the nature of these compounds — whether they are alcohols, phenols, or ethers. The following observations were made:

Sample X	Sample Y:
Has a pleasant fruity smell. Does not react with neutral $FeCl_3$ solution. Shows no visible reaction with sodium metal. Undergoes cleavage with HI to give alcohol and alkyl iodide.	Gives a violet coloration with neutral $FeCl_3$ solution. Is slightly soluble in water. Does not react with Lucas reagent at room temperature

i) **Identify the class of each compound (alcohol, phenol, or ether). Justify your answer using the given observations.**

Hint-ether, phenol, alcohol

ii) Which compound is most likely a tertiary alcohol? Explain your reasoning.

Hint-The reactivity of alcohols towards Lucas reagent follows the order: tertiary > secondary > primary

iii) **Write a balanced chemical equation for the reaction of sample Z with sodium metal.**

Hint – reaction of alcohol with sodium metal

iv) What role does Lucas reagent play in the identification of alcohols, and what does the reaction time indicate about the alcohol structure?

Hint -based on the speed at which corresponding insoluble alkyl chlorides (R-Cl) are formed post reaction

SECTION –E (5 MARKS)

Q1 Give reasons for the following: -

(a) The usual halogenation of benzene takes place in the presence of a Lewis acid, but In case of phenol, the reaction takes place even in the absence of Lewis acid.

Hint- activating effect of - OH group.

(b) Pure phenol is a colorless solid but why it is converted into pink after some time?

Hint-oxidation of phenol.

(c) why does ethers possess a dipole moment even if the alkyl radicals in the molecules are identical

Hint -bond polarity and bond angle in ethers .

(d) boiling point of glycol is higher than the alcohol of same molecular mass

Hint- hydrogen bonding

(e) The K_a for p- nitro hydroxybenzene is 6.9 x10^{-8} whereas o-nitro hydroxybenzene is 6.0 x10^{-8}

Hint-hydrogen bonding between the -OH group and the nitro group.

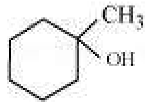
Q2 How would you obtain

i) (a) phenol from benzene (b) acetophenone from phenol (c) ethane-1,2-diol from Ethanol

Hint -a) preparation of phenol; b) Friedel-Crafts acylation reaction.; c) dehydration reaction followed by addition of Baeyer's reagent

ii) **Show how would you synthesize the following alcohols from appropriate alkenes?**

(a)



(b)

Hint-acid catalyzed hydration of appropriate alkene

CHAPTER-8

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

SUMMARY:

Nature of Carbonyl Group

- The carbon and oxygen of the carbonyl group are sp^2 hybridised and the carbonyl double bond contains one sigma-bond and one π-bond with the bond angle 120^0.
- The electronegativity of oxygen is much higher than that of the carbon, so their electron cloud is shifted towards the oxygen. Therefore, C—O bond is polar in nature .

  In carboxylate ion –ve charge is delocalized on two electronegative O-atoms hence shows resonance which indicate that CO group is not a true carbonyl group in carboxylic acids.

Nomenclature

(i) Nomenclature of **Aldehydes** **IUPAC** system, the suffix ‘e’ of alkane is replaced by the suffix ‘al’. **e.g.**

Compound	**Common name**	**IUPAC name**
HCHO	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal

(ii) Nomenclature of **ketones** **IUPAC** system, the suffix “e” of alkane is replaced by ‘one’**. e.g.**

Compound	**Common name**	**IUPAC name**
H_3CCOCH_3	Dimethyl ketone (acetone)	Propanone
$H_3CCOC_2H_5$	Ethyl methyl ketone	Butanone

(iii) Nomenclature of carboxylic acids **IUPAC** system, the suffix “e” of alkane is replaced by ‘oic’acid. **e.g.**

Compound	**Common name**	**IUPAC name**
HCOOH	Formic acid	Methanoic acid
H_3CCOOH	Acetic acid	Ethanoic acid
$CH_3(CH_2)_2COOH$	Butyric acid	Butanoic acid

Reactivity of aldehyde and Ketones :

$HCHO > RCHO > RCOR > RCOOR > RCONH_2$.

Physical Properties of Aldehydes and Ketones

1. **Methanal (HCHO**) is a gas at room temperature, and its 40% aqueous solution is known as f**ormalin**, which is used to preserve biological specimens .

It is used in silvering of mirrors and decolourising vat dyes.

2. **Ethanal (CH_3CHO)**

It is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.

- The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular mass due to high magnitude of dipole-dipole interactions.
- Aldehydes and ketones have lower boiling point than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.
- The lower members of aldehydes and ketones are miscible with water due to the formation of hydrogen bond with water. However, the solubility decreases with increase in length of alkyl chain.

- Acetophenone is a hypnotic (sleep producing drug) so used as a medicine under the name hypnone.
- 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.
- **Preparation of Aldehydes** :

  a. Dehydrogenation of primary alcohols

  b. Controlled oxidation of primary alcohols.

  c. Controlled and selective reduction of acyl halides Aromatic aldehydes can be prepared by-

  (i) Oxidation of toluene with chromyl chloride or CrO_3 in the presence of acetic anhydride

  (ii) Formylation of arenes with carbon monoxide and Hydrochloric acid in the presence of anhydrous aluminium chloride / Cuprous chloride

  (iii) Hydrolysis of benzal chloride
- **Preparation of Ketones** :

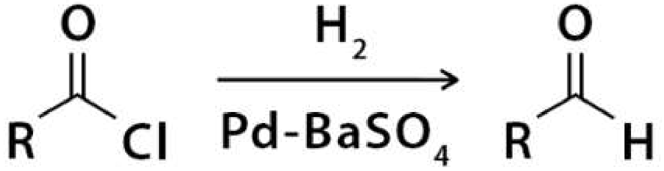
  a. oxidation of secondary alcohols b. Hydration of alkenes

  c. Reaction acyl chlorides with dialkylcadmium d. By friedel crafts reaction
- **Preparation of Carboxylic acids** :

  a. oxidation of primary alcohols, aldehydes and alkenes b. hydrolysis of nitriles

  c. Treatment of grignard reagent with carbon dioxide.
- **IMPORTANT NAMED REACTIONS**

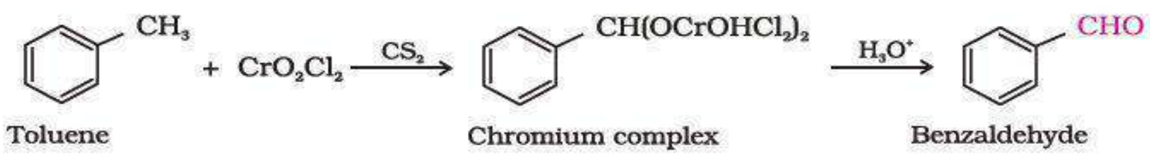
.1. **ROSENMUND REDUCTION**:



2. STEPHEN REACTION

RCN + $SnCl_2$ + HCl → RCH=NH $\xrightarrow{H_3O^+}$ RCHO

3. ETARD REACTION:



This reaction is called Etard reaction.

4. CLEMMENSEN REDUCTION

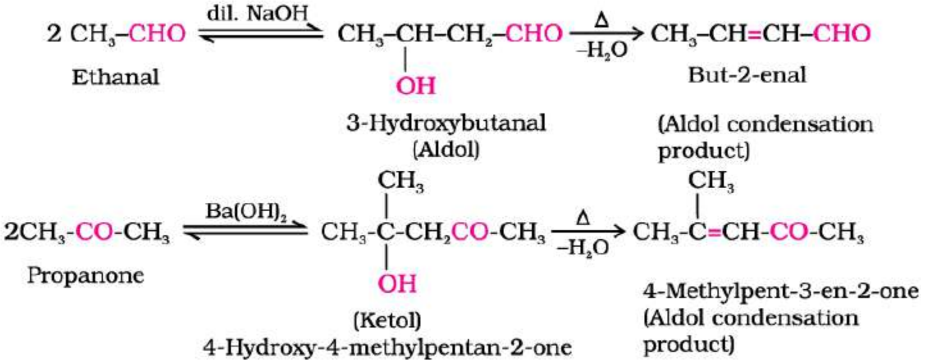
$>C=O \xrightarrow{\text{Zn-Hg/HCl}} >CH2 + H2O$

5. WOLFF-KISHNER REDUCTION

$>C=O \xrightarrow{NH_2NH_2} >C=NNH_2 \xrightarrow{\text{KOH/ethylene glycol /}H_2O} >CH_2 + N_2$

6. ALDOL CONDENSATION

Aldehydes and ketones having at least one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxyaldehydes (aldol) or β-hydroxy ketones (ketol). The reaction is given below:



$$2\,CH_3\text{–}CHO \overset{\text{dil. NaOH}}{\rightleftharpoons} CH_3\text{–}\underset{OH}{\underset{|}{CH}}\text{–}CH_2\text{–}CHO \xrightarrow[-H_2O]{\Delta} CH_3\text{–}CH{=}CH\text{–}CHO$$

Ethanal

3-Hydroxybutanal (Aldol)

But-2-enal (Aldol condensation product)

$$2CH_3\text{-}CO\text{-}CH_3 \overset{Ba(OH)_2}{\rightleftharpoons} CH_3\text{-}\overset{CH_3}{\underset{OH}{C}}\text{-}CH_2CO\text{-}CH_3 \xrightarrow[-H_2O]{\Delta} CH_3\text{-}\overset{CH_3}{C}{=}CH\text{-}CO\text{-}CH_3$$

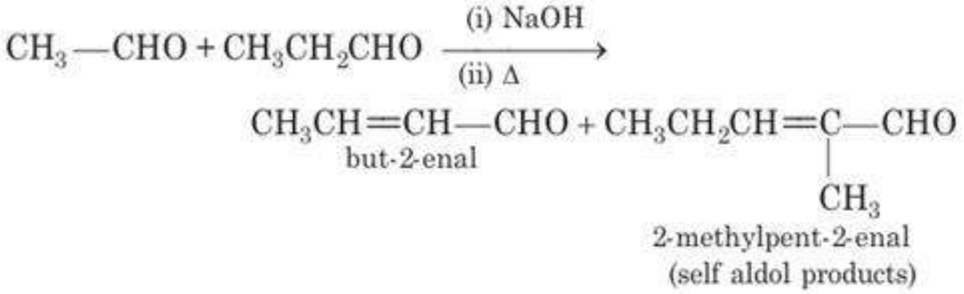
Propanone

(Ketol) 4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one (Aldol condensation product)

7. CROSS- ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.



$$CH_3\text{—}CHO + CH_3CH_2CHO \xrightarrow[\text{(ii) }\Delta]{\text{(i) NaOH}}$$

$$CH_3CH{=}CH\text{—}CHO + CH_3CH_2CH{=}\underset{CH_3}{\underset{|}{C}}\text{—}CHO$$

but-2-enal

2-methylpent-2-enal

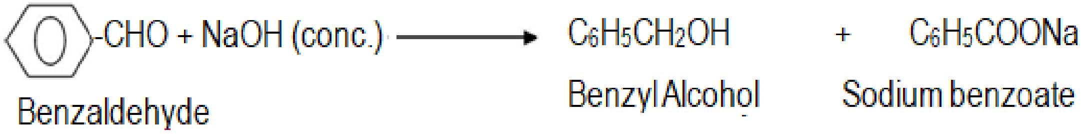
(self aldol products)

8. CANNIZZARO REACTION

Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (dispropotionation) reaction on treatment with concentrated alkali,to yield carboxylioc acid salt and an alcohol respectively.

$H\text{-}CHO + H\text{-}CHO + \text{Conc.}KOH \longrightarrow CH_3OH + HCOOK$

Formaldehyde	Methanol	Potassium Formate



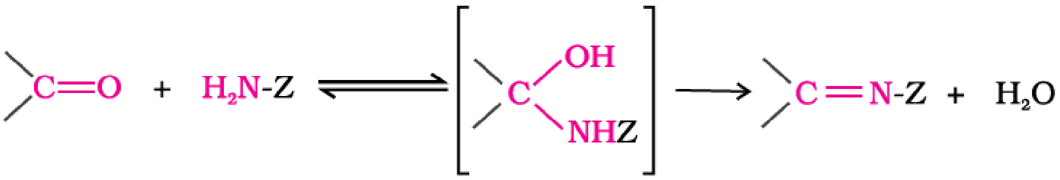
$C_6H_5\text{-}CHO + NaOH\ (\text{conc.}) \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$

Benzaldehyde

Benzyl Alcohol

Sodium benzoate

ADDITION OF AMMONIA AND ITS DERIVATIVES:



$$\rangle C{=}O + H_2N\text{-}Z \rightleftharpoons \left[\rangle C\langle^{OH}_{NHZ}\right] \longrightarrow \rangle C{=}N\text{-}Z + H_2O$$

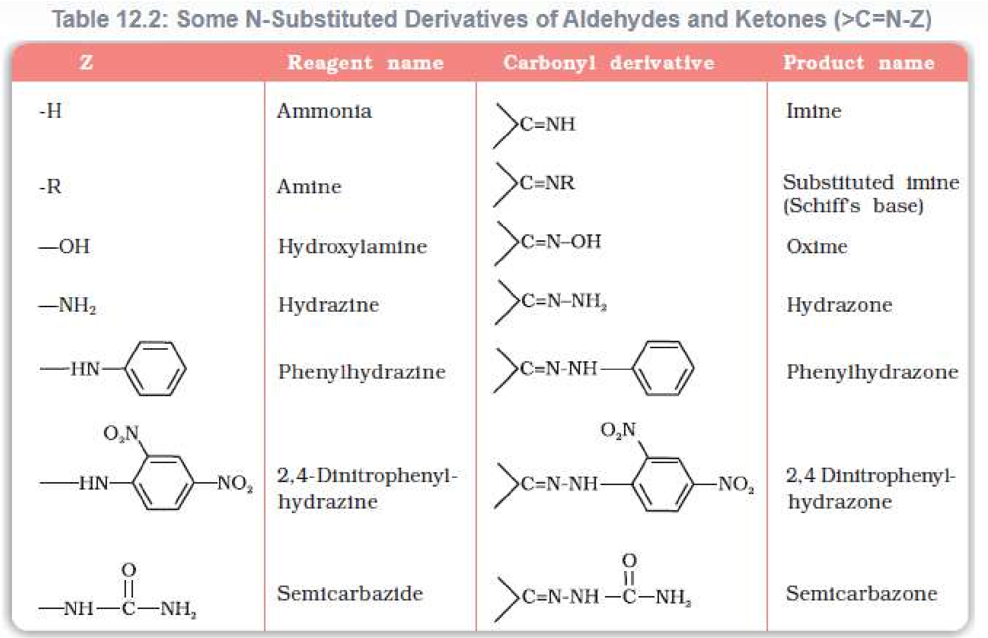
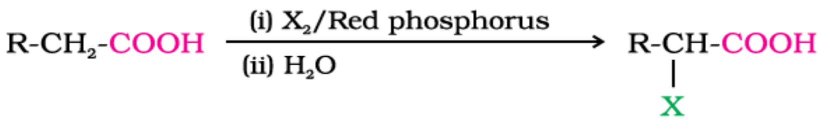


Table 12.2: Some N-Substituted Derivatives of Aldehydes and Ketones (>C=N-Z)

Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	>C=NH	Imine
-R	Amine	>C=NR	Substituted imine (Schiff's base)
—OH	Hydroxylamine	>C=N–OH	Oxime
—NH_2	Hydrazine	>C=N–NH_2	Hydrazone
—HN—	Phenylhydrazine	>C=N-NH—	Phenylhydrazone
O_2N —HN— —NO_2	2,4-Dinitrophenyl-hydrazine	>C=N-NH— O_2N —NO_2	2,4 Dinitrophenyl-hydrazone
—NH—C(=O)—NH_2	Semicarbazide	>C=N-NH —C(=O)—NH_2	Semicarbazone

REACTIONS OF CARBOXYLIC ACID:

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)



$$\text{R-CH}_2\text{-COOH} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) X}_2\text{/Red phosphorus}} \underset{\substack{|\\ \text{X}}}{\text{R-CH-COOH}}$$

X = Cl, Br

α – Halocarboxylic acid

2. ESTERIFICATION

$$\text{RCOOH} \quad + \quad \text{R'OH} \overset{H^+}{\rightarrow} \quad \text{RCOOR} \quad + \quad H_2O$$

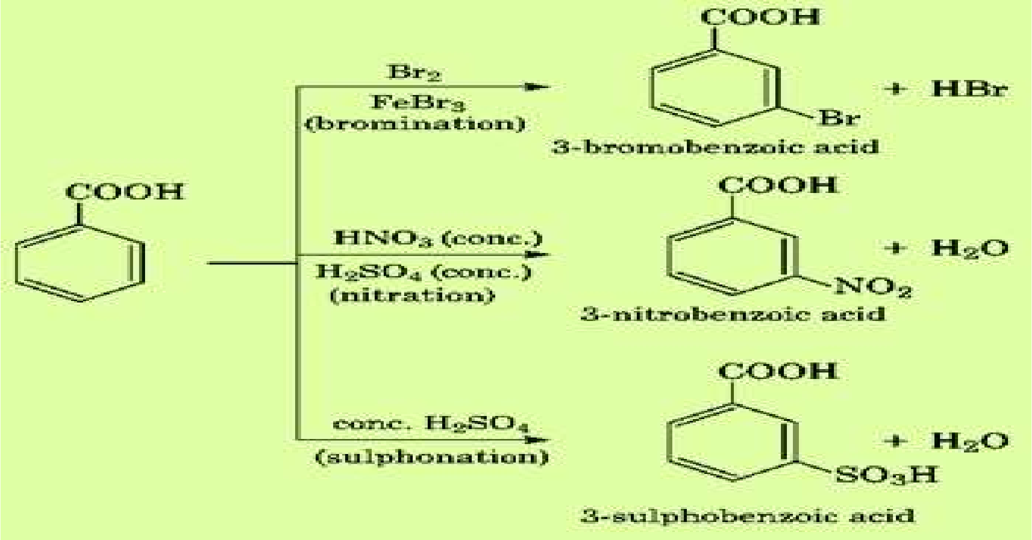
Carboxylic acid   alcohol

3. DECARBOXYLATION

$$\text{R-COONa} \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} \text{R-H} + Na_2CO_3$$

sodalime = NaOH and CaO in the ratio of 3 : 1

REACTIONS OF BENZOIC ACID



DISTINCTION OF ORGANIC PAIRS

Distinguish between :-

Alcohol	**Phenol**
It does not give $FeCl_3$ test	It gives neutral $FeCl_3$ (violet) test
Benzaldehyde	**Acetophenone**
It give Fehling's solution test and Tollens reagent test	It doesn't give Fehling's solution test and Tollens reagent test
Acetic acid	**Formic acid**
It doesn't gives tollen's reagent and fehling's solution test	It gives tollen's test and fehling's solution test
Ethanal	**Propanal**
It gives iodoform test	It doesn't give iodoform test
Propanol	**Ethanol**
It doesn't give iodoform test	It gives iodoform test
Pentan-2-one	**Pentan-3-one**
It gives iodoform test	It doesn't gives iodoform
Benzoic acid	**benzene**
On adding $NaHCO_3$ effervescence of CO_2 produced	No effervescence obtained

Note: Learn properly since one question on distinguish between organic pairs is ask

SECTION –A (1 MARK)

1. Name the compound $CH_3COCH(CH_3)_2$ as per the IUPAC nomenclature:
(a) 2-methyl-3-butanone (b) 4-methylisopropyl ketone
(c) 3-methyl-2-butanone (d) Isopropylmethyl ketone

2 . Predict the acid which cannot be prepared by Grignard reagent:
(a) Acetic acid (b) Succinic acid (c) Formic acid (d) All of the above

3. Which is highly soluble in water:
(a) Methanal (b) Propanal (c) Propanone (d) Butanone

4. Benzaldehyde reacts with ethanoic KCN to give product :
(a) $C_6H_5CHOHCN$ (b) $C_6H_5CHOHCOC_6H_5$
(c) $C_6H_5CHOHCOOH$ (d) $C_6H_5CHOHCHOHC_6H_5$

5. Name the compound not responding to the Iodoform test :
(a) 2-Pentanone (b) Ethanol (c) Ethanal (d) 3-Pentanone

6. Precipitate produced when acetaldehyde is heated with Fehling's solution :
(a) Cu (b) CuO (c) Cu_2O (d) $Cu(OH)_2$

7. Test used to distinguished between Aldehydes and ketones would be :
(a) Lucas test (b) Tollen's test (c) KMnO4 solution (Baeyer's test) (d) None of these

8. Name the compound called Imine derivatives of aldehyde and ketones :
(a) Schiff's reagent (b) Fehling's reagent (c) Schiff's base (d) Schiff's acid

9.Predict the pair of compounds will undergo Aldol and Cannizzaro reaction respectively :
(i) acetone; benzaldehyde (ii) acetaldehyde; butan–2–one
(iii) propanone; formaldehyde. (iv) cyclopentanone, benzaldehyde :
(a) (i) and (iii) (b) (ii) and (iii) (c) (ii), (iii) and (iv) (d) (iii) and (iv)

10. Carboxylic acids are more acidic than phenol and alcohol due to :
(a) intermolecular hydrogen bonding (b) formation of dimers
(c) highly acidic hydrogen (d) resonance stabilization of their conjugate base

ASSERTION-REASON TYPE QUESTIONS

Directions : Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer.

You have to select one of the codes (a), (b), (c) and (d) given below:

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

11. **Assertion**:The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.
Reason: There is a weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.

12. **Assertion**: Formaldehyde is a planar molecule.
Reason: It contains sp^2 hybridised carbon atom.

13. **Assertion**: Compounds containing –CHO group are easily oxidised to corresponding carboxylic acids.
Reason: Carboxylic acids can be reduced to alcohols by treatment with $LiAlH_4$

14. **Assertion**: The molecular mass of acetic acid in benzene is 120 instead of 60.
Reason: The carboxylic acids exist as cyclic dimers in which the two molecules of the acid are held together by two strong hydrogen bonds

15. **Assertion:** The PK_a of acetic acid is lower than that of phenol.
Reason: Phenoxide ion is more resonance stabilized than acetate ion.

ANSWER KEY for MCQ

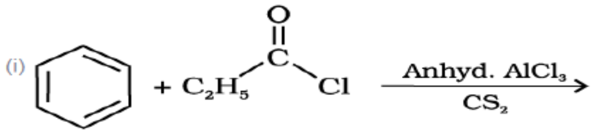
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
C	C	A	B	D	C	B	C	A	D	A	A	B	A	C

SECTION – B [02 Marks Each]

1. Arrange the following compounds in increasing order of their boiling points.
CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$
[Hint: is given by: $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$]
2. 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.
[Hint: Consider steric effect and Inductive effect.:
(i) Butanone < Propanone < Propanal < Ethanal
(ii) Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde]

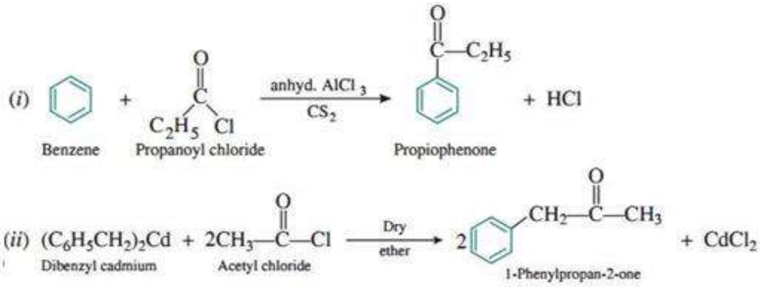
3 . Give the IUPAC names of the following compounds: (i) $PhCH_2CH_2COOH$
(ii) $(CH_3)_2C=CHCOOH$
[Hint: (i) 3-Phenylpropanoic acid (ii) 3-Methylbut-2-enoic acid]

4. Predict the product of the following reactions::



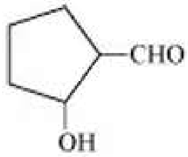
(ii) $(C_6H_5CH_2)_2Cd + 2\ CH_3COCl \rightarrow$

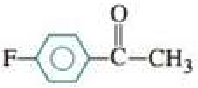
Hint:



4 Draw the structures of the following compounds:
(i) 2-Hydroxycyclopentane carbaldehyde (ii) 4-Fluoroacetophenone

Hint:

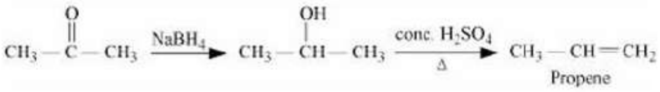




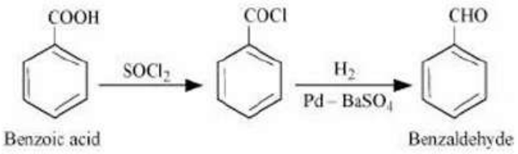
SECTION –C [03 Marks Each]

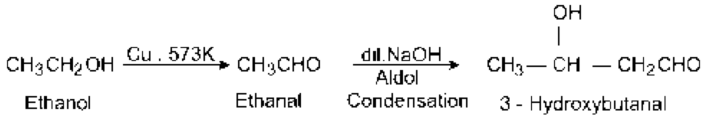
1. How will you convert ethanal into the following compounds:
(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid
[Hint: (i) On treatment with dilute alkali, ethanal produces 3-hydroxybutanal gives butane-1, 3 diol on reduction. (ii) On treatment with dilute alkali, ethanal gives 3-hydroxybutanal which on heating produces but-2-enal. (iii) When treated with Tollen's reagent, But-2-enal produced in the above reaction produces but-2-enoic acid]
Note: try to draw the structure of all the compounds involved in these reactions
2. Give simple chemical tests to distinguish between the following pairs of compounds:
(i) Methanol and Ethanol
(ii) Benzaldehyde and Formic acid
(iii) Phenol and Benzoic acid
[Hint: As per the text summary]
3. How will you bring about the following conversions in not more than two steps: (i) Propanone to Propene (ii) Benzoic acid to Benzaldehyde (iii) Ethanol to 3-Hydroxybutanal
[Hint:

(i)



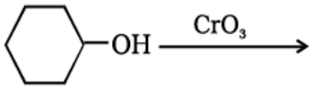
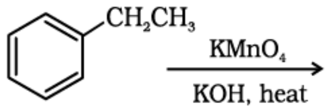
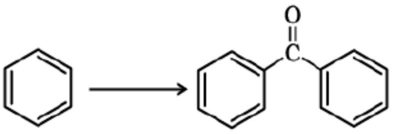
(ii)



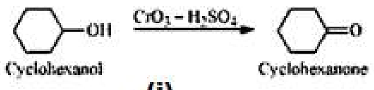
(iii) 

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{Cu\ .\ 573K} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{Aldol Condensation}]{dil.NaOH} \underset{\text{3 - Hydroxybutanal}}{CH_3-\overset{OH}{\overset{|}{CH}}-CH_2CHO}$$

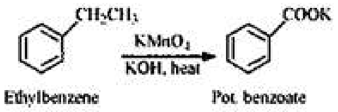
4. Complete each synthesis by giving missing starting material, reagent or products:

(i)  ; (ii)  ; (iii) 

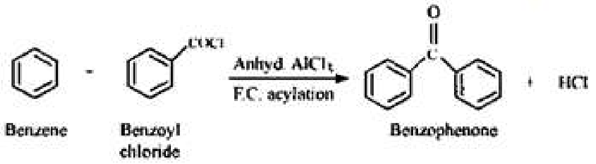
Hint:



(i)



(ii)



(iii)

5. Account for 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.

[Hint: (i) Methyl groups at α-positions offer steric hindrances and as a result, CN^- cannot attack effectively in later case

(ii) The electron density on one of the $-NH_2$ group involved in the resonance decreases. As a result, it cannot act as a nucleophile.

(iii) Ester along with water is formed reversibly, therefore, to shift the equilibrium in the forward direction i.e., to produce more ester, either of the two should be removed.

SECTION – D CASE BASED STUDY QUESTIONS [04 MARKS]

1. Read the passage carefully and answer the questions that follow. [1+1+2]

The following questions are case-based questions Aldehydes and ketones having at least one methyl group linked to the carbonyl carbon atom (methyl ketones) are oxidised to sodium salts of corresponding carboxylic acids having one carbon atom less than that of carbonyl compound. The methyl group is converted to haloform. This oxidation does not affect a carbon-carbon double bond, if present in the molecule. An aromatic organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It neither reduces Tollens' reagent nor does it decolourise bromine water.

An aromatic organic compound 'A' with molecular formula C_8H_8O gives positive DNP and iodoform tests. It neither reduces Tollens' reagent nor does it decolourise bromine water.

(i) $(CH_3)_3C-CHO$ does not undergo aldol condensation.
(ii) Benzoic acid does not give Friedel craft reaction.
(iii) Sodium bisulphite is used for purification of ketones and aldehydes

[Hint; (i) Due to unavailability of α-hydrogen in the given compound it does not undergo aldol condensation.

(ii) Catalyst $AlCl_3$ is a Lewis acid that gets bonded to the carboxyl group making it less reactive.

(iii) Due to formation of addition compound with $NaHCO_3$ whereas impurities do not.

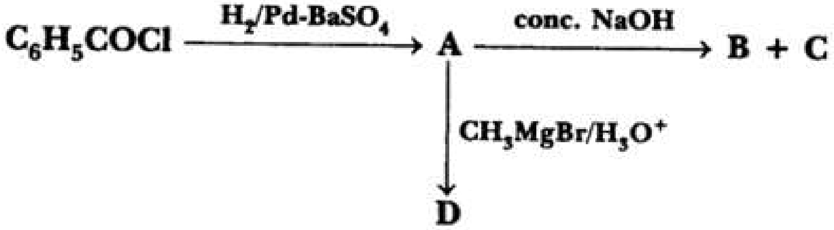
SECTION –E [05 MARKS EACH]

1. An organic compound A, having the formula C_3H_8O, on treatment with copper at 573 Kgives B. B does not reduce Fehling's solution but gives a yellow precipitate of the compound C with I_2 / NaOH. Deduce the structures of A, B, and C. Also write the respective chemical reactions.

Hint: (A) Compound A: Propan -2-ol (C_3H_8O)
(B) Compound B: Propanone (CH_3COCH_3)
(C) Compound C: Iodoform (CHI_3)

Reactions: (i) $C_3H_8O \xrightarrow{Cu/573K} CH_3 - CO - CH_3$
(ii) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COO - Na + CHI_3 + 3NaI + 3H_2O$

2 . Write the structures of A, B, and C in the following reactions.



Hint:- A-C_6H_5CHO, B-C_6H_5COONa ,C-$C_6H_5CH_2OH$, D-$C_6H_5CHOHCH_3$

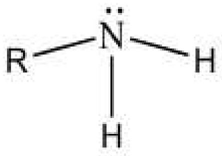
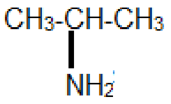
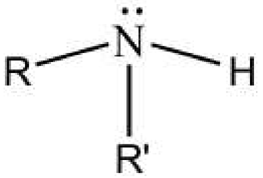
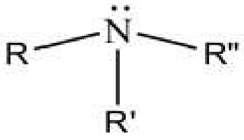
(b) Name the reagents used for the following conversions:
(i) Hexan-1-ol to hexanal (ii) Ethanenitrile to ethanal
[Hint: (i) $C_5H_5NH^+CrO_3Cl^-$ (PCC); (ii)(Di isobutyl) aluminium hydride (DIBAL-H)

****

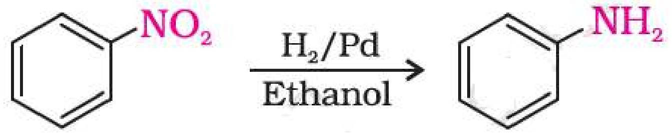
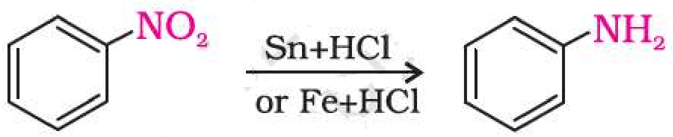
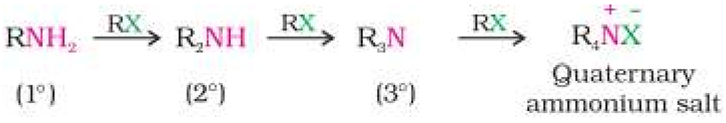
CHAPTER : 9 AMINES

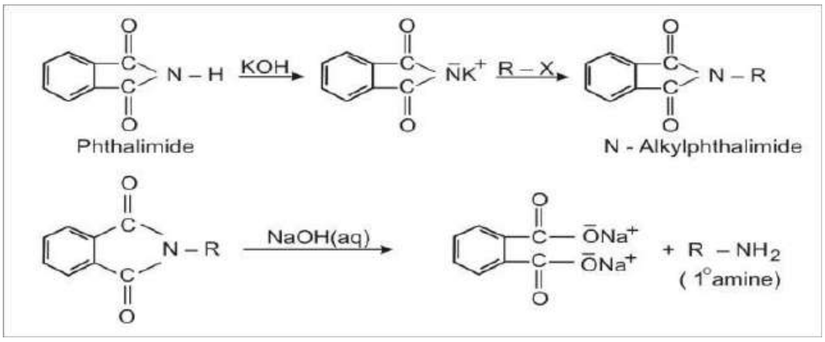
SUMMARY

1. Amines are alkyl / aryl derivatives of ammonia. In amines nitrogen atom is sp3 hybridized and contains one lone pair.
2. Amines can be classified as 10, 20 and 30 based on the number of hydrogen atom present on nitrogen.

1^0 Amine	2^0 Amine	3^0 Amine
 CH_3-NH_2 = Methanamine  $\underset{\underset{NH_2}{\vert}}{CH_3\text{-}CH\text{-}CH_3}$ Propan-2-amine	 CH_3-NH- CH_3 N-methylmethanamine	 $(CH_3)_3N$ N,N-dimethylmethanamine

➢ **PREPRATION OF AMINES**

. Reduction of Nitro compound gives aliphatic and aromatic amines (reducing agent Sn/HCl,Fe/HCl) Reduction with Fe/HCl is preferred as $FeCl_2$ is formed during reduction get hydrolyzed to release HCl	(i)  (ii) 
. **Ammonolysis of alkyl halides**: - Reagent: Ethanolic solution of ammonia.	 Disadvantage: Mixture of amines formed
. **Reduction of nitriles** Reducing agents: - $LiAlH_4$, H_2/Ni, Na/C_2H_5OH	$R-CN \xrightarrow{(H_2/Ni \text{ or } Na(Hg)/C_2H_5OH} R{-}CH_2NH_2$
. **By the reduction of amides**	$CH_3CONH_2 + (LiAlH_4 + H_2O) \rightarrow CH_3CH_2NH_2$

5. **Hoffmann bromamide** Reaction: An amide is heated with Bromine in aq. solution of NaOH/KOH gives primary amine.	$R - CONH_2 + Br_2 + 4NaOH \rightarrow R - NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$
6. **Gabriel phthalimide synthesis**: Only primary aliphatic amines are prepared by this method, primary aromatic amine cannot be prepared because aryl halides do not undergo substitution reaction.	

PHYSICAL PROPERTIES: (i) Primary amines are water soluble as H-bonding follows $1^0 > 2^0 > 3^0$.

(ii) The order of boiling points of isomeric amines is as follows:

Primary > Secondary > Tertiary (Directly depends on the extent of hydrogen bonding)

CHEMICAL PROPERTIES:

1. **Basic Nature-** Amines are basic in nature, it accepts proton from an acid.

- $3^0>2^0>1^0>NH_3$(Basic nature in gaseous phase)
- $2^0>3^0>1^0>NH_3$(Basic nature of ethyl substituted amines in aqueous phase)
- $2^0>1^0>3^0>NH_3$(Basic nature of Methyl substituted amines in aqueous phase)
- Aniline is weaker base than ammonia (Its pKb value is large, lone pair of electrons are involved in resonance)

Acetylation: Replacement of H-atom from $–NH_2$ or >NH by Acid chloride, anhydride and esters

$(C_2H_5)_2NH + CH_3COCl \rightarrow CH_3CON(C_2H_5)_2 + HCl$

3. **Reaction with Nitrous acid:** Forms aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols after reacting with water

4. **Reaction with Hinesberg reagent($C_6H_5SO_2Cl$): (Test for 1^0,2^0, and 3^0 amines)**

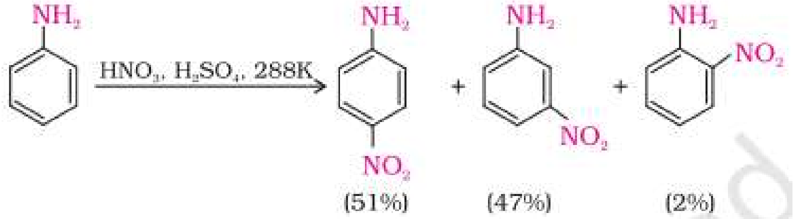
a. 1^0 amine forms a salt which is soluble in alkali
b. 2^0 amine forms a salt which is insoluble in alkali
c. 3^0amine do not react with Hinsberg reagent

5. **Carbylamine reaction: (i)** Primary aliphatic and aromatic amine reacts with chloroform and KOH to form alkyl/aryl isocyanides(foul smell compound distinguish test for primary amine from secondary and tertiary amine

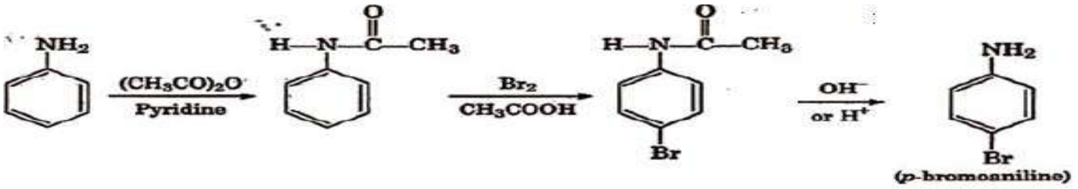
$$R\text{-}NH_2 + CHCl_3 + 3KOH \rightarrow R\text{-}NC + 3KCl + 3H_2O$$

6. **REACTIONS OF ANILINE**

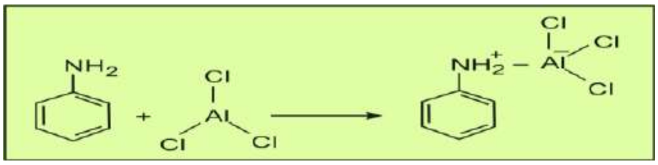
$–NH_2$ group is ortho and para directing and a powerful activating group. Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives.



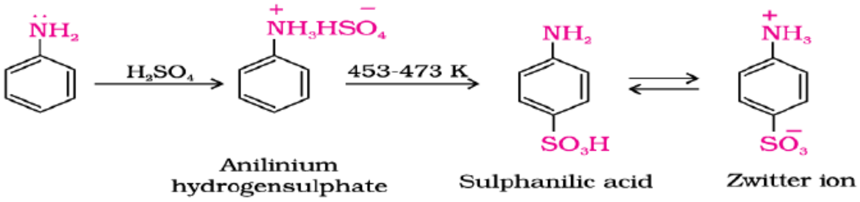
Aniline is converted into acetanilide by acetylation with acetic anhydride and then the desired substitution is carried out followed by hydrolysis the lone pair on nitrogen is less available for donation to benzene ring by resonance. Therefore, activating effect of -$NHCOCH_3$ group is less than that of amino group.



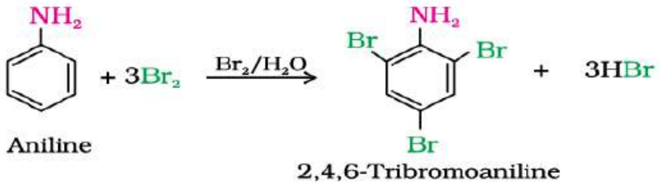
- Aniline do not undergo Friedel craft reaction as it forms salt with the catalyst $AlCl_3$



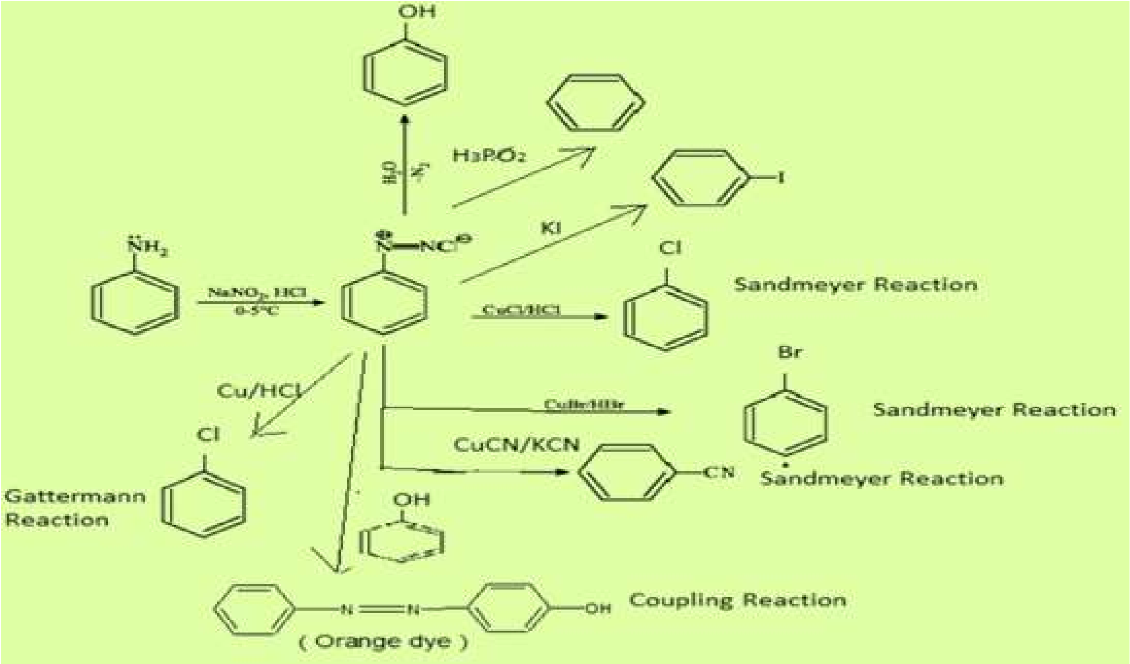
Sulphonation: Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate, which on heating at 453–473 K yields p-aminobenzene sulphonic acid (sulphanilic acid) as the major product.



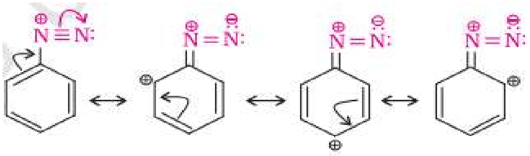
Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



7..REACTIONS OF BENZENE DIAZONIUM CHLORIDE



Note: Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K). The stability of arenediazonium ion is explained on the basis of resonance.



SECTION – A (1 Mark)

Q1. A compound which is formed when hydrogen gas is passed through nitrobenzene in the presence of finely divided nickel is…

(a) Aniline (b) 2-Nitroaniline (c) 3-Nitroaniline (d) 2,4- dinitroaniline

Q2. Aniline reacts with Br_2 water to give……

(a) 1-bromoaniline (b) 1,2- dibromoaniline (c) 2,4,6-tribromoaniline (d) No reaction

Q3. The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is…………….

(a) excess H_2 (b) Br_2 in aqueous NaOH

(c) iodine in the presence of red phosphorus (d) $LiAlH_4$ in ether

Q4**.** ……….. of the following compound will not undergo azo-coupling reaction with benzene diazonium chloride**?**

(a) Aniline (b) Phenol (c) Anisole (d) Nitrobenzene

Q5.The correct IUPAC for $CH_3CH_2CH_2NCH_3C_2H_5$ is……..

(a) N-methyl-N-ethylpropan-1-amine (c) N-ethyl-N-methylpropan-1-amine

(b) N,N diethylpropane-1-amine (d) N,N-dimethylpropan-1-amine

Q6. Raghu 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 (b) Hinsberg's Test

(c) Gabriel Phthalimide reaction (d) Carbylamine reaction

Q7. The correct increasing order of basic strength for the following compounds

(i) CH_3NH_2 (ii) $(CH_3)_2NH$ (iii) $C_6H_5NH_2$ (iv) NH_3

(a) i,ii,iii,iv (b) ii,iii,i,iv (c) iv,iii,i,ii (d) iii,iv,ii,i

Q8. Hinsberg's reagent is:

(a) Phenylisocyanide (b) p- toluenesulphonic acid

(c) benzensulphonyl chloride (d) o-dichlorobenzene

Q9.The conversion of benzene diazonium chloride to bromobenzene can be accomplished by

(a) Reimer-Tiemann reaction (b) Friedel-Crafts reaction

(c) Gattermann reaction (d) Azo-Coupling reaction

Q10. Identify the false statement about amines.

(a) Alkylamines are stronger bases than arylamines.

(b) Alkylamines react with nitrous acid to produce alcohols.

(c) Alkylamines are stronger bases than ammonia.

(d) Arylamines react with nitrous acid to produce phenols

The following questions has two statements; one is assertion and second is reason write;

(a) If assertion and reason both are true and R is correct explanation of A

(b)Assertion and reason both are correct but R is not the correct explanation

(c) A is true but R is false (d) A is false but R is true

Q11. ASSERSTION(A): Amines being basic in nature react with acids to form salt.

REASON(R): Aromatic amines are stronger bases than ammonia.

Q12. Assertion (A): Solubility of amines decreases with increase in the molar maas of amine.

Reason (R): The hydrophobic alkyl part increases with the increase in molar masses of amines.

Q13. ASSERTION(A): Gabriel phthalimide synthesis Is not used for the preparation of primary aromatic amines.

REASON(R): Aryl halide do not undergo substitution reaction.

Q14. ASSERTION(A): Hoffmann bromamide reaction is given by primary amines only.

REASON(R): Primary amines are more basic than secondary amines.

Q15. Assertion(A): Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (273-278 K).

Reason(R): Alkyldiazonium salt is more stable than arenediazonium salts

ANSWERS KEY:

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

SECTION - B (2 marks)

Q1.The -NH_2 group in aniline is acetylated before nitration, cite possible reason for it.

[Hint: Direct nitration of aniline gives tarry oxidation product]

Q2.Arrange the following in the increasing order of dipole moment.

(I)$CH_3CH_2CH_3$ (II)$CH_3CH_2NH_2$ (III) CH_3CH_3OH

[Hint: $CH_3CH_2CH_3 < CH_3CH_2NH_2 < CH_3CH_2OH$]

Q3.A compound Z with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid insoluble in alkali, identify Z

[Hint: 2^0 amine gives insoluble salt in alkali]

Q4.Write the structure and name of:

(a) The amide which gives propanamime by Hoffmann bromamide reaction

(b) The amine produced by Hoffmann degradation of Benzamide

[Hint: (a) Butanamide, (b) Aniline]

Q5.Give a chemical test to distinguish between the following pair of compounds

(a) Aniline & Methanamine (b) Ethanamine & N-methylethanamine

[Hint: a- azodye test, b- Carbyl amine or Hinsberg test]

SECTION – C (3 marks)

Q1. Arrange the following in increasing order of their basic strength:

(i) $C_2H_5NH_2$, $C_6H_5NH_2$, NH_3, $C_6H_5CH_2NH_2$ and $(C_2H_5)_2NH$

(ii) $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, $C_6H_5NH_2$

(iii) CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$, $C_6H_5NH_2$, $C_6H_5CH_2NH_2$.

[Hint:ref,NCERT Ch.9 q.n. 9.4]

Q2. Illustrate the following reactions:

(a) Sandmeyer's reaction

(b) Gabriel phthalimide reaction

(C) Carbylamine reaction

[Hint: ref summary]

Q3. Cite the reasons for the following :
(i) pK_b value for aniline is more than that for methylamine.
(ii) Ethylamine is soluble in water whereas aniline is not soluble in water.
(iii) Primary amines have higher boiling points than tertiary amines
[Hint: ref, Summary]

Q4. Predict the structure of A, B and C in the following reactions:

$$(i)\ CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiA/H_4} B \xrightarrow[0°C]{HNO_2} C$$

$$(ii)\ CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOH + Br_2} B \xrightarrow{CHCl_3 + Alc.KOH} C$$

[Hint: (i)A-CH_3CH_2CN, B-$CH_3CH_2CH_2NH_2$, C-$CH_3CH_2CH_2OH$]
(ii)A-CH_3CONH_2, B-CH_3CH_2OH ,C-CH_3CH_2NC

Q5. Identify and give names to the following reactions:
(a) $C_6HN_2Cl + CUCl + H^+ \rightarrow C_6H_5Cl$
(b) $CH_3CH_3NH_2 + CHCl_3 + KOH \rightarrow CH_3CH_3NC + KCl + H_2O$
(c) $C_6H_5CONH_2 + Br_2 + KOH \rightarrow C_6H_5NH_2 + KBr$
[Hint: a- Sandmeyers reaction, b- Carbylamine reaction c- Hoffmann rkn]

SECTION D Case Based Questions (4 Marks)

Q1. Read the following passage carefully and give answers of following questions:

Amines are alkyl or aryl derivatives of ammonia formed by replacement of one or more hydrogen atoms. Alkyl derivatives are called aliphatic amines and aryl derivatives are known as aromatic amines. The presence of aromatic amines can be identified by performing dye test. Aniline is the simplest example of aromatic amine. It undergoes electrophilic substitution reactions in which - NH_2 group strongly activates the aromatic ring through delocalization of lone pair of electrons of N-atom. Aniline undergoes electrophilic substitution reactions. Ortho and para positions to the -NH_2 group become centers of high electrons density. Thus,
-NH_2 group is ortho and Para-directing and powerful activating group.

(i) Aniline when treated with conc, HNO_3 and H_2SO_4 gives
(a) m-nitro Aniline (b) Phenylhydroxylamine (c) Nitrobenzene (d) p-Benzoquinone
(ii) Aniline on reaction with HNO_2 at 0 to 50c gives:
(a) Phenol (b) Nitrobenzene (c) Benzene (d) Benzene diazonium chloride
(iii) Cyclohexylamine and aniline can be distinguished by
(a) Azo dye test (b) Carbylamine test (c) Hinsberg test (d) Lassaigne test
(iv) Aniline do not undergo friedel craft reaction why?
[Hint: i-a, ii- d, iii-a,iv- Forms salt/adduct with $AlCl_3$]

Q2.Read the passage given below and answer the following questions:
The amines are basic in nature due to the presence of a lone pair of electron on N-atom of the -NH_2 group. Aliphatic amines are stronger bases than NH_3 because of the +I effect of the alkyl groups. Thus, the order of basic nature of amines is expected to be 3° > 2° > 1° (in gaseous phase), however the observed order is 2° > 1° > 3° (for Methyl substitution) and 20 > 30 >10(for ethyl substitution).This is explained on the basis of crowding on N-atom of the amine by alkyl groups which hinders the approach and bonding by a proton, consequently, the electron pair which is present on N is unavailable for donation. Aromatic amines are weaker bases than ammonia and aliphatic amines. Electron -donating groups such as -CH_3 , -OCH_3 , etc. increase the basicity while electron-withdrawing substitutes such as -NO_2 , -CN,

halogens, etc. decrease the basicity of amines. The effect of these substituents is more at p than at m-positions.

(i) Which one of the following is the strongest base in aqueous solution

(a) Methyl amine (b) Trimethylamine (c) Aniline (d) Dimethylamine

(ii) Choose the correct statement

(a) Methylamine is slightly acidic (b) Methylamine is stronger base than ammonia

(c) Methylamine is less basic than ammonia (d) Methylamine forms salt with alkali

(iii) The electron donating groups like $–OCH_3$,$-CH_3$ etc. increases basicity of amines, Comment on the statement.

(iv) The decreasing order of basicity of primary, secondary and tertiary ethylamines and NH_3 will be…….

(a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (b) $(C_2H_5)_3N> (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(c) $(C_2H_5)_2NH >C_2H_5NH_2 > (C_2H_5)_3N > NH_3$ (d) $(C_2H_5)_2NH> (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

[Hint: (i)-d,(ii)-b, (iii)-Resonance,(iv)-d]

SECTION –E (5 Marks)

Q1.a. complete the reactions:

(i) $CH_3CONH_2 + Br_2 + NaOH \rightarrow$………. + $Na_2CO_3 + H_2O$

(ii) ………. $\xrightarrow{\text{Pd, } H_2}$ $CH_3\text{-}CH_2\text{-}NH_2$ (iii) $CH_3CONH_2 \xrightarrow[\text{ii.} H_2O]{\text{i. } LiAlH_4}$

b. Illustrate the reactions with statement involved in Gabriel phthalimide reaction

[Hint: a i-CH_3NH_2,ii-$CH_3CH_2NO_2$,ii-$CH_3CH_2NH_2$: b- ref summary]

Q2. a. $C_6H_5N_2Cl$ reacts with the following reagents to give :

(i) $H_3PO_2 + H_2O$ (ii) CuCN/KCN (iii) H_2O

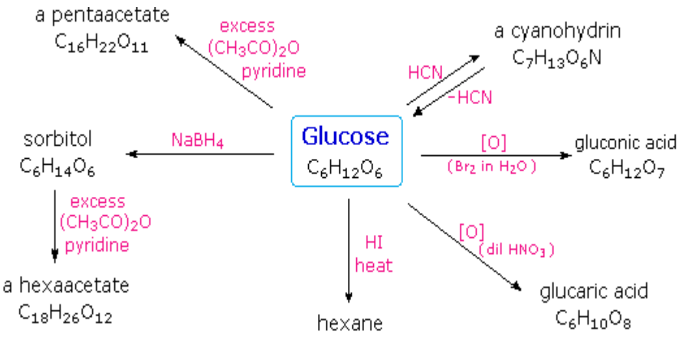
b.Complete the following reaction equations:

(i) $C_6H_5N_2Cl + C_6H_5OH \rightarrow$ (ii) $C_2H_5NH_2 + C_6H_5SO_2Cl \rightarrow$

[Hint: a. i-C_6H_6,ii-C_6H_5CN,iii- C_6H_5OH,b.i- p-hydroxyazobenzene ii-N-thylbenzenesulphonylchloride]

10 BIOMOLECULES

- **Monosaccharides** : Cannot be hydrolysed further to simpler molecules. Example: Glucose, fructose, Ribose etc.
- **Reactions of glucose (Open Chain structure):**



- **Reactions of glucose could not be explained by open chain structure.**

1. Glucose does not give Schiff's test and it does not form the hydrogensulphite.
2. The pentaacetate of glucose does not react with hydroxylamine (due to absence of free —CHO group.)
3. Glucose is found to exist in two different crystalline forms which are named as α and β.

Reducing sugars	**Non reducing sugars**
Aldehydic/ ketonic groups free so reduce Fehling's/ Tollens solution and. Eg- maltose and lactose.	Aldehydic/ ketonic groups are bonded so cannot reduce Fehling's solution and Tollens' reagent. Eg- Sucrose Anomers

Anomer: 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

Disaccharides: Hydrolysis, they generally give two monosaccharides unit. The linkage between two monosaccharide units through oxygen atom is called **glycosidic linkage**. Example:

Disaccharides	Monomers
(i) Sucrose	α-D-glucose and of β-D-fructose
(ii) Lactose	β-D-galactose and β-D-glucose.
(iii) Maltose	Two α-D-glucose

Polysaccharides: Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages.

Starch (i) Main storage of plants

(ii) polymer of α-glucose and consists of two components— Amylose and Amylopectin.

Amylose	**Amylopectin**
It is water soluble which constitutes about 15-20% of starch.	It is insoluble in water and constitutes about 80-85% of starch.
It is a long unbranched.	It is a branched chain polymer
α-D-(+)-glucose units held together by C1– C4 glycosidic linkage.	branching occurs by C1–C6 glycosidic linkage

Cellulose: it is the most abundant organic substance in plant kingdom and main constituents of cell wall.Cellulose is a straight chain polysaccharide composed only of β-D-glucose units which are joined by glycosidic linkage between C1 of one glucose unit and C4 of the next glucose unit.

Glycogen: The carbohydrates are stored in animal body as glycogen. It is also known as animal starch. It is present in liver, muscles and brain. It is polysaccharides of α-D glucose.

Proteins: All proteins are polymers of α-amino acids.

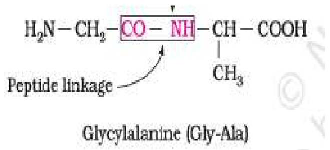
Amino Acids:

Essential amino acids	**Non- essential amino acids**
• which cannot be synthesised in the body and must be obtained through diet, • eg- Valine, Leucine.	• 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

(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.



Glycylalanine (Gly-Ala)

Primary (1^0) structure of proteins	**Secondary (2^0) structure of proteins**	**Tertiary (3^0) structure of proteins**
sequence of amino acids that is said to be the primary structure of protein.	(i) Secondary structure of protein refers to the shape in which a long polypeptide chain can exist. (ii) Exist in two types of structures viz. α -helix and β -pleated sheet structure and the binding force is hydrogen bond	**:** (i) Further folding of the secondary structure. It gives rise to two major molecular shapes viz. fibrous and globular. (ii) The main **forces** which stabilise the 3° structures of proteins are **hydrogen bonds, disulphide linkages, van der Waals and electrostatic forces of attraction**

Fibrous proteins	**Globular proteins**
Polypeptide chains run parallel and water insoluble.	Globular proteins chains of polypeptides coil around to give a spherical shape. water soluble.
Eg- are keratin(in hair, wool, silk) and myosin (present in muscles).	Eg-Insulin and albumins Stab.

Denaturation of Proteins: (i) 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.eg- The coagulation of egg white on boiling, curdling of milk
(ii) During denaturation 2° and 3° structures are destroyed but 1° structure remains intact.

Enzymes: Enzymes are essential biological catalysts which are required to catalyse biological reactions, e.g., maltase, lactase, invertase, etc. Almost all the enzymes are globular proteins

Vitamins: Organic compounds required in the diet in small amounts to perform specific biological functions for normal maintenance of optimum growth and health of the organism.

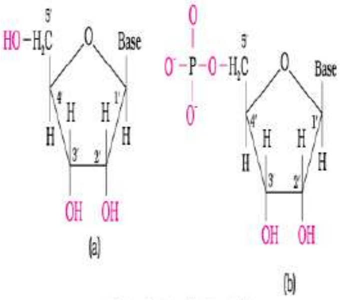
Fat soluble vitamins: These are vitamins A, D, E and K. They are stored in liver and adipose (fat storing) tissues.

Water soluble vitamins: Vitamin B, C. these vitamins must be supplied regularly in diet because they are readily excreted in urine and cannot stored in human body.

Vitamin	Deficiency diseases	Vitamin	Deficiency diseases
Vitamin A	Xerophthalmia (hardening of cornea of eye) Night blindness	Vitamin B6	Convulsions
Vitamin B1 (Thiamine)	Beriberi	Vitamin C(Ascorbic acid)	Scurvy (bleeding gums)
Vitamin B 2	Cheilosis	Vitamin D	Rickets, osteomalacia
Vitamin B12	Pernicious anaemia	Vitamin E	fragility of RBCs and muscular weakness
Vitamin K	Increased blood clotting time		

Nucleic acid

- Particles in nucleus of the cell, responsible for heredity, are called chromosomes which are made up of proteins and another type of biomolecules called nucleic acids.
- Two types of nucleic acid that is deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).nucleic acids are long chain polymers of nucleotides, so they are also called polynucleotides.
- Complete hydrolysis of DNA (or RNA) produces a pentose sugar, phosphoric acid, and nitrogen-containing heterocyclic compounds known as bases.
- A unit formed by the attachment of a base to $1^{'}$ position of sugar is known as nucleoside.When nucleoside is linked to phosphoric acid at $5^{'}$-position of sugar moiety, we get a nucleotide.

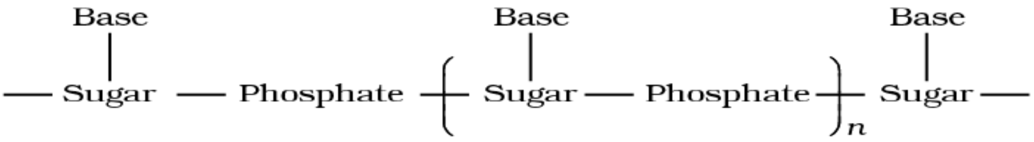


Structure of (a) a nucleoside and (b) a nucleotide

DNA	RNA
β-D-2-deoxyribose sugar is present.	**β-** b-D-ribose sugar is present
DNA contains four bases viz. adenine (A), guanine (G), cytosine (C) and thymine (T)	RNA also contains four bases adenine (A), guanine (G), cytosine (C) and uracil (U).
DNA has a double strand helix structure. The two strands are complementary to each other. The two strands held together by hydrogen bonds between pairs of bases	RNA has a single stranded **α-helix structure.** RNA molecules are of three types and they perform different functions. They are (i) messenger RNA(m-RNA), (ii) ribosomal RNA (r-RNA) and (iii) transfer RNA (t-RNA).
DNA has a unique property of replication	RNA usually does not replicate.
DNA controls the transmission of hereditary effects	RNA controls the synthesis of proteins.

Nucleotides are joined together by phosphodiester linkage between $5^{'}$ and $3^{'}$ carbon atoms of the pentose sugar.

A simplified version of nucleic acid chain is as shown below.



$$-\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}\left[\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-\text{Phosphate}\right]_n\overset{\text{Base}}{\overset{|}{\text{Sugar}}}-$$

SECTION - A (1 MARKS)

Q.1 The structure of glycogen is similar to __________.
(a) Amylose (b) Amylopectin (c) Cellulose (d) Glucose

Q.2 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.

Q.3 Which of the following acids is a vitamin?
(a) Aspartic acid (b) Ascorbic acid (c) Adipic acid (d) Saccharic acid

Q.4 Which of the following base is not present in RNA?
(a) Adenine (b) Uracil (c) Thymine (d) Cytosine

Q.5 Which of the following B group vitamins can be stored in our body?
(a) Vitamin B1 (b) Vitamin B2 (c) Vitamin B6 (d) Vitamin B12

Q.6 On hydrolysis, which of the following carbohydrates give glucose and fructose?
(a) Sucrose (b) Starch (c) Lactose (d) Maltose

Q.7 Curdling of milk is an example of
(a) breaking of peptide linkage (b) hydrolysis of lactose
(c) breaking of protein into amino acid (d) denaturation of protein

Q.8 Nucleosides are composed of
(a) a pentose sugar and phosphoric acid
(b) a nitrogenous base and phosphoric acid
(c) a nitrogenous base and a pentose sugar
(d) a nitrogenous base, a pentose sugar and phosphoric acid

Q.9 Which of the following naturally occurring α- amino acids is optically inactive?
(a) Glycine (b) Alanine (c) Leucine (d) Valine

Q10 Which carbon atoms of pentose sugar of nucleotides are Phosphodiesterlinkages present?
(a) 5’ and 3’ (b) 1’ and 5’ (c) 5’ and 5’ (d) 3’ and 3’

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

Q.11 ASSERTION – Vitamin C can’t be stored in our body.
REASON – Vitamin C is water soluble and is excreted from the body through urine.

Q.12 Assertion: Glycine must be taken through diet.
Reason: It is a non-essential amino acid.

Q.13 Assertion : Polysaccharides are called non-sugars.
Reason : Carbohydrates which yield a large number of monosaccharide units on hydrolysis are called polysaccharides.

Q.14 Assertion: Purine bases present in DNA are adenine and guanine
Reason: The base thymine is present in RNA while base uracil is present in DNA.

Q.15 Assertion: Two strands of DNA are complementary to each other.
Reason: Adenine form hydrogen bond with guanine whereas cytosine form hydrogen bond with thiamine.

Answer key:

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

SECTION –B (2 MARKS)

Q.1 Identify the main sugar found in milk and name the monosaccharide units it contains.

(Hint: Lactose, monomers- β –D – Glucose and β –D –Galactose)

Q.2 Sucrose is dextrorotatory but the mixture obtained after hydrolysis is laevorotatory. Explain.

(Hint: Invert Sugar)

Q.3 Compare (i) Nucleotides and Nucleosides (ii) Essential and Non- essential amino acids.

(Hint: refer to the summary of chapter)

Q.4 The iodine test is used to detect the presence of starch. Why does iodine specifically bind to starch, and how does this interaction lead to the characteristic blue-black coloration?

hint: Iodine molecules fit into the helical structure of amylose, a component of starch. This inclusion forms a starch-iodine complex, which absorbs light at specific wavelengths

Q.5 In which part of body and tissue fat soluble vitamins are stored?

{Hint: liver (adipose tissues)}

SECTION -C (3 MARKS)

Q.1 Which moieties of nucleosides are involved in the formation of phosphodiester linkages present in di-nucleotides? What does the word diester in the name of linkage indicate? Which acid is involved in the formation of this linkage?

(Hint: 3' –OH of one sugar and 5' – phosphate of the next sugar.phosphodiesterlinkage , acid involved Phosphoric acid .

Q.2I)The primary structure of a protein determines its three-dimensional shape. Evaluate how changes in the primary structure can lead to alterations in the protein's function.

II) Name the disease caused when valine replaces glutamic acid at the sixth position of the beta-globin chain of the haemoglobin.

Hint i)denaturation of proteinii)sickle cell anemia

Q.3 Activation energy for the acid catalysed hydrolysis of sucrose is 6.22 kJ mol–1 , while the activation energy is only 2.15 kJ mol–1 when hydrolysis is catalysed by the enzyme sucrase. Explain.

Hint-enzymes are bio catalyst ,reduce the magnitude of activation energy .

Q.4I)Structures of glycine and alanine are given below. Show the peptide linkage in glycylalanine.

$H_2N{-}CH_2{-}COOH \quad ; \quad H_2N{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}COOH$

(Glycine) (Alanine)

ii)α-Helix is a secondary structure of proteins formed by twisting of polypeptide chain into right handed screw like structures. Which type of interactions are responsible for making the α-helix structure stable?

Hint i)refer summary ii) hydrogen bonding

Q5i) Why does glucose not give a 2,4-DNP test despite having an aldehyde group?

II) Why is fructose a reducing sugar despite being a ketose?

Hint-i)glucose's aldehyde group is involved in the ring structure

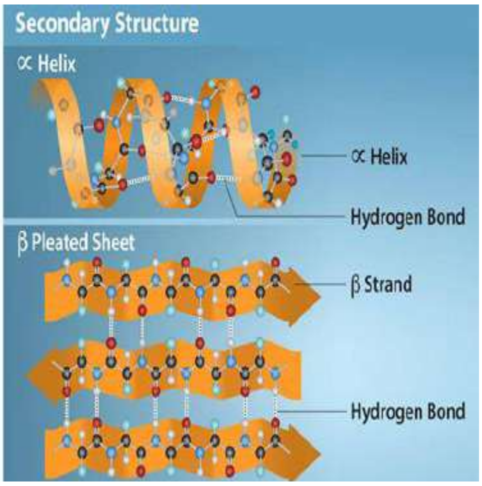
ii)Fructose contains a free aldehyde group

SECTION –D CASE STUDY BASED QUESTIONS (4 MARKS)

Read the passage carefully and answer the questions.

Q1.

Ridhima was reading her Chemistry textbook and came across the section on biomolecules. She learned that proteins are complex polymers made up of amino acids. She also read that proteins play vital roles in biological systems and that their function is determined by their structure. Curious, she asked her teacher how proteins like enzymes and hormones can be so specific in their action. Her teacher explained the four levels of protein structure and how peptide bonds, hydrogen bonds, disulfide bridges, and other interactions stabilize them.



(i) **Which of the following best describes the primary structure of a protein?**

a) 3D structure of protein b) Sequence of amino acids linked by peptide bonds

c) Helical or pleated arrangement d) Combination of several polypeptide chains

(ii) **The secondary structure of proteins includes:**

a) Only α-helix b) Only β-pleated sheet

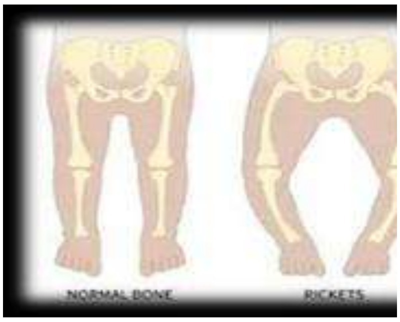
c) Both α-helix and β-pleated sheet d) Random folding of chain

(iii) Name the bonds that help to stabilize the tertiary level of protein structure.

Hint: (i) b (ii) c (iii) Hydrogen bonds, disulfide bonds, ionic interactions, and hydrophobic interactions.

Q2.

Meena lives in a region with limited sunlight during winter. Over time, she started feeling bone pain and muscle weakness. Her doctor diagnosed her with rickets, a disease related to bone development. The doctor explained that this condition is due to Vitamin D deficiency, often occurring when people don't get enough sunlight or consume insufficient vitamin D-rich foods like fish oil and fortified milk



(i) Identify the scientific name assigned to Vitamin D.

(ii) Is Vitamin D fat-soluble or water-soluble?

(iii)Name one deficiency disease caused by the lack of Vitamin D in adults and Suggest two food sources rich in Vitamin D.

Hint: (i). **Calciferol.**(ii). fat soluble

(iii). Osteomalacia ,Food sources**: Fish liver oil** and mushroom

LONG ANSWER TYPE QUESTIONS (5 MARKS)

Q.1i) Explain mutarotation of D-G lucose. ii) Predict the product when glucose reacts with

(a) HI (b) bromine water (c) HNO_3

Hint –I)$\alpha - D\ Glucose \leftrightharpoons open\ chain\ structure \leftrightharpoons \beta - D\ Glucose$

ii) a)n-hexane b) gluconic acid c) saccharic acid

QUESTION PAPER CLASS XII
CHEMISTRY THEORY (043)

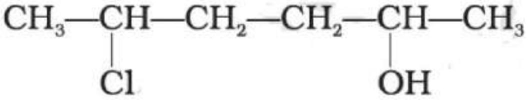
Max Marks:70 **Time: 3 hours**

(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 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.

Q.1 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 (b) 2-Hydroxy-5-chlorohexane
(c) 5-Chlorohexan-2-ol (d) 2-Chlorohexan-5-ol

Q 2. In order to make alcohol undrinkable pyridine or methanol are added to it. The resulting alcohol is called

(a) Power alcohol (b) Proof spirit
(c) Denatured spirit (d) Poison alcohol

Q.3. The positive value of the standard electrode potential of Cu2+/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 cannot displace H_2 from acid.

Q4. Which of the following is the right temperature coefficient (n) expression?

a) n = Rate constant at T + 10°/Rate constant at T°
b) n = Rate constant at T + 20°/Rate constant at T°
c) n = Rate constant at T + 30°/Rate constant at T°
d) n = Rate constant at T + 40°/Rate constant at T°

Q5. The reaction rate constant can be defined as the rate of reaction when each reactant's concentration is ……..

a) Zero b) Unity
c) Doubled the initial concentration d) Infinite

Q6 Which one is electrophilic reagent during nitration of aromatic compounds

a)NO_2^+ b) NO_3^-
c) NO_2 d) NO^+

Q.7. Lanthanoid contraction is due to increase in

a) Atomic number b) Effective nuclear charge
(c) Atomic radius d) Valence electrons

Q.8 Which of the following products are obtained when Na2CO3 is added to a solution of copper sulphate?

(a) Basic copper carbonate, sodium sulphate and CO2
(b) Copper hydroxide, sodium sulphate and CO2
(c) Copper carbonate, sodium sulphate and CO2
(d) Copper carbonate and sodium sulphate

Q.9.Which compound undergoes Cannizzaro reaction?

a) Ethanol b)Propanal c)Acetone d)Benzaldehyde

Q10.What is the product of the oxidation of a primary alcohol with PCC (pyridinium chlorochromate)?

a))Aldehyde b)Ketone c) Carboxylic acid d) Alcohol

Q.11. RNA lacks the nitrogen base of
a)Thymine b) Cytosine
b)Uracil c)Adenine

Q.12.The acylation reaction of amines is carried out in presence of pyridine because
(a) Pyridine is absorbed ammonia formed.
(b) Pyridine is weaker base than amine.
(c) Pyridine is stronger base than amine and it removes HCl formed and shifts the equilibrium to the right hand side.
(d) Pyridine removes HCl formed and shifts the equilibrium to the left hand side.

Q.13.Assertion: Aldehydes are generally more reactive than ketones towards nucleophilic addition reactions.
Reason: Aldehydes have a more electrophilic carbonyl group due to the presence of an H atom, making them more susceptible to nucleophilic attack.
(a) Both Assertion and Reason are true and the reason is the correct explanation of assertion.
(b) Both Assertion and Reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true

Q.14.Assertion: Amino acids are amphoteric in their function.
Reason: All amino acids are necessary for our body.
(a) Both Assertion and Reason are true and the reason is the correct explanation of assertion.
(b) Both Assertion and Reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true

Q 15. Assertion : boiling points of alcohols are much higher than those of alkanes, halo alkanes or ethers of comparable molecular masses.
Reason : Strong intermolecular hydrogen bonding exists in Alcohols.
(a) Both Assertion and Reason are true and the reason is the correct explanation of assertion.
(b) Both Assertion and Reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true

Q.16 Assertion : Mercury cell does not give steady potential.
Reason : in the cell reaction, ions are not involved in solution.
(a) Both Assertion and Reason are true and the reason is the correct explanation of assertion.
(b) Both Assertion and Reason are true but the reason is not the correct explanation of assertion.
(c) Assertion is true but Reason is false.
(d) Assertion is false but Reason is true

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.

Q.17.H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Q18. Radioactive decay follows first - order kinetics. The initial amount of two radioactive elements X and Y is 1 gm each. What will be the ratio of X and Y after two days if their half-lives are 12 hours and 16 hours respectively? .

Q.19.Arrange the following compounds in increasing order of their property as indicated(**any two**):
(i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4- Methoxybenzoic acid (acid strength)

Q.20. Define the following as related to proteins
(i)Peptide linkage (ii) Denaturation.

Q.21 Write structures of different dihalogen derivatives of propane.

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.

Q.22 The molar conductivity of 0.025 mol L^{-1} methanoic acid is 46.1 S cm2 mol−1. Calculate its degree of dissociation and dissociation constant. Given λ ° (H+) = 349.6 S cm2 mol−1 and λ ° ($HCOO^-$) = 54.6 S cm^2 mol.

Q.23 The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N2O5 is 2.33 mol L–1 and after 184 minutes, it is reduced to 2.08 mol L–1. The reaction takes place according to the equation

$$2\ N_2O_5\,(g) \rightarrow 4\ NO_2\,(g) + O_2\,(g)$$

Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?

Q.24. Draw the structures of all the eight structural isomers that have the Molecular formula $C_5H_{11}Br$. Name each isomer according to IUPAC system and classify them as primary, secondary or tertiary bromide.

Q.25.An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Q.26 (a)Write the mechanism of Acid catalyzed hydration of Alkene to Alcohol.

(b)Give a chemical test to distinguish between the following pair of compounds.

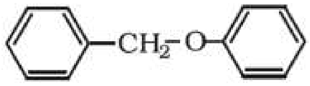
1-Propanol and ethanol

OR

(a)While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

(b) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

(c) Give major products that are formed by heating of the following ethers with HI



Q.27 What happens when D-glucose is treated with the following reagents?

(i) HI (ii) Bromine water (iii) HNO_3

Q.28- Explain the nature of bonding(hybridization ,magnetism & spin) in the following coordination entities on the basis of valence bond theory: $[Co(NH_3)_6]^{3+}$

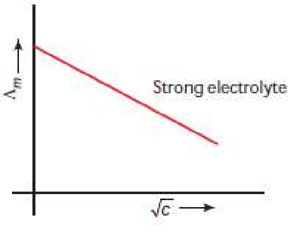
SECTION D

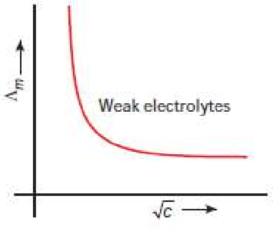
The following questions are case -based questions. Each question has an internal choice and carries 4 (1+1+2) marks each. Read the passage carefully and answer the questions that follow.

Q.29. Case Based Question

Read the passage given below and answer the questions that follow

The conductivity or specific conductivity of an electrolytic solution varies with the concentration of the solutions of different electrolytes. For comparing the conductances of the solutions of different electrolytes, it is essential that the solutions should have equal volumes and they must contain definite amount of the electrolytes which give ions carrying the same total charge. The conducting power of an electrolytic solution can be expressed in terms of equivalent conductance and molar conductance. The equivalent conductance of a solution does not vary linearly with concentration and it is related with specific conductance. The effect of equivalent conductance can be studied by plotting values against the square root of the concentration. Following two figures show the behaviour of strong and weak electrolytes with change of concentration.





(a). Write the relationship between specific conductivity and molar conductivity?

(b). Which equation gives the relationship between equivalent or molar conductivity and concentration of a strong electrolyte?

(c). What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte and strong electrolyte

OR

The conductivity of a 0.20M solution of KCl at 298K is 0.0248 S cm^{-1}. Calculate molar conductivity.

Q 30 . **Read the passage given below and answer the questions that follow**

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 systems, industry and medicine, Formation of coordination compounds is largely used in analytical chemistry for the qualitative detection and quantitative estimation of metal ions. Coordination compounds also find several important applications in the field of medicine. Several coordination compounds are also used as antidote to poisoning caused by the ingestion of poisonous metals by human beings.

Answer the following questions:

(i) Which complexing material is added to vegetable oils to remove the ill effects of undesired metal ions?

(ii) Which complex is used in the treatment of cancer?

(iii) How would you detect the presence of nickel in a food sample?

OR

What is Chelation therapy?

SECTION E

The following questions are long answer type and carry 5 marks each. All questions have an internal choice.

Q.31 a) Explain giving reasons:

(i)Actinides contraction is greater from element to element than lanthanoids contraction.

(ii)The enthalpies of atomization of the transition metals are high.

(iii)The transition metals generally form coloured compounds.

(b) write ionic equation of: acidified permanganate solution react with (i) iron (II) ions (ii) oxalic acid

OR

a) Indicate the steps in the preparation of $K_2Cr_2O_7$ from chromite ore.

b) Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) Iodide (ii) H_2S Write the Ionic equations.

Q32(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.

(b) Arrange the following:

(i)In decreasing order of the pKb values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii)In increasing order of boiling point:

C_2H_5OH,$(CH_3)_2NH$,C_2H_5NH

OR

(a) Aniline does not undergo Friedel-Crafts reaction.

(b) Aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis?

(c)Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(d).Accomplish the following conversions:

(i) Aniline to p-bromoanilineBenzamide to Benzene

Q.33.(a) Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of acid if the density of the solution is 1.504 g mL^{-1} ?.

(b)(i) Why is glycol and water mixture used in car radiators in cold countries?

(ii)Aquatic species are more comfortable in cold waters rather than in warm waters. Why

OR

(a) Calculate the mass of a non-volatile solute (molar mass 40g $mol^{-1)}$ which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

(b) What are Azeotropes? Give one example each of minimum boiling and maximum boiling azeotropes.

Model question paper 2
CHEMISTRY THEORY(043)

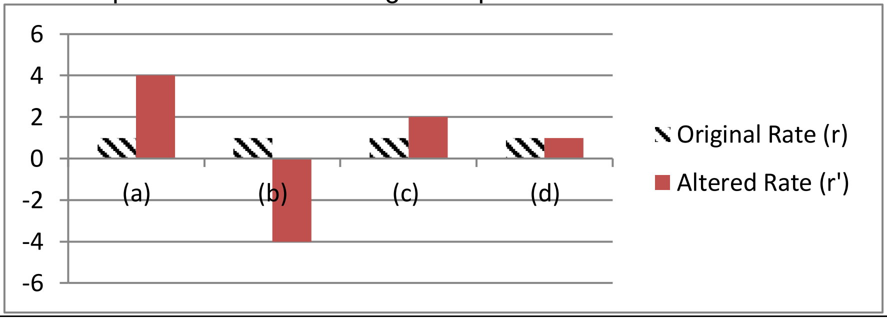
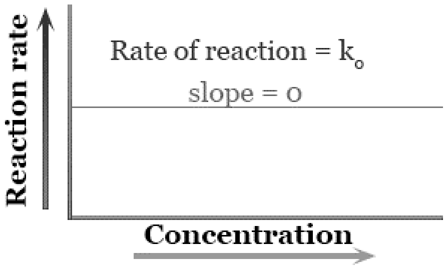
MM:70 **Time: 3 hours**

General Instructions:

(a) There are 33 questions in this question paper with internal choice.
(b) **SECTION A** comprises **16** multiple -choice questions carrying 1 mark each.
(c) **SECTION B** comprises **5** short answer questions carrying 2 marks each.
(d) **SECTION C** comprises **7** short answer questions carrying 3 marks each.
(e) **SECTION D** comprises **2** case - based questions carrying 4 marks each.
(f) **SECTION E** comprises **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	The charge required for the reduction of 1 mol of MnO_4^- to Mn^{2+} is :		1
	(a) 1 F	(b) 3 F	
	(c) 5 F	(d) 6 F	
2	For the reaction, $A + 2B \longrightarrow AB_2$, the order w.r.t. reactant A is 2 and w.r.t. reactant B is 1. What will be change in rate of reaction if the concentration of A is doubled and B is halved? Choose the correct option from the following chart pattern  		1
3	The following graph represents  		1
	(a) Zero order reaction	(b) First order reaction	
	(c) Second order reaction	(d) Third order reaction	
4	Which of the following has magnetic moment value of 1.73 BM ?		1
	(a) Fe^{2+} (Z= 26)	(b) Fe^{3+}(Z= 26)	
	(c) Ni^{2+}(Z= 28)	(d) Cu^{2+}(Z= 29)	
5	Which of the following **is a bidentate ligand?**		1
	(a) Br^-(Bromide ion)	(b) CH_3NH_2	
	(c) $C_2O_4^{2-}$	CH_3CN	
6	The complex ions $[Co(NH_3)_5(NO_2)]^{2+}$ and $[Co(NH_3)_5(ONO)]^{2+}$ are called :		1

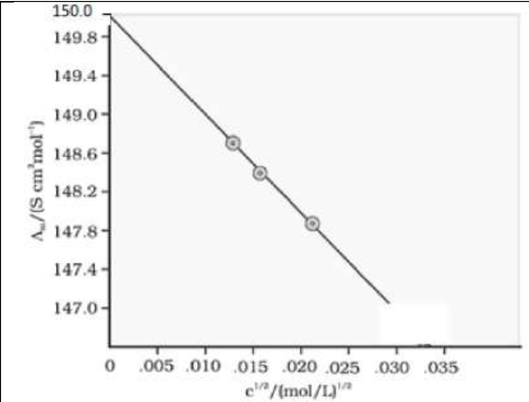
	(a) Ionization isomers	(b) Linkage isomers	
	(c) Co-ordination isomers	(d) Geometrical isomers	
7	Which of the following haloalkanes has the highest boiling point?		1
	2-Bromo-2-methylpropane	(b)2-Bromobutane	
	(c) Bromomethane	(d) 1-Bromobutane	
8	Picric Acid is prepared by treating Phenol with Conc. Sulphuric acid followed by Conc. Nitric acid. What is the correct IUPAC name of Picric acid :		1
	(a) 3-nitroophenol	(b) 4-nitrophenol	
	(c) 4,6-dinitrophenol	(d) 2,4,6-trinitrophenol	
9	Lucas Test : The Lucas test is a chemical test that uses Lucas reagent to distinguish between primary, secondary, and tertiary alcohols  The alcohol which does not react with Lucas reagent is :		1
	(a) 2-Methylpropan-2-ol	(b) 2-Methylbutan-2-ol	
	(c) 3-Methylbutan-2-ol	(d) 3-Methylbutan-1-ol	
10	Iodoform test is ***not***given by :		1
	(a) Propan-2-ol	(b) Ethanal	
	(c) Pentan-2-one	(d) Pentan-3-one	
11	Out of the following, the strongest base is **(in aqueous phase)** :		1
	(a) Methylamine ($pK_b = 3.38$)	(b) Dimethylamine ($pK_b = 3.27$)	
	(c) Trimethylamine ($pK_b = 4.22$)	(d) Aniline ($pK_b = 9.38$)	
12	Ammonolysis of benzyl chloride and reaction of amine so formed with one mole of CH_3Cl , gives an amine that		1
	(a) Reacts with Hinsberg reagent to form a product soluble in an alkali.	(b) On reaction with Nitrous acid, produced nitrogen gas	
	(c) Reacts with Benzenesulphonyl chloride to form a product that is insoluble in alkali.	(d) Does not react with Hinsberg reagent.	
13	Given below are two statements labelled as Assertion (A) and Reason (R) **Assertion: There is a continuous decrease in size among lanthanoids , called as Lanthanoid contraction .** **Reason : Lanthanoid contraction is less than actinoid contraction.** Select the most appropriate answer from the options given below:		1
	(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.	

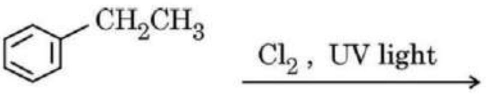
	(c) A is true but R is false.	(d) A is false but R is true.	
14	Given below are two statements labelled as Assertion (A) and Reason (R) **Assertion (A): An ether is more volatile than an alcohol of comparable molecular mass.** **Reason (R): Ethers are polar in nature.** Select the most appropriate answer from the options given below:		1
	(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.	
15	Given below are two statements labelled as Assertion (A) and Reason (R) **Assertion (A): Tertiary amines are more basic than corresponding secondary and primary amines in gaseous state.** **Reason (R): Tertiary amines have three alkyl groups which cause +I effect.** Select the most appropriate answer from the options given below:		1
	(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.	
16	Given below are two statements labelled as Assertion (A) and Reason (R) **Assertion (A) :Sucrose is a non-reducing sugar.** **Reason (R) :InSucrose two monosaccharide units are linked by glycosidic linkage.** Select the most appropriate answer from the options given below:		1
	(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.	
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 first-order reaction takes 77.78 min for 50% completion. What is the time required for 30% completion of this reaction. (Given: log 10 = 1, log 7 = 0.8450, log 2 = 0.3010)		2
18	Account for the following: (a) There are 5 OH groups in glucose (b) Glucose is a reducing sugar **OR** What happens when D – (+)– Glucose is treated with the following reagents (a) Bromine water (b) HCN		1 1 1 1
19	(a) Arrange the following alkyl halide in the increasing order of reactivity towards S_N^2 reaction 2-Bromopentane, 2-Bromo-2-methylbutane, 1-Bromopentane (b) Write the compound which is optically active (chiral) in the question 19 (a).		1 1
20	When a co-ordination compound $CrCl_3.6H_2O$ is mixed with $AgNO_3$, 2 moles of $AgCl$ are precipitated per mole of the compound. Write		1 1

	(a) Structural formula of the complex. (b) IUPAC name of the complex.	
21	Write the IUPAC name of the final product and reaction involved when Propanal is treated with Methyl magnesium bromide followed by hydrolysis.	**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	The following figure , represents variation of (Λ_m) vs √c for an electrolyte. Here $\mathbf{\Lambda_m}$is the molar conductivity and **c** is the concentration of the electrolyte.  (a) Identify the nature of electrolyte on the basis of the above plot. Justify your answer. (b) Determine the value of Λ^O_m for the electrolyte. (c) Write the relationship betweenΛ^O_m **,** Λ_m and concentration of strong electrolyte.	1 1 1
23	The rate constants of a reaction at 500K and 700K are $2 \times 10^{-2}\ s^{-1}$ and $4 \times 10^{-2}\ s^{-1}$ respectively. Calculate the values of $E_{a.}$ (log 2 = 0.3010, log 4 = 0.6020 , R = 8.314 J/mol.K)	3
24	Carry out the following conversions : (a) Phenol to Salicylaldehyde (b) t-Butylchloride to t-butyl ethyl ether (c) Propene to Propan-2-ol	1 1 1
25	Using Valence bond theory, explain the following in relation to the complex $[Mn(L)_6]^{3-}$ **($\triangle_o$ > P)** (L = Monodentate Ligand with one unit negative charge) (a) Type of hybridization (b) Magnetic property (c) Type of complex (inner or outer orbital complex)	1 1 1
26	Answer the following questions: (a) Explain why are the tanks used by scuba divers filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen)? (b) When 2.5 g of a nonvolatile solute was dissolved in 50 gm of water, it gave boiling point elevation of $0.52\ ^{O}C$. Find the molar mass of the solute. (K_b for Water = 0.52 Km^{-1})	1 2
27	Give the structures of **A** and **B** in the following sequence of reactions : (a) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B$ (b) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[0^O-5^O C]{NaNO_2+HCl} B$ (c) $C_6H_5N_2^+Cl^- \xrightarrow[\Delta]{CuCN} A \xrightarrow{H_2O/H^+} B$	1 1 1
28	(a) Identify the major product formed when 2-cyclohexylchloroethane undergoes a dehydrohalogenation reaction in the presence of alcoholic KOH. (b) Why is chloroethane participate in nucleophilic substitution reaction but chlorobenzene does not ? (c) Chlorobenzene reacts with CH_3Cl in the presence of $FeCl_3$ giving ortho and para chloro compounds. Write the IUPAC name of one of the product.	1 1 1

	OR (a) Write the major product in the reaction :  (b) Identify **A and B** in the following: 1-Bromo-2-methylpropane + Alcholic KOH →**A** + HBr →**B** (Major)	1 2
	ECTION D **The following questions are case -based questions. Each question has an internal choice and carries 4 marks.**	
29	When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law. The osmotic pressure of a solution is the excess pressure that must be applied to asolution to prevent osmosis, i.e., to stop the passage of solvent molecules through a Semipermeable membrane into the solution. Osmotic pressure is colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity (Mole/litre), C of the Solution at a given temperature T. Thus: **Π = C R T**, Here Π is the osmotic pressure and R is the gas constant. Π = (n / V) RT (a) Define ideal solution. (b) What kind of deviation is found in solution of alcohol in water? **OR** Why Osmotic Pressure is used to measure the molar mass of biomolecules? (c) 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.	1 1 2
30	The carbohydrates may also be classified as either reducing or nonreducing sugars. All those carbohydrates which reduce Fehling's solution and Tollens' reagent are referred to as reducing sugars. All monosaccharides whether aldose or ketose are reducing sugars. Fructose also has the molecular formula $C_6H_{12}O_6$ and on the basis of its reactions it was found to contain a ketonic functional group at carbon number 2 and six carbons in straight chain as in the case of glucose. It belongs to D-series and is a laevorotatory compound. It is appropriately written as D-(–)-fructose. Its open chain structure is as shown. Polysaccharides contain a large number of monosaccharide units joined together by glycosidic linkages. These are the most commonly encountered carbohydrates in nature. They mainly act as the food storage or structural materials. Protein found in a biological system with a unique three-dimensional structure and biological activity is called a native protein. When a protein in its native form, is subjected to physical change like change in temperature or chemical change like change in pH, the hydrogen bonds are disturbed. (a) Sucrose cannot reduce the Tollen's reagent .why? (b) The optical activity of sucrose is changed to from dextro to leavo after sometime. Explain it. (c) What is denaturation of protein? Which structure of protein remains intact during denaturation? **OR** What is the significance of D and L and + and - sign in sugars.	1 1 2
	SECTION E **The following questions are long answer type and carry 5 marks each. All questions have an internal choice**	
31	**(a)** Account for the following : (i) Copper (I) compounds are white whereas Copper (II) compounds are coloured. (iii) Zn, Cd, Hg are considered as d-block elements but not as transition elements. **(b)** Give reason:	1 1 1 1

	(i) Sc^{3+} (Exhibit diamagnetic behavior) (ii) Cr (High melting point) **(c)** Complete the reaction: MnO_4^{2-} + SO_3^{2-} + $H^+ \rightarrow$ **OR** When a chromite ore (A) is fused with sodium carbonate in free excess of air and the product is dissolved in water, a yellow solution of compound (B) is obtained. After treatment of this yellow solution with sulphuric acid, compound (C) can be crystallized from the solution. When compound (C) is treated with KCl, orange crystals of compound (D) crystallise out. Identify A to D and also explain the reactions.	1
32	A hydrocarbon (A) with molecular formula C_5H_{10} on ozonolysis gives two products (B) and (C). Both (B) and (C) give a yellow precipitate when heated with iodine in presence of NaOH while only (B) give a silver mirror on reaction with Tollen's reagent. (a) Identify (A), (B) and (C). (b) Write the reaction of B with Tollen's reagent (c) Write the equation for iodoform test for C (d) Write down the equation for aldol condensation reaction of B and C. **OR** An organic compound (A) with molecular formula $CH_3CH\ (Cl)CO_2H$ is obtained when (B) reacts with Red P and Cl_2. The organic compound (B) can be obtained on the reaction of ethyl magnesium chloride with dry ice followed by acid hydrolysis. (a) Identify B . (b) Write down the reaction for the formation of A from B. (c) Give any one method by which organic compound B can be prepared from its corresponding acid chloride. (d) Which will be the more acidic compound (A) or (B) ? (e) Write down the reaction to prepare Ethane from the compound (B).	1 1 1 2 1 1 1 1 1
33	Consider the foloowing redox reaction taking place in an Electrochemical Cell $Mg(s) + Cu^{2+}_{(0.01\ M)} \longrightarrow Mg^{2+}_{(0.001\ M)} + Cu(s)$ $E^O_{cell} = 2.71\ V$ (a) Calculate E_{cell} for the reaction. (b) Write Cell representation of above cell reaction. (c) Write the direction of flow of current when an external opposite potential applied is more than 2.71 V. **OR** (a) What is the role of zinc chloride in dry cell? (b) $\Lambda^o m$ for NaCl, HCl and NaAc are 126.4, 425.9 and 91.0 S cm^2/mol respectively. Calculate Λ^o m for HAc. (c) Write the chemical reactions taking place at the electrodes during discharging of lead storage battery.	3 1 1 1 3 1

CBSE QUESTION PAPER 2025
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) This 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

1. Which of the following is a polysaccharide ?

(A) Maltose (B) Glucose (C) Cellulose (D) Sucrose

2. The Gabriel Phthalimide Synthesis is used for the preparation of

(A) Secondary amines (B) Primary aromatic amines

(C) Tertiary amines (D) Primary aliphatic amines

3. The compound which undergoes dehydration most easily is

(A) 2-Methylpropan –2– ol (B) Ethanol

(C) 2-Methylbutan –2– ol (D) Propan –1– ol

4. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as

(A) an addition reaction (B) a substitution reaction

(C) a dehydrohalogenation reaction (D) a dehydration reaction

5. Which of the following transition metals does not show variable oxidation states ?

(A) Cu (B) Sc (C) Ti (D) Fe

6. An azeotropic mixture of two liquids has a boiling point higher than that of either of the two liquids when it

(A) obeys Raoult's law. (B) shows positive deviation from Raoult's law.

(C) shows negative deviation from Raoult's law. (D) obeys Henry's law.

7. Kohlrausch gave the following relation for strong electrolytes at low concentration :

$\Lambda_m = \Lambda_m{}^o - A\sqrt{C}$ Which of the following equality holds true ?

(A) $\Lambda_m = \Lambda_m^0$ as $C \rightarrow \sqrt{A}$ (B) $\Lambda_m = \Lambda_m^0$ as $C \rightarrow 0$

(C) $\Lambda_m = \Lambda_m^0$ as $C \rightarrow \infty$ (D) $\Lambda_m = \Lambda_m^0$ as $C \rightarrow 1$

8. The rate of reaction X + Y → products, is given by the equation

Rate = k[X] [Y].

If Y is taken in large excess, the order of the reaction would be

(A) 0 (B) 1 (C) 2 (D) ½

9. The synthesis of alkyl fluoride is best accomplished by

(A) Sandmeyer reaction (B) Finkelstein reaction (C) Wurtz reaction (D) Swarts reaction

10. Benzene diazonium chloride on hydrolysis gives

(A) Chlorobenzene (B) Phenol (C) Anisole (D) Aniline

11. Solubility of gases in liquid decreases with increase in

(A) pressure (B) volume (C) number of solute particles (D) temperature

12. Δ_rG^o and E_{cell}^o for a spontaneous reaction will respectively be

(A) positive and positive (B) positive and negative

(C) negative and positive (D) negative and negative

For question 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 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) : Zinc is not regarded as a transition element.

Reason (R) : Zinc has completely filled 3d orbitals in its ground state as well as in its oxidised state.

14. Assertion (A) : In a first order reaction, if the concentration of the reactant is doubled, its half-life is also doubled.

Reason (R) : The half-life of a reaction does not depend upon the initial concentration of the reactant in a first order reaction.

15. Assertion (A) : $(CH_3)_3C–O–CH_3$ gives $(CH_3)_3C–I$ and CH_3OH on treatment with HI.

Reason (R) : The reaction occurs by S_N1 mechanism.

16. Assertion (A) : Nucleophilic substitution reaction of chlorobenzene is easier than that of chloroethane.

Reason (R) : C – Cl bond in chlorobenzene has partial double bond character due to resonance.

SECTION – B

17. (a) Why does the cell potential of mercury cell remains constant throughout its life ?) of CH3α

(b) Calculate the degree of dissociation (α) of CH_3COOH if Λ_m and Λ_m^o of CH_3COOH are 50 S $cm^2\ mol^{-1}$ and 400 S $cm^2\ mol^{-1}$ respectively.

18. Using the E^0 values of P and Q, predict which one is better for coating the surface of iron $E^0_{(Fe2+/Fe)}$ = –0.44 V] to prevent corrosion and why ?

$E^0_{(P^{2+}/P)} = -2.37\ V,\ E^0_{(Q^{2+}/Q)} = -0.14\ V$

19. 19. (a) A reaction is second order in ‘A’ and first order in ‘B’. How is the rate affected when the concentrations of both ‘A’ and ‘B’ are doubled ?

(b) Write the unit of ‘k’ for zero order reaction.

20. 20. (a) How do you convert the following ?

(i) Ethanenitrile to Ethanamine

(ii) Benzenediazonium chloride to benzonitrile

OR

(b) (i) Write a simple chemical test to distinguish between ethanamine and dimethylamine.

(ii) What happens when CH_3CONH_2 is heated with Br_2 and an aqueous solution of NaOH ?

21. What is the effect of denaturation on the structures of protein ? Give one example each of fibrous protein and globular protein.

SECTION – C

22. What happens when

(a) Ethanal is treated with CH_3MgBr followed by hydrolysis ?

(b) Phenol is treated with Zinc dust?

(c) Anisole is treated with HI?

23. The rate constant of a first order reaction increases from 0.04 s^{-1} to 0.08 s^{-1} when the temperature increases from 27 ^oC to to 37 ^oC. Calculate the energy of activation (Ea).

[Given : 2.303R = 19.15 $JK^{-1}mol^{-1}$]

[log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021]

24. Give reactions for the following :

(i) Aniline does not undergo Friedel – Crafts reaction.

(ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution.

(iii) Ethyl amine is soluble in water whereas aniline is insoluble.

25.. (a) When a co-ordination compound $CoCl_3.6NH_3$ is mixed with excess of $AgNO_3$ solution, 3 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex

(ii) IUPAC name of the complex

iii) Hybridization of the complex using valence bond theory [Atomic number: Co = 27]

OR

(b) (i) Write IUPAC name of $[Pt(NH_3)_2Cl(ONO)]$.

(ii) Why $[Co(en)_3]^{3+}$ is more stable complex than $[Co(NH_3)_6]^{3+}$?

(iii) Predict the hybridization of $[Ni(CO)_4]$ on the basis of valence bond theory. [Atomic number : Ni = 28]

26. Explain the following reactions :

(a) Rosenmund's Reduction (b) Cannizzaro's reaction (c) Hell-Volhard Zelinsky reaction

27. Calculate Δ_rG° and log K_C for the following cell at 25 ^oC:

$$Zn/Zn^{2+} \parallel Cd^{2+}/Cd$$

$$\text{Given that : } E^0_{Zn^{2+}/Zn} = -0.76 \text{ V}, \ E^0_{Cd^{2+}/Cd} = 0.40 \text{ V}$$

$$1 \text{ F} = 96500 \text{ C mol}^{-1}.$$

28. Define Racemization. Out of S_N1 and S_N2 reactions, which is accompanied by racemization?

Give reason in support of your answer.

SECTION – D

The following questions are case based questions. Each question has an internal choice and carries 4 (2 + 1 + 1) marks each. Read the passage carefully and answer the questions that follow :

29. Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups –

monosaccharides, oligosaccharides and polysaccharides. Monosaccharides are held together by glycosidic linkage to form disaccharides like sucrose, maltose.

Another biomolecule : proteins are polymers of α-amino acids which are linked by peptide bonds. On the basis of number of amino group and carboxyl group, amino acids are classified as acidic, basic or neutral amino acids. Amino acids are amphoteric in nature.

(a) What is difference between glycosidic linkage and peptide linkage ? The pentacetate of glucose does not react with Hydroxyl amine. What does it indicate ?

(b) Define Oligosaccharides with an example.

OR

(b) Why amino acids are amphoteric in nature ?

(c) Define Acidic amino acids.

30. Werner proposed the concept of a primary valence and a secondary valence for a metal ion. The primary valences are normally ionisable and are satisfied by negative ions. The secondary valences are non-ionisable. These are satisfied by neutral molecules or negative ions. The secondary valency is equal to the co-ordination number and is normally fixed for a metal. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of co-ordination compounds whereas the Crystal Field Theory (CFT) is based on the effect of different crystal fields on the degeneracy of d orbitals energies of the central metal atom / ion.

(a) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why? [Atomic number : Cr = 24, Ni = 28]

(b) Write one difference between a primary valence and a secondary valence.

(c) What is crystal field splitting energy ?

OR

(c) On the basis of CFT, write the electronic configuration of d^4 orbitals when $\Delta_o > P$.

SECTION – E

31. (A) (a) Account for the following :

(i) Transition metals and their compounds show catalytic activities.

(ii) Mn^{3+} is a strong oxidising agent.

(iii) Cu^+ is not stable in aqueous solution.

(b) Write the preparation of $KMnO_4$ from Pyrolusite ore (MnO_2).

OR

(B) (i) Write the preparation of $Na_2Cr_2O_7$, from $FeCr_2O_4$.

(ii) What is Lanthanoid contraction ? Write its two consequences.

(iii) Name two elements of 3d series which show anomalous electronic configuration.

32. (A) (a) ‘A’ and ‘B’ are two functional isomers of compound C_4H_8O. On heating with NaOH and I_2, isomer ‘B’ forms yellow precipitate of iodoform whereas isomer ‘A’ does not form any precipitate.

(i) Identify ‘A’ and ‘B’.

(ii) What happens when isomer ‘A’ is treated with Zn(Hg) in the presence of Conc. HCl ?

(iii) Write the reaction of isomer ‘B’ with NaOH and I_2.

(b) Arrange the following in the increasing order of their property as indicated :

(i) Ethanol, Ethanoic acid, Ethanal (boiling point).

(ii) Ethanal, Methanal, acetone (reactivity towards addition of HCN).

OR

(B) (a) Explain Aldol Condensation with an example. Why alpha(α) hydrogen of aldehydes and ketones are acidic in nature ?

(b) Give simple chemical test to distinguish between the following compounds :

(i) Benzoic acid and Benzaldehyde (ii) Ethanal and Propanal

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