रसायन विज्ञान
Chemistry

कक्षा / Class XII

2026-27

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Student Support Material

केन्द्रीय विद्यालय संगठन~Kendriya Vidyalaya Sangathan

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संदेश

शिक्षा केवल पुस्तकों तक सीमित ज्ञान नहीं है; यह स्वयं को पहचानने, अपने विचारों को विस्तार देने और जीवन की चुनौतियों का आत्मविश्वास से सामना करने की सतत् यात्रा है। केन्द्रीय विद्यालय संगठन का सदैव यह प्रयास रहा है कि प्रत्येक विद्यार्थी के लिए ऐसा शिक्षण वातावरण हो, जहाँ जिज्ञासा को प्रोत्साहन मिले, सीखना आनंददायी बने और प्रत्येक बालक अपनी अंतर्निहित क्षमताओं को पहचानकर उन्हें विकसित कर सके।

राष्ट्रीय शिक्षा नीति 2020 ने शिक्षा को सिर्फ रटने से समझने, सूचना से ज्ञान और ज्ञान से जीवनोपयोगी दक्षताओं की ओर अग्रसर किया है। आज का समय कृत्रिम बुद्धिमत्ता (Artificial Intelligence – AI), डिजिटल नवाचार और निरंतर बदलती तकनीकों का है। ऐसे युग में केवल तथ्यों का ज्ञान पर्याप्त नहीं है; आवश्यक है कि विद्यार्थी मनन- चिंतन करना सीखें, प्रश्न पूछें, समस्याओं का समाधान खोजें और नए विचारों के साथ आगे बढ़ें। यही क्षमताएँ उन्हें भविष्य के लिए तैयार करेंगी।

इन्हीं उद्देश्यों को ध्यान में रखते हुए केन्द्रीय विद्यालय संगठन के पाँचों आंचलिक शिक्षा एवं प्रशिक्षण संस्थानों (ZIETs) के माध्यम से, समर्पित एवं अनुभवी शिक्षकों द्वारा कक्षा 9 से 12 के विद्यार्थियों के लिए यह विद्यार्थी सहायक सामग्री तैयार की गई है। यह केवल परीक्षा की तैयारी की संकलन सामग्री नहीं है, बल्कि विषयों को सरलता से समझने, अवधारणाओं को स्पष्ट करने, नियमित अभ्यास करने और आत्मविश्वास के साथ आगे बढ़ने का एक विश्वसनीय साथी है।

इस सामग्री में विषय-वस्तु को विद्यार्थियों की आवश्यकताओं के अनुरूप सरल, व्यवस्थित एवं दक्षता-आधारित दृष्टिकोण से प्रस्तुत किया गया है। मुझे प्रसन्नता है कि इसे हमारे शिक्षकों के अनुभव, नवाचार और विद्यार्थियों के प्रति उनकी प्रतिबद्धता ने समृद्ध बनाया है। मुझे विश्वास है कि यह सामग्री विद्यार्थियों की सीखने की यात्रा को अधिक सहज, रोचक और प्रभावी बनाएगी तथा उन्हें बोर्ड परीक्षाओं के साथ-साथ जीवन की व्यापक चुनौतियों के लिए भी तैयार करेगी।

मेरा विश्वास है कि जब एक जिज्ञासु विद्यार्थी, प्रेरित शिक्षक और सार्थक शिक्षण संसाधन एक साथ आते हैं, तब शिक्षा केवल उपलब्धि का माध्यम नहीं रहती, बल्कि व्यक्तित्व निर्माण की एक सशक्त प्रक्रिया बन जाती है। यही भावना इस विद्यार्थी सहायक सामग्री के केंद्र में है।

मेरी हार्दिक शुभकामनाएँ हैं कि आप सभी सीखने की इस यात्रा में निरंतर आगे बढ़ें, अपने सपनों को नए आयाम दें और ज्ञान, संवेदनशीलता तथा नवाचार के साथ राष्ट्र निर्माण में अपना महत्वपूर्ण योगदान दें।

शुभकामनाओं सहित।

(विकास गुप्ता)

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INDEX

UNIT - 1 SOLUTIONS (7 Marks)

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

Key Concepts-

SOLUTION- A homogeneous mixture of two or more substances is known as solution.

TYPES OF SOLUTIONS: *(Based on nature of solute and Solvent)*

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

➢ ***In the formulae given below, A represents solvent and B represents solute, also***
M_A = Molar mass of solvent M_B = Molar mass of solute, W_A = Mass of solvent W_B = Mass of solute
V = Volume of solution, d = Density of solution, n_A = No. of moles of solvent, n_B = No. of moles of solute

Mass percentage (w/w %): mass of solute per 100 g of solution.	$= \frac{Mass\ of\ solute}{Total\ mass\ of\ the\ solution} \times 100$	$= \frac{W_B}{W_A + W_B} \times 100$
Parts per million (ppm): parts of a component present in per million (10^6) parts of the solution.		
Mole Fraction (*X*)- Ratio of the number of moles of one component (solute or solvent) to the total number of moles of all the components.	Mole fraction of solvent $X_A = \frac{n_A}{n_A + n_B}$	Mole fraction of solute $X_A = \frac{n_B}{n_A + n_B}$
	$X_A + X_B = 1$	
Molarity /Molar /mole per litre conc.(M)- number of moles of solute dissolved in one litre of solution.	$= \frac{No.of\ moles\ of\ solute}{Volume\ of\ the\ solution(L)}$	$= \frac{n_B}{V\ (\text{in } L)} = \frac{W_B}{M_B \times V\ (\text{in } L)}$
Molality or molal conc. (m) = no. of moles of solute dissolved in 1kg of solvent	$= \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$	$= \frac{n_B}{W_A(\text{in kg})}$ or $m = \frac{W_B \times 1000}{M_B \times W_A\ (in\ g)}$
Relation between molarity and density of solution $M = \frac{ww\ \%\ x\ d\ x\ 10}{molar\ mass\ of\ solute}$	**Molarity Vs. Molality** ***Molality is preferred over molarity as molality does not change with temperature change but molarity changes due to change in volume with temperature.***	**Dilution formula**: If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2 then **$M_1V_1 = M_2V_2$** *M_1= molarity before dilution* *M_2= molarity before dilution*

Solubility of gases in liquid:

Effect of pressure on solubility : Henry's law - At constant temperature the solubility of gas in the solution is directly proportional to the partial pressure of gas in the vapour phase.

Mathematical formulation- **$p \alpha X_B$ or $p = K_H X_B$ (K_H= Henry's constant)**

K_H *value depends upon nature of gas, 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* (11.7% Helium, 56.2% Nitrogen and 32.1% Oxygen).

3.Anoxia- At high altitudes, low blood oxygen causes climbers to become weak and make them unable to think clearly.

Effect of temperature on Solubility: Solubility of gas in liquid decreases with increase in temperature.

- e.g. *Solubility of oxygen in water is greater at low temperature*, hence aquatic animals feel more *comfortable in cold water rather than warm water*.

➢ **Vapour pressure: -**The pressure exerted by the vapours in the equilibrium with liquid at a given temperature is called vapour pressure. (V.P. α T)

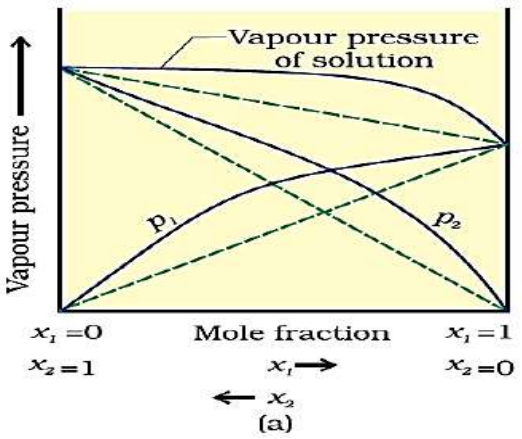
➢ **Raoult's law: -** The partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction in solution.

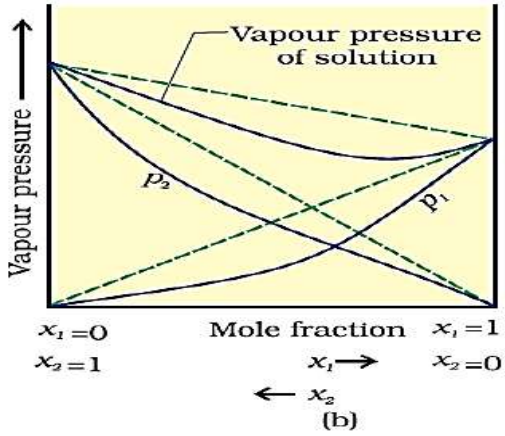
$$P_A \alpha X_A \qquad P_B \alpha X_B$$

$$P_A = P_A^o X_A \quad P_B^o X_A$$

Total V.P. of solution , $P_T = P_A + P_B$ (Daltons Law)

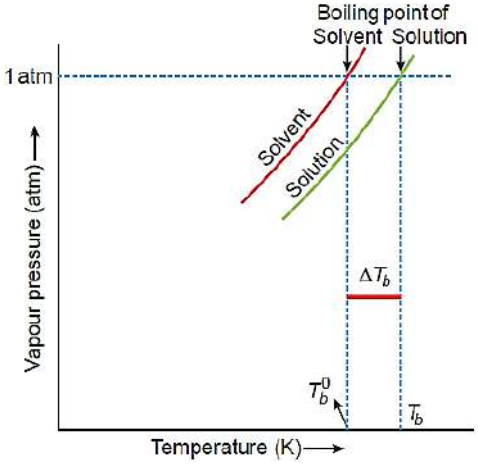
Ideal solutions	**Non-Ideal solutions**
Obeys Raoult's law over the entire range of composition. e.g. Solution of n-hexane and n-heptane	Don't Obey Raoult's law over the entire range of composition.
A-A interaction = B-B int. = A-B interactions	A-A & B-B interaction ≠ A-B interactions
$P_{Total} = P^0_A X_A + P_B^0 X_B$	$P_{Total} \neq P^0_A X_A + P_B^0 X_B$
$\Delta_{mix} H = 0$ $\Delta_{mix} V = 0$ ($V_{sol} = V_A + V_B$)	$\Delta_{mix} H \neq 0$, $\Delta_{mix} V \neq 0$ ($V_{sol} \neq V_A + V_B$)
Can be separated by fractional distillation	Can not be separated by fractional distillation.
Positive deviation	**Negative deviation**
$P_{Total} > P^0_A X_A + P_B^0 X_B$, ΔV_{mix}=+ve, ΔH_{mix}=+ve	$P_{Total} < P^0_A X_A + P_B^0 X_B$, ΔV_{mix}= -ve, ΔH_{mix}=-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
Produce **Minimum boiling Azeotrope**	Produce Maximum boiling Azeotrope

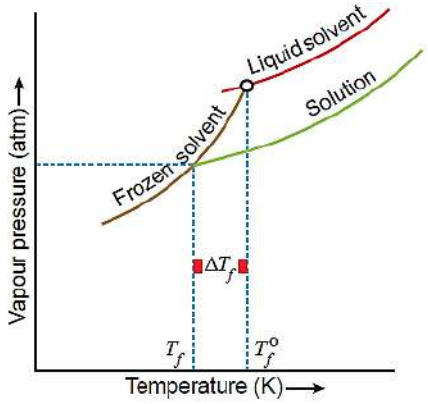




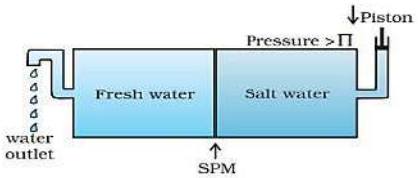
- **Azeotrope**(Greek: boiling without change) Mixtures having same composition in liquid and vapour phase, boil at a constant temperature and cannot be separated by fractional distillation
- **Colligative properties: -** The properties of solutions which depend only on the number of particles of the solute (molecules or ions) dissolved in a definite amount of the solvent and do not depend on the nature of solute(Size, shape, charge etc.)

Relative lowering in vapour pressure	**Elevation in boiling point (ΔT_b)**	**Depression in freezing point (ΔT_f)**	**Osmotic pressure (π)**
$\frac{p_A^o - p}{p_A^o} = x_B$ $X_B = n_B / n_A + n_B$ [for a very dilute solution $n_B << n_A$] **$P_A^o - P/P_A^o = n_B/n_A$** $\frac{p_A^o - p}{p_A^o} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$	**$\Delta T_b = T_b - T_b^o$** T_b =BP of Solution T_b^o =BP of pure solvent **$\Delta T_b = K_b$ m** $\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$ **K_b** = molal elevation or EBULLIOSCOPIC constant. ***It is the elevation in boiling point of 1 molal solution***.	**$\Delta T_f = T_f^o - T_f$** **T_f** = FP of Solution T^o_f = FP of pure solvent **$\Delta T_f = K_f$ m** $\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$ **K_f**= molal depression or CRYOSCOPIC constant. ***It is the depression in freezing point of 1 molal solution***.	**π = CRT** = $\frac{nRT}{V}$ **C=** Molar conc. **Unit of T Kelvin** **R**= 0.082 L atm K^{-1} Mol^{-1} ***The external pressur applied on solution side which just prevents the osmotic flow of solvent olecules is called OSMOTIC PRESSURE.***



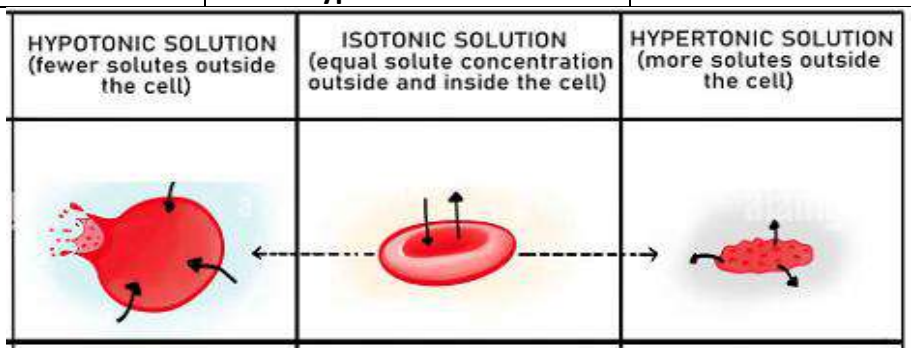


- **OSMOSIS**-The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to a more concentrated solution through a *semipermeable membrane* (spm) is called **OSMOSIS.**
- **Examples of SPM : Natural**- cell membranes, animal bladders, parchment paper.
  Synthetic (artificial) - cellulose acetate, cellophane, and Potassium Ferrocyanide Film.
- **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 seawater, residential drinking water purification
- **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



Applications of osmosis :

- Plant roots absorb water from soil due to osmosis. Concentration of cell sap inside the root hair cells is higher than that of water present in the soil. Water enters the root cells due to endosmosis.
- Red blood cells are isotonic with 0.9% w/v NaCl solution (normal saline) , RBCs burst when placed in distilled water; it is due to endosmosis.
- Use of salt and sugar in pickles and jams acts as preservatives. It prevents growth of bacteria and fungi by osmosis.
- Dead bodies swell under water due to endosmosis.
- When dried fruits , raisin and vegetables are placed in water, they slowly swell and return to the original form. It is again due to the endosmosis of water into the fruits and vegetables.
- **Edema**: Due to excess intake of salt by a person, the tissues become puffy, it is called edema. It is due to retention of water in the tissue owing to endosmosis.

- The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.
- ***IMPORTANT POINTS:***
- Antifreeze agent: **ethylene glycol used in car radiators at hill stations (Depression in freezing point)**
- **De-icing agents:** common salt (NaCl) or calcium chloride (CaCl2) is scattered on the roads to melt ice in cold countries (**Depression in freezing point)**
- **Abnormal molar mass: ELECTROLYTIC SOLUTIONS:** - When the molar mass of a substance (solute) become higher or lower due to 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
- $\mathbf{i} = \frac{observed\ value\ of\ Colligative\ Property}{calculated\ value\ of\ C.P.}$

Colligative property after abnormal molar masses: -

- Lowering of vapour pressure: - $\mathbf{X_B = i(P^o_A - P_s / P^o_A)}$
- Elevation in boiling point: - $\mathbf{\Delta T_b = i\ K_b\ m}$
- Depression in freezing point: - $\mathbf{\Delta T_f = i\ K_f\ m}$
- Osmotic pressure**: - π = iCRT**

PROPERTY	ASSOCIATION	DISSOCIATION
Colligative property	Value decreases	Value Increases
Molar mass	Greater than theoretical value	lesser
i=1	i < 1	i > 1
α (extent) =degree of dissociation or association	α = $\frac{i-1}{\frac{1}{n}-1}$ [n = no. of particles associated to give a single particle]	α= $\frac{i-1}{n-1}$ (n = no. of particles obtained after dissociation)
Examples	2 CH_3COOH $\xrightarrow{benzene}$ $(CH_3COOH)_2$ (n = 2 , dimerisation)	Na_2SO_4 $2Na^+ + SO_4^{2-}$ (n = 3)

Molal elevation constant and enthalpy of Vapourisation

$$K_b = \frac{R \times M_A \times (T_b^o)^2}{1000 \times \Delta_{vap} H}$$

$\Delta_{vap}H$ = Enthalpy of vapourisation, M_A= molar mass of solvent

Molal depression constant and enthalpy of Fusion

$$K_f = \frac{R \times M_A \times (T_f^o)^2}{1000 \times \Delta_{fus} H}$$

$\Delta_{fus.}H$ = Enthalpy of fusion

Unit-1: Solutions

SOLUTION

A homogeneous mixture of two or more substances.
The substance present in larger amount is called **SOLVENT** and the substance present in smaller amount is called **SOLUTE**.

CHARACTERISTICS OF SOLUTIONS

- Homogeneous
- Stable
- Particles size < 1 nm
- Do not scatter light (Tyndall effect)
- Do not settle down

TYPES OF SOLUTIONS

- Gaseous solutions
- Liquid solutions
- Solid solutions

EXPRESSIONS OF CONCENTRATION

1. MASS PERCENTAGE (w/w %)

$$w/w\,\% = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

2. VOLUME PERCENTAGE (v/v %)

$$v/v\,\% = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

3. MASS BY VOLUME PERCENTAGE (w/v %)

$$w/v\,\% = \frac{\text{Mass of solute (g)}}{\text{Volume of solution (mL)}} \times 100$$

4. MOLARITY (M)

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution (L)}}$$

5. MOLALITY (m)

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}}$$

6. MOLE FRACTION (χ)

$$\chi_A = \frac{\text{Moles of component A}}{\text{Total moles of all components}}$$

(For a solution, $\chi_{solute} + \chi_{solvent} = 1$)

7. PARTS PER MILLION (ppm)

$$ppm = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

8. PARTS PER BILLION (ppb)

$$ppb = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^9$$

Colligative Properties Of Solutions

1. RELATIVE LOWERING OF VAPOUR PRESSURE

$$\frac{P^0 - P}{P^0} = X_B$$

(Raoult's Law)

- P^0 = Vapour pressure of pure solvent
- P = Vapour pressure of solution
- X_B = Mole fraction of solute

2. ELEVATION IN BOILING POINT

$$\Delta T_b = K_b\, m$$

- K_b = Ebullioscopic constant
- m = Molality of solution

3. DEPRESSION IN FREEZING POINT

$$\Delta T_f = K_f\, m$$

- K_f = Cryoscopic constant
- m = Molality of solution

4. OSMOTIC PRESSURE

$$\Pi = C\,R\,T$$

- C = Molarity of solution
- R = Gas constant
- T = Absolute temperature (K)

5. APPLICATION OF OSMOTIC PRESSURE

- Absorption of water by plant roots
- Swelling of raisins
- Insertion of IV fluids
- Working of reverse osmosis/desalination

IDEAL SOLUTIONS

- Obey Raoult's law at all compositions
- A–A, B–B and A–B interactions are similar
- $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$
- Example: *n*-Hexane + *n*-Heptane

NON-IDEAL SOLUTIONS

- Do not obey Raoult's law at all compositions
- A–B interactions differ from A–A or B–B
- $\Delta H_{mix} \neq 0$ and/or $\Delta V_{mix} \neq 0$

POSITIVE DEVIATION (A–B interactions weaker)

- Vapour pressure ↑
- Boiling point ↓
- Forms minimum boiling azeotrope
- Example: Ethanol + Water

NEGATIVE DEVIATION (A–B interactions stronger)

- Vapour pressure ↓
- Boiling point ↑
- Forms maximum boiling azeotrope
- Example: Acetone + Chloroform

AZEOTROPIC MIXTURES

- Mixtures that boil at constant temperature with constant composition.
- Show no change in composition on boiling.
- Separated by fractional distillation.

Solute lowers the escaping tendency of solvent molecules, causing changes in colligative properties which depend only on the number of solute particles and not on their nature.

SECTION -A (1 Mark)

Q1. K_H value for Ar(g), CO_2(g), HCHO (g) and CH_4(g) are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.

a) HCHO < CH_4 < CO_2 < Ar b) HCHO < CO_2 < CH_4 < Ar

c) Ar < CO_2 < CH_4 < HCHO d) Ar < CH_4 < CO_2 < HCHO

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

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

Q3. Water- HCl mixture will

I. shows positive deviations II. forms minimum boiling azeotrope

III. Shows negative deviations IV. forms maximum boiling azeotrope

a) I and II b) II and III c) I and IV d) III and IV

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

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

Q6. An azeotropic solution of two liquids has boiling point lower than either of them when solute solvent interactions are:

a) Equal to solute solute and solvent solvent interactions

b) Stronger than solute solute and solvent solvent interactions

c)Weaker than solute- solute and solvent-solvent interactions

d)None of the above

Q7. The value of van't Hoff factor for ethanoic acid in benzene is

(a) 1.0 (b) 1.5 (c) 0.5 (d) 2

Q8. The system that forms maximum boiling azeotropes is:

(a) ethyl alcohol-water (b) benzene-toluene

(c) acetone-chloroform (d) carbon disulphide-acetone

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):** Cooking time is reduced in pressure cooker.

Reason (R): Boiling point of water inside the pressure cooker is elevated

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):** the aquatic species more comfortable in cold water in comparison to warm water

Reason(R): the solubility of oxygen in water decreases with decrease in temperature.

Q14.**Assertion(A) :** mercuric iodide is added to an aqueous solution of KI, the freezing point is raised

Reason(R): the formation of complex $K_2[HgI_4]$, number of particles in the solution decreases

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
C	C	D	D	A	C	C	C	B	B	A	A	C	A	C

SECTION - B (2 Marks)

Q1.What type of deviation is shown by ethanol and acetone mixture? Give reason. What type of azeotropic mixture is formed by that deviation?

Hint : Positive deviation, minimum boiling azeotrope.

Q2. a) How the osmotic pressure of 5 % aqueous solution of glucose (π_1) is related to that of 5 % aqueous solution of urea (π_2)?

b) Why do salt water fish die when they are suddenly transferred to a fresh water aquarium?

Hint : a) $\pi_1 < \pi_2$

b) Water from aquarium enters in cell causing them to expand and get ruptured

Q3.Explain why on addition of 1 mol of NaCl to 1L 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.(i) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y?

(ii) What happens when we place the blood cell in water (hypotonic solution)? Give reason.

Hint: i) The solution will show negative deviation from Raoult's law. Temperature will rise.

(ii) Due to endosmosis water enters into the cell .

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.Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation.(Kb for water = 0.52 K kg mol^{-1})

Hint*:* *i= 3, $T_s = T^o + \Delta T_b$, &*

$$\Delta T_b = \frac{i \times K_b \times W_B \times 1000}{M_B \times W_A}$$

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 ; b) Apply formula

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

P_s=23.55 mmHg

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

Hint: $\Delta T_f = i K_f m$, $\alpha = (i-1)/n-1$ (n=4), i=3.65, α =0.8833

Q4. a) Why do Scuba divers use Oxygen cylinders diluted with He .Explain

b) Which cold drink you prefer one chilled or other one at room temperature and why?

c)At the same temperature hydrogen is more soluble in water than Helium. Which of them will have higher value of KH and why?

Hint: refer summary page-2

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

Certain membranes allow solvent molecules to pass through them but not solute molecules, particularly not those of large molecular mass. Such a membrane is called semipermeable and might be an animal bladder, a vegetable tissue, or a piece of cellophane.Osmosis is the phenomenon of solvent flow through a semipermeable membrane to equalize the solute concentrations on both sides of the membrane. When two solutions of the same solvent are separated by a semipermeable membrane, solvent molecules migrate through the membrane in both directions. However, the solvent migration is faster from the solution of low concentration to the solution of high concentration.The osmotic pressure is a colligative property of a solution equal to the pressure that, when applied to the solution, just stops osmosis. The osmotic pressure, π , of a solution is related to the molar concentration of solute, C:

$$\pi = CRT$$

Here R is the gas constant and T is the absolute temperature.

(Source : General Chemistry by Ebbing)

Answer the following questions-

a. Name one artificial and one natural SPM which can be used in the process of reverse osmosis.
b. Which one of the following will have higher osmotic pressure in 1 M KCl or 1 M urea solution?
c. Calculate the osmotic pressure at 20C of an aqueous solution containing 5.0 g of sucrose, $C_{12}H_{22}O_{11}$, in 100.0 mL of solution. (R= 0.082 L atm K^{-1} mol^{-1})

Hints-

b) 1M KCl , electrolyte>dissociation , c) $\boldsymbol{\pi = CRT = \frac{nRT}{V(mL)} \quad x\ 1000}$

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) Sucrose is a non-electrolyte that dissolves in water without dissociating into ions. Based on this understanding, determine the van't Hoff factor (i) for sucrose and explain your reasoning. (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 When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (Sx).

[K_f for CS_2 = 3.83 K kg mol–1, Atomic mass of Sulphur = 32 g mol^{-1}]

Hint : *b) calculate molar mass of associated molecule (Sx),*

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A} \qquad x = \frac{molar\ mass\ of\ Sx}{molar\ mass\ of\ S}$$

Q2. a) Blood cells are isotonic with 0.9 % sodium chloride solution. What happens if we place blood cells in a solution containing

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

b) 2 g of benzoic acid (C_6H_5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol^{-1}. What is the percentage association of acid if it forms dimer in solution?

Hints- a) (i) cell shrink ,exosmosis (ii) cells swell, endosmosis

b) $\Delta T_f = i\, K_f\, m$, calculate i

$$\alpha\ (asso.) = \frac{i-1}{\frac{1}{n}-1} \quad ; \qquad \alpha = 0.992 \text{ or } 99.2\ \%$$

UNIT-2. ELECTROCHEMISTRY (9 MARKS)

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

Key Concepts-

Conductors: Materials that allow flow of electrons. These are of two types

Electronic or Metallic Conductors	**Electrolytic or Solution 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.	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.

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 is 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.

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.

Electrical Conductance	**Specific Conductance or Conductivity**
The property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it. Conductance =1/ Resistance Unit : mho^{-1}	In a conductor if length is 1 cm. And 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

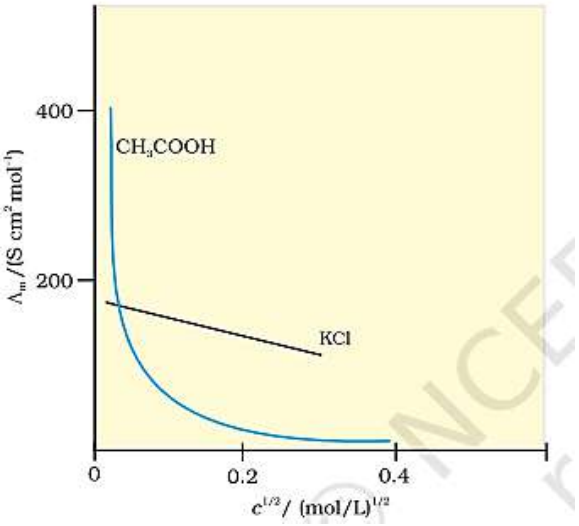
the conductance of all the ions produced by ionization of 1 g-mole of an electrolyte when present in V ml of solution. It is denoted by Λm.

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

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

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

Molar conductivity versus $c^{½}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions



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:

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

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

Applications of Kohlrausch's Law :

1. Determining Λ^0 m of a weak electrolyte:
2. Degree of dissocition,

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

3. Determination of solubility of sparingly soluble salt:

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

where, C is molarity of solution and hence solubility

4. Determination of ionic product of water

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

(complete dissociation of water)

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

Then. $K_W = C^2$

Ionic mobility :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 potential difference develops between the electrode and the electrolyte which is called **electrode potential**. When the concentrations of all the species involved in a half-cell is unity then the electrode potential is known as **standard electrode potential**. According to IUPAC convention, standard reduction potentials are now called standard electrode potentials.

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

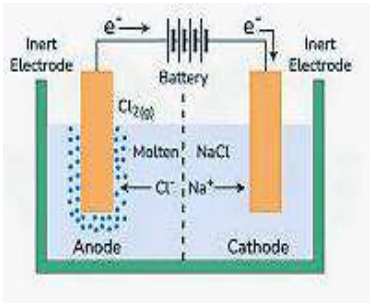
$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \text{ or } E^\circ_{cell} = E^\circ_{right\ electrode} - E^\circ_{left\ electrode}$$

ELECTROCHEMICAL CELLS

ELECTROLYTIC CELLS

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)



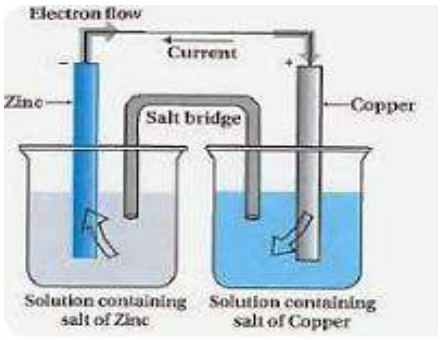
Cell reaction :

$$NaCl + H_2O \rightleftharpoons Na^+ + OH^- + H_2 + Cl_2$$

DANIEL CELLS

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.

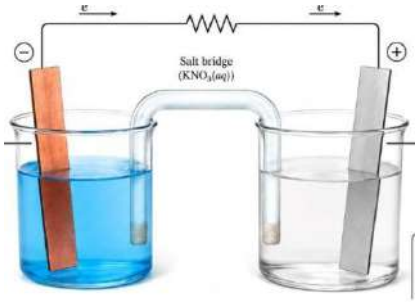
Cell representation :



Zn/Zn^{+2} (aq.) II Cu^{+2}(aq.)/Cu

GALVANIC CELLS

A broader term encompassing any electrochemical cell that converts chemical energy to electrical energy through a spontaneous redox reaction.



Cell representation :

Cu/Cu^{+2} (aq.)IIAg+(aq) /Ag

QUICK COMPARISION

ELECTROLYTIC CELLS	DANIEL CELLS	GALVANIC CELLS

1. Redox reaction **2. Non spontaneous** **3. E^ocell is negative** **4. Anode is +ve** **5. Cathode is -ve** **6. flow of electron anode to cathode** **Electrolysis, electroplating**	**Redox reaction** **Spontaneous** **E^ocell is positive (+ve)** **Anode is -ve** **Cathode is +ve** **Anode to cathode** **Cell**	**Redox reaction** **Spontaneous** **E^ocell is positive** **Anode is -ve** **Cathode is +ve** **Anode to cathode** **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

$$z = \frac{M}{nF}$$

$$w = \frac{M.I.t}{nF}$$

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 law can be combined

$$W = ZQ = \frac{E}{F} \times Q = \frac{Q}{F} \times E = \frac{Q}{F} \times \frac{M}{z} = \frac{C \times t}{F} \times \frac{M}{z}$$

Nernst Equation : (For calculating E_{cell} or emf)

For a general reaction; $aA + bB \longrightarrow cC + dD$

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

eg: For the cell, Ni /Ni^{+2}(aq) II Ag^+(aq)/ Ag

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

The **Nernst equation** can be written as

$$E_{(cell)} = E^\circ_{(cell)} - \frac{RT}{2F} \ln \frac{[Ni^{2+}]}{[Ag^+]^2}$$

Equilibrium Constant from Nernst Equation

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

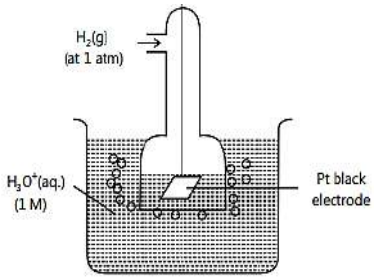
Electrochemical Cell and Gibbs Energy of the Reaction

$\Delta G^o = -nFE^o_{cell}$

Salt bridge completes the circuit, maintains electroneutrality and also minimises liquid junction potential.

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

lati
nu
m

Electrolyte: 1M HCl

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

PRODUCTS OF ELECTROLYSIS

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.

electrolyte	elect rode	Cathodic reaction	Anodic reaction	Remarks if any
1. Molten NaCl	Pt	$2Na^+ + 2e^-$ 2Na	$2Cl^-$ $Cl_2 + 2e^-$	One cation and one anion
2.Molten $PbBr_2$	Pt	$Pb^{2+} + 2e^-$ Pb	$2Br^-$ $Br_2 + 2e^-$	**--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 $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^\circ = -1.0$ V; $Na^+(l) + e^- \rightarrow Na(l)$ $E^\circ = -2.71$V. At anode : both water and chloride ion can be oxidised. $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ $E^\circ = -1.42$ V; $2Cl^- \rightarrow Cl_2 + 2e^-$ $E = -1.36$V		

A.) <u>Very dilute aq. NaCl solution</u>

water with high reduction potential is reduced at cathode

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

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

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

B. **<u>High Concentration of Sodium Chloride :</u>** **Hydogen 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

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

B. **) MERCURY CELL**

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

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

overall reaction does not involve any ion in solution

on is represented by

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

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 :

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Overall cell reaction- Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

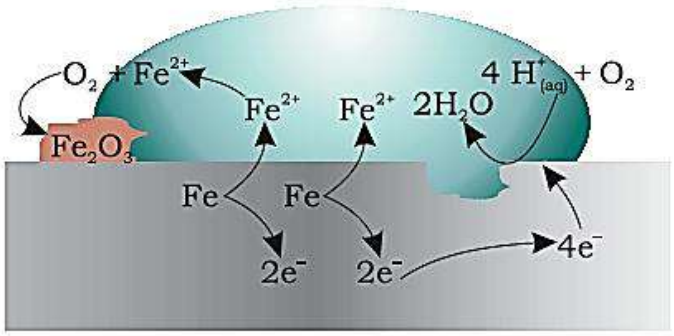
FUEL CELLS :Electrical cells that are discharged to convert the energy from the combustion of fuels (hydrogen, carbon monoxide, methane, etc.) directly into the electrical energy are called fuel cells.

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

H_2-O_2 fuel cell was used in Apollo space program.

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.



Oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

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

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

PREVENTION OF RUSTING :

BARRIER PROTECTION: 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 /SACRIFICIAL 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.

Unit-3: Electrochemistry

ELECTROCHEMISTRY

Study of chemical change produced by electricity and the production of electricity from chemical change.

1. REDOX REACTIONS

- Oxidation, Reduction
- Redox Reactions
- Oxidising & Reducing Agents
- Balancing Redox Reactions

2. ELECTROCHEMICAL CELLS

- Galvanic / Voltaic Cell
- Spontaneous Redox Reaction
- Components of a Cell
- Cell Representation
- Salt Bridge – Function

3. ELECTRODE POTENTIALS AND ELECTROCHEMICAL SERIES

- Electrode Potential
- Standard Electrode Potential ($E°$)
- Electrochemical Series
- Significance of $E°$ Values

4. NERNST EQUATION

- Need for Nernst Equation
- Derivation

$$E = E° - \frac{0.0591}{n} \log Q$$

(at 298 K)

- Applications

5. RELATION BETWEEN ELECTRODE POTENTIAL AND GIBBS ENERGY

- Gibbs Energy change (ΔG)
- Derivation of $\Delta G = -nFE$
- Spontaneity of Redox Reactions
- Equilibrium Constant (K)

$$\Delta G° = -nFE° = -2.303\ RT \log K$$

6. CONDUCTANCE IN ELECTROLYTIC SOLUTIONS

- Electrolytic Solutions
- Specific Conductance (κ)
- Molar Conductance (Λ_m)
- Variation of Λ_m with Concentration
- Strong vs Weak Electrolytes
- Kohlrausch's Law

7. ELECTROCHEMICAL CELLS AND THEIR APPLICATIONS

- Primary Cells (Zn–C, Leclanché Cell)
- Secondary Cells (Lead Storage Cell, Ni–Cd Cell)
- Fuel Cells (H_2–O_2 Fuel Cell)
- Corrosion and its Prevention (Galvanisation, Cathodic Protection, Alloying, Painting, Greasing, Sacrificial Anode)

8. ELECTROLYSIS

Process of decomposition of an electrolyte by the passage of electricity.

- Electrolytic Cell – Components
- Electrodes: Anode (+), Cathode (–)
- Electrolysis of Molten Compounds
- Electrolysis of Aqueous Solutions
- Discharge of Ions – General Rules
- Products at Electrodes

9. FARADAY'S LAWS OF ELECTROLYSIS

First Law

Mass of substance deposited (or liberated)

$$W \propto Q \quad \text{or} \quad W = ZQ$$

Second Law

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

- Significance and Applications

10. APPLICATIONS OF ELECTROLYSIS

- Electroplating
- Electrorefining
- Extraction of Metals (e.g., Al, Na, Mg)
- Electrolytic Purification of Metals

11. NUMERICALS & PROBLEMS

- Based on Nernst Equation
- Based on $\Delta G° - E° - K$ Relationship
- Based on Conductance
- Based on Faraday's Laws
- Based on Electrolysis & Applications

HOW THE TOPICS ARE INTERLINKED

1. provides the foundation (concept of redox) for 2, 3 and 8.
2. describes the cell in which redox reactions occur and connects to 3.
3. provides $E°$ values used in 4, 5 and 7.
4. (Nernst Equation) uses $E°$ from 3 and helps in calculating cell potentials.
5. links $E°$ (from 3/4) to spontaneity and equilibrium (K).
6. explains the conducting nature of the electrolyte used in cells (2, 8).
7. uses principles of 2, 3 and 6 and shows real-life applications.
8. applies redox (1) and uses electricity to bring about chemical change.
9. quantifies the amount of substances changed in 8.
10. practical uses of 8 and 9.
11. numericals integrate all concepts.

KEY FORMULAE (QUICK RECALL)

- Nernst Equation : $E = E° - \frac{0.0591}{n} \log Q$ (298 K)
- $\Delta G = -nFE$
- $\Delta G° = -nFE° = -2.303\ RT \log K$
- Conductance : $\kappa = \frac{1}{R} \times \frac{l}{A}$
- Molar Conductance : $\Lambda_m = \frac{\kappa \times 1000}{c}$
- Faraday's First Law : $W = ZQ = ZIt$
- Faraday's Second Law : $\frac{W_1}{W_2} = \frac{E_1}{E_2}$

SYLLABUS COVERED (NCERT)

This flow chart covers all CBSE Class XII topics from the Electrochemistry chapter.

(Redox Reactions, Electrochemical Cells, Electrode Potentials, Nernst Equation, ΔG and K, Conductance, Cells & Applications, Electrolysis, Faraday's Laws & Applications)

LEGEND (FLOW INDICATION)

- Foundation / Prerequisite
- Builds / Extends
- Used in / Derived From
- Supports / Related To
- Application / Outcome
- Leads to / Solved Through

QUESTION BANK

SECTION- A (1 MARK)

Q.1). An electrochemical cell can behave like an electrolytic cell when _____.

(a) $E_{cell} = 0$ (b) $E_{cell} > E_{ext}$

(c) $E_{cell} = E_{ext}$ (d) $E_{ext} > E_{cell}$

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 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) $\Lambda^o_m(NH_4OH)$ is equal to_____

(a) $\Lambda^o_m(NH_4OH) + \Lambda^o_m(NH_4Cl) - \Lambda^o_m(HCl)$

(b) $\Lambda^o_m(NH_4Cl) + \Lambda^o_m(NaOH) - \Lambda^o_m(NaCl)$

(c) $\Lambda^o_m(NH_4Cl) + \Lambda^o_m(NaCl) - \Lambda^o_m(NaOH)$

(d) $\Lambda^o_m(NaOH) + \Lambda^o_m(NaCl) - \Lambda^o_m(NH_4Cl)$

Q6. 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.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 | Zn^{2+} (0.1M) || Cu^{2+} (1.0M)|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:** Assertion : E_{Cell} should have a positive value for the cell to function.

Reason: Ecathode < Eanode

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 :** Electrolysis of NaCl solution gives chlorine at anode instead of O_2.

Reason: Formation of oxygen at anode requires overvoltage.

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.d	5.b
6.d	7.c	8.c	9.a	10.b

ASSERTION REASON QUESTIONS

11.d	12.c	13.c	14.a	15.a

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,Pt**. 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^-, H_2O, F^- are in the following order. $Br^- > H_2O > F^-$

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, $E^0_{Cu2+/Cu} = +0.34$V)

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 (4Marks)

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]

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

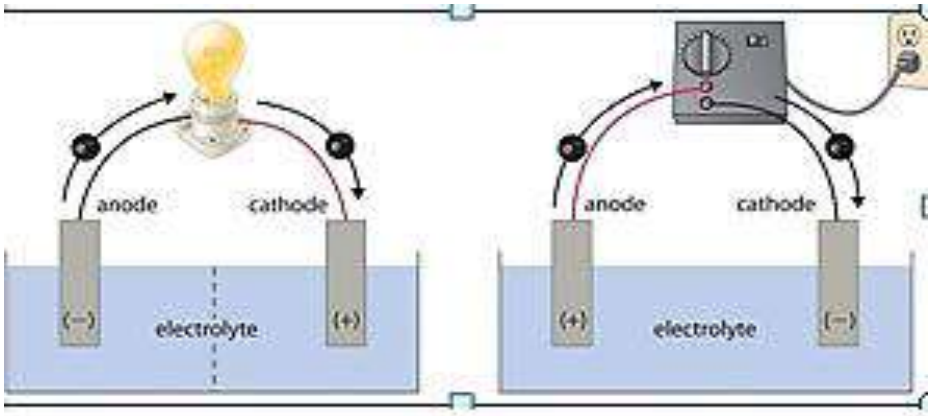
Remaining thickness = 6.0 mm.

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

$\Lambda m = (0.00635\ S\ cm^{-1} \times 1000) / 0.01\ mol\ L^{-1} = 635\ S\ cm^2\ mol^{-1}$

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

Molar Conductivity After Dilution

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

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

UNIT-3: CHEMICAL KINETICS (7 Marks)

Rate of a reaction (Average and instantaneous), factors affecting rate of reaction: concentration, temperature, catalyst; order and molecularity of a reaction, rate law and specific rate constant, integrated rate equations and half-life (only for zero and first order 10 reactions), concept of collision theory (elementary idea, no mathematical treatment), activation energy, Arrhenius equation.

Key Concepts

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

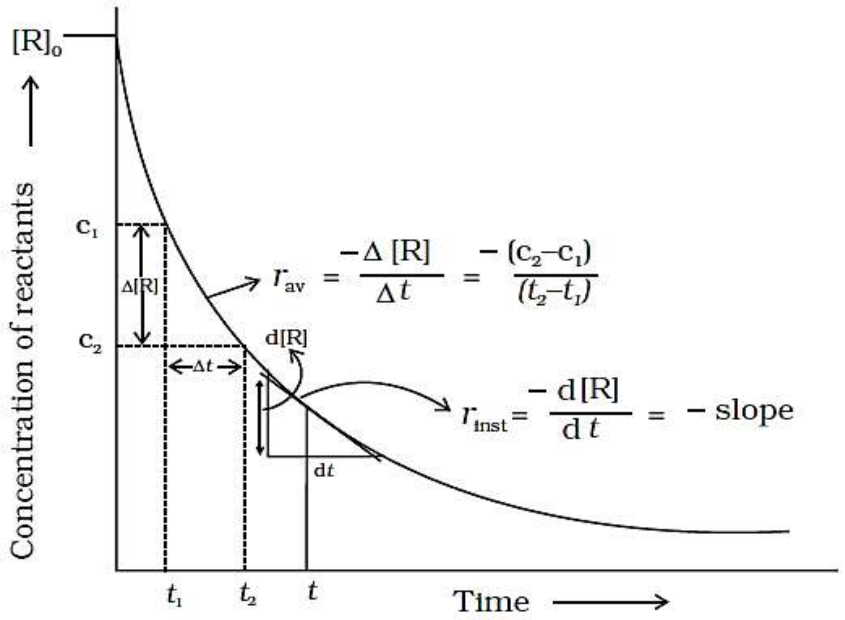
Units of rate of a reaction: mol $L^{-1}s^{-1}$

Expression for rate of reaction:

Consider a reaction, R → P

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

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.



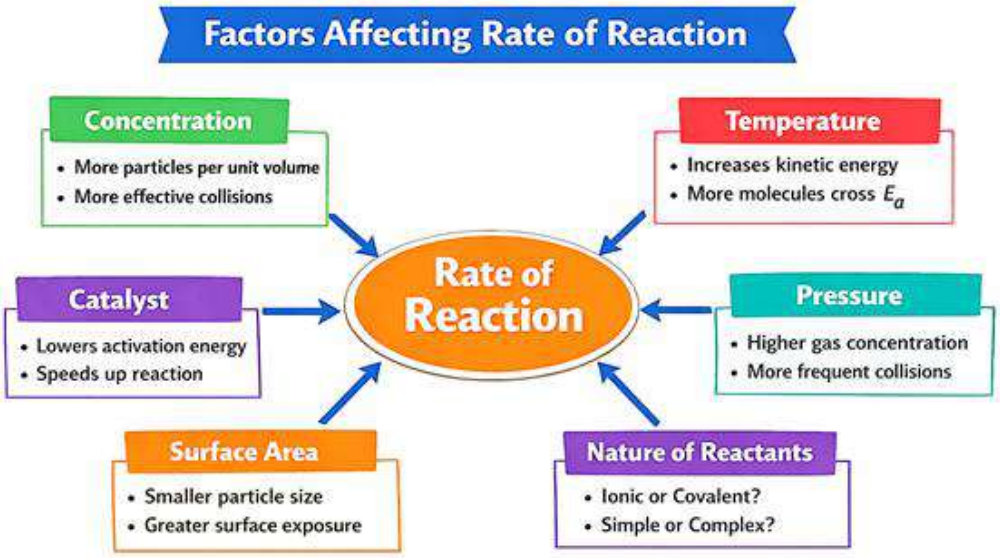
Consider a given reaction : aA +Bb →cC + dD

$$r_{av} = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

$$r_{inst} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Rate of disappearance of A = - Δ[A] / Δt , **Rate of disappearance of B** = - Δ[B] / Δt

Rate of appearance of C = + Δ[C] / Δt **Rate of appearance of D** = +Δ[D] / Δt



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.

- **For a given reaction : A → B**
- **Rate = k [A]^X X= Order of reaction k= Rate constant**

General unit of **K** = [Mol L $^{-1}$] $^{1-X}$ time $^{-1}$

(***Where time may be second, minutes or hours , days or years)***

Order	Unit	Examples
0	[Mol L $^{-1}$] Sec.$^{-1}$ (or any other unit of time)	$2NH_3(g) \xrightarrow{Pt} N_2(g) + 3H_2(g)$
1	Sec. $^{-1}$	$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
2	[Mol $^{-1}$ L] Sec. $^{-1}$	$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

S.N.	ORDER	MOLECULARITY
1	Sum of powers to which conc. terms are raised in rate law.	No. of molecules taking part in elementary reaction.
2.	Can be zero or fractional.	Can neither be zero or fractional or more than 3
3.	Determined Experimentally	Theoretical concept
4.	Applicable to elementary as well as complex reaction	Applicable to only elementary reaction

The integrated rate equations

Zero order reaction

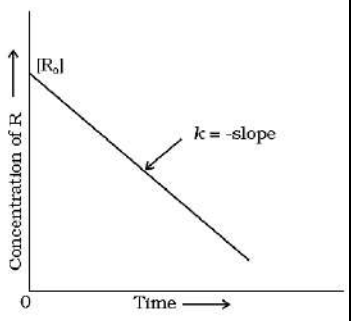
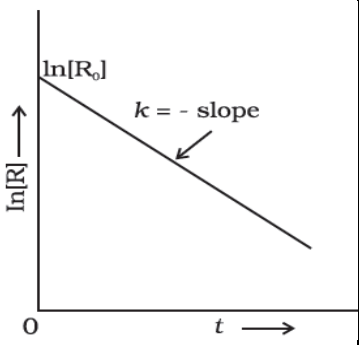
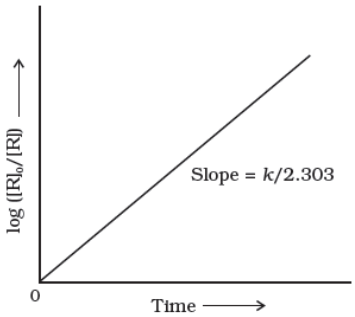
$$k = \frac{[R]_0 - [R]}{t}$$

First order reaction

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

Where $[R]_0$ = initial concentration of reactant, [R] = the final concentration at time 't' , t = time taken

➢ **Integrated Rate Law & Important Graph plots for zero order and first order reaction-**

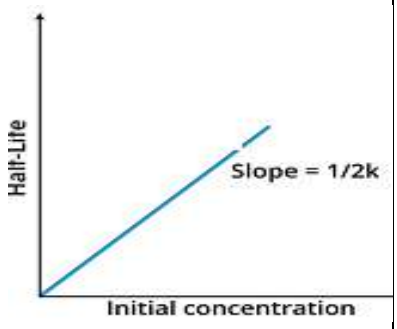
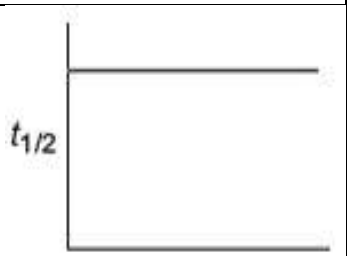
	(zero order reaction)	(First order reaction)	(First order reaction)
Integrated rate equations	$k = \frac{[R]_0 - [R]}{t}$	$k = \frac{2.303}{t} \log \frac{[R]o}{[R]}$	-
Line equation	$[R] = -kt + [R]_0$	$\ln[R] = -kt + \ln[R]_0$	$\log \frac{[R]_0}{[R]} = \frac{kt}{2.303}$
Graph			
Plot	[R] vs time	ln[R] vs time	Log $\frac{[R]0}{[R]}$ vs time
Slope	–k	-k	k/2.303
Intercept	$[R]_0$	ln $[R]_0$	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 is constant, i.e., it is independent of initial concentration of the reacting species.

Graph plots for half life period of reaction-

	Zero order reaction	First order of reaction
Line equation	$t_{1/2} = \frac{[R]0}{2k}$	$t_{1/2} = 0.693/ k$
Graph		
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)

Pseudo first order reactions: Such reactions in which the molar concentration of reactant remain unchanged and small change in concentration does not effect the rate of reaction are called Pseudo first order reactions.

1. Inversion of cane sugar :

$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

Cane sugar — Glucose — Fructose

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

2. Hydrolysis of ester:

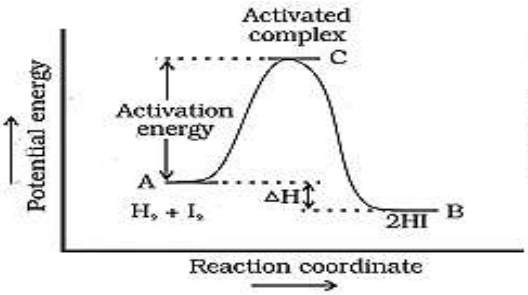
$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3OOH + C_2H_5OH$

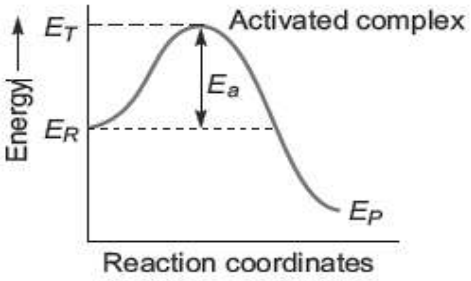
Rate = K $[CH_3COOC_2H_5]$

- **Activation Energy**(E_a) = The minimum amount of extra energy required by reactant molecules to initiate a chemical reaction and transform into products.
- According to Kinetic theory of Molecular gases, the average kinetic energy of reacting gaseous molecules is directly proportional to absolute temperature.

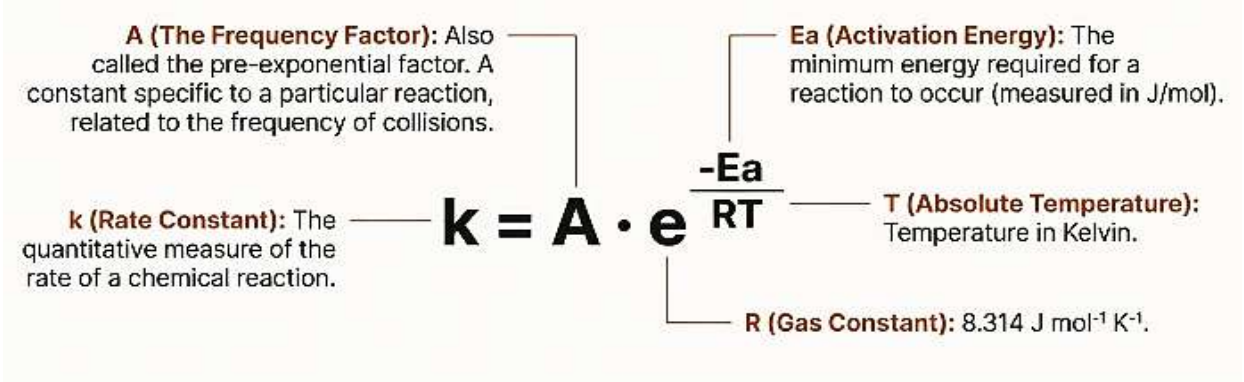
  K.E α T

  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 which the reactant must possess in order to convert into products is known as **threshold energy**.





Arrhenius equation



NOTE: Increasing the temperature or decreasing the activation energy results in exponential increase in rate constant (K)

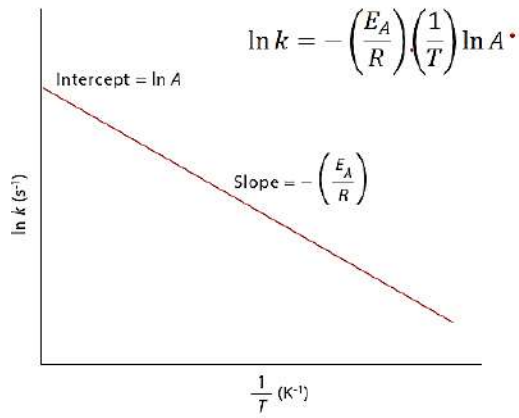
- **Important formula to relate activation energy , temperature and rate constant-**

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

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

E_a = Activation energy, R= Gas constant

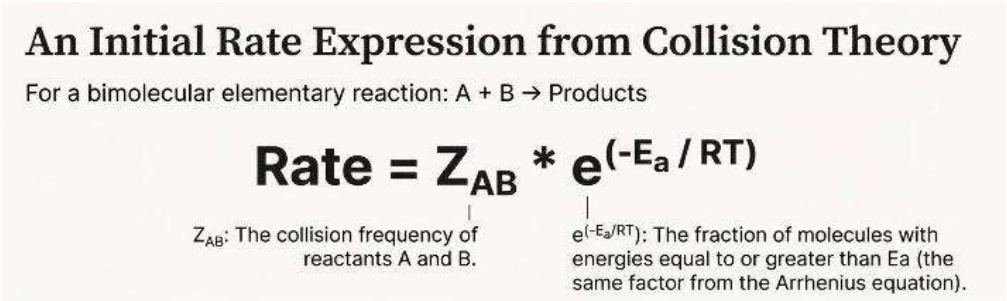
- **Graph:-**



Plot between ln k vs 1/T ,
Straight line equation ln k = $-\frac{Ea}{R}$ + lnA
slope = $-\frac{Ea}{R}$ and intercept = ln*A*

- **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 theory of Reaction Rate

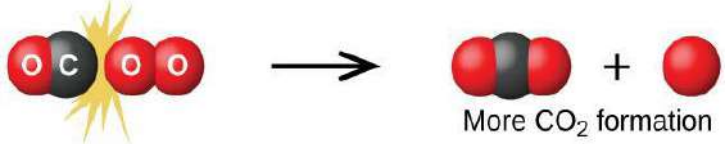


Importance of Molecular Orientation:

Not all collisions lead to product formation.They must have sufficient kinetic energy (threshold energy) and proper orientation to be effective**.**

No reaction

Improper orientation



Proper orientation

- **Collision frequency**: The number of collisions per second per unit volume of the reaction mixture is known as collision 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.

The Probability Factor (Steric Factor) (P) :

It accounts for the orientation of molecules.

Criteria for reaction: 1. Sufficient activation energy 2. Proper orientation.

$$\textbf{Rate} = P.Z_{AB}.e^{(-Ea/RT)}$$

Drawback: It considers molecules to be hard spheres.

For a typical first order gas phase reaction

A(g) --> B(g) + C(g)

The rate law will be

$$k = \frac{2.303}{t}\log\frac{p_i}{(2p_i - p_t)}$$

here, p_i is the initial pressure at time t = 0 & P_t is the total pressure at time t

e.g.

The following data were given for thermal decomposition of SO_2Cl_2 at a constant volume :

$$SO_2Cl_2\ (g) \rightarrow SO_2\ (g) + Cl_2\ (g)$$

Exp.	Time/s	Total p/atm
1	0	0.5
2	100	0.6

Calculate the rate constant of the reaction

Hint- P_i= 0.5, P_t= 0.6 use formula

$$k = \frac{2.303}{t}\log\frac{P_1}{(2P_1 - P_t)}$$

K=2.23x 10^{-3} s^{-1}

Unit-3

CHEMICAL KINETICS

Study of the rate of chemical reactions and the factors affecting the rate.

RATE OF REACTION

Change in concentration of reactants or products per unit time.

RATE EXPRESSION (General)

For aA + bB ⟶ Products

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} - \frac{1}{b}\frac{d[B]}{dt} = +\frac{d[P]}{dt}$$

1. RATE OF A REACTION

A. AVERAGE RATE

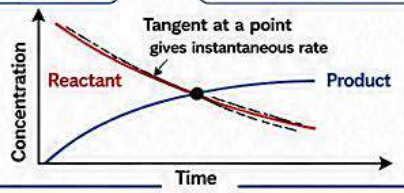
$$\text{Average rate} = -\frac{\Delta[A]}{\Delta t} \text{ (or) } \frac{\Delta[P]}{\Delta t}$$

(Over a time interval Δt)

B. INSTANTANEOUS RATE

$$\text{Instantaneous rate} = -\frac{d[A]}{dt} \text{ (or) } \frac{d[P]}{dt}$$

(At a particular moment)



2. FACTORS AFFECTING RATE OF REACTION

- Nature of reactants
- Concentration of reactants
- Temperature
- Presence of catalyst
- Surface area (in case of solids)
- Pressure (in case of gases)
- Light (in photochemical reactions)
- Solvent
- Presence of inhibitors / promoters

3. RATE LAW AND ORDER OF REACTION

Rate law gives the relationship between rate and concentration of reactants.

$$\text{Rate} = k[A]^m [B]^n$$

- k = Rate constant (Independent of concentration but depends on temperature & nature of reactants)
- m, n = Order w.r.t. A and B
- Overall order = (m+n) (Sum of powers)

Order can be 0, fractional or integral but not negative.

4. DETERMINATION OF ORDER

- From Rate Law (if mechanism known)
- Initial Rate Method
- Half-Life Method
- Integrated Rate Equation Method
- Differential Method (Graphical)

5. IMPORTANT POINTS

- Rate is independent of stoichiometric coefficients.
- Order is determined experimentally.
- Overall order is the sum of powers.
- Unit of k depends on the order of reaction.

6. INTEGRATED RATE EQUATIONS

(i) ZERO ORDER REACTION

(aA ⟶ Products)

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

Integrated form:

$$[A]_t = [A]_0 - kt$$

Half-life:

$$t_{1/2} = \frac{[A]_0}{2k}$$

Unit of k: $\text{mol L}^{-1}\text{ s}^{-1}$

Plot: [A] vs t ⟶ Straight line, slope = −k

(ii) FIRST ORDER REACTION

(aA ⟶ Products)

$$\text{Rate} = k[A]$$

Integrated form:

$$\ln[A]_t = \ln[A]_0 - kt$$

$$[A]_t = [A]_0 e^{-kt}$$

Half-life:

$$t_{1/2} = \frac{0.693}{k}$$ (Independent of $[A]_0$)

Unit of k: s^{-1}

Plot: ln[A] vs t ⟶ Straight line, slope = −k

(iii) SECOND ORDER REACTION

(aA ⟶ Products)

$$\text{Rate} = k[A]^2$$

Integrated form:

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt$$

Half-life:

$$t_{1/2} = \frac{1}{k[A]_0}$$ (Depends on $[A]_0$)

Unit of k: $\text{L mol}^{-1}\text{ s}^{-1}$

Plot: $\frac{1}{[A]}$ vs t ⟶ Straight line, slope = k

(iv) n^{th} ORDER REACTION ($n \neq 0,1$)

$$\text{Rate} = k[A]^n$$

Integrated form:

$$[A]_t^{1-n} = [A]_0^{1-n} + (n-1)kt$$

Half-life:

$$t_{1/2} = \frac{2^{n-1} - 1)}{(n-1)\,k\,[A]_0^{n-1}}$$

Unit of k: $\text{L}^{n-1}\text{ mol}^{1-n}\text{ s}^{-1}$

Plot: $[A]^{1-n}$ vs t ⟶ Straight line, slope = (n − 1)k

7. INITIAL RATE METHOD

For aA + bB ⟶ Products

Keep one reactant in large excess and vary the concentration of other.

$$\text{Rate} = k[A]^m [B]^n$$

By comparing initial rates:

Exp.	[A] (mol L⁻¹)	[B] (mol L⁻¹)	Initial Rate (mol L⁻¹ s⁻¹)
1	a_1	b_1	r_1
2	a_2	b_1	r_2
3	a_1	b_2	r_3
4	a_2	b_2	r_4

$$m = \frac{\log(r_2/r_1)}{\log(a_2/a_1)}$$ (Keeping [B] constant)

$$n = \frac{\log(r_3/r_1)}{\log(b_2/b_1)}$$ (Keeping [A] constant)

8. HALF-LIFE METHOD

$t_{1/2}$ = Time taken for the concentration of a reactant to become half of its initial concentration.

Order	Half-life ($t_{1/2}$)
Zero	$\frac{[A]_0}{2k}$
First	$\frac{0.693}{k}$
Second	$\frac{1}{k[A]_0}$
n^{th} ($n \neq 1$)	$\frac{2^{n-1} - 1}{(n-1)\,k\,[A]_0^{n-1}}$

Use: To determine order and rate constant.

9. TEMPERATURE DEPENDENCE (ARRHENIUS EQUATION)

$$k = Ae^{-\frac{E_a}{RT}}$$

- k = Rate constant
- A = Frequency factor (pre-exponential factor)
- E_a = Activation energy
- R = Gas constant (8.314 J $\text{mol}^{-1}\text{ K}^{-1}$)
- T = Absolute temperature (K)

Two point form:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Higher E_a ⟶ Greater temperature sensitivity.

10. CATALYSIS

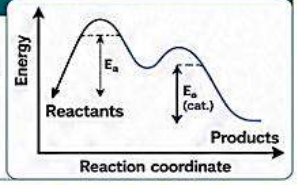
- Catalyst increases rate by providing an alternate pathway with lower activation energy.
- Does not change ΔG, equilibrium constant or the stoichiometry.
- Types:
  - (i) Homogeneous catalysis (Reactant & catalyst in same phase)
  - (ii) Heterogeneous catalysis (Different phases)
  - (iii) Enzyme catalysis (Biocatalysis)
- Poisoning – Decrease in catalytic activity due to foreign substances.

11. MECHANISM OF A REACTION

A complex reaction occurs by a series of elementary steps.

Reactants $\xrightarrow{\text{Step 1}}$ Intermediate $\xrightarrow{\text{Step 2}}$ Intermediate $\xrightarrow{\text{Step 3}}$ Products

- The slowest step is called the rate determining step.
- Overall order is determined by the rate determining step.
- Sum of steps = Overall reaction.



12. COLLISION THEORY

- Reaction occurs by collision of reactant molecules.
- For effective collision:
  - (i) Colliding molecules must have energy ≥ E_a.
  - (ii) Proper orientation must exist.
- Rate ∝ Number of effective collisions.

KEY TAKEAWAY

The rate of a reaction depends on the concentration, nature of reactants, temperature, catalyst and other factors. Understanding rate laws, order, and mechanisms helps in controlling and predicting chemical reactions.

QUESTION BANK

Section – A (1 Mark)

Q.1: For the reaction $2P + Q \rightarrow P_2Q$, the order with respect to P and Q is 2 and 0 respectively .what will be the effect on the reaction rate if the concentration of reactant P is doubled and the concentration of reactant Q is decreased by half?"

(a) increase 2 times (b) increase 4 times

(c) decrease 2 times (d) remain the same

Q.2: The value of rate constant for a reaction is 3.96×10^{-30} $Mol^{-1}Ls^{-1}$. 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 :

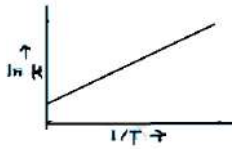
(a) equilibrium constant (b) Δ_rG (c) Δ_rH (d) E_a

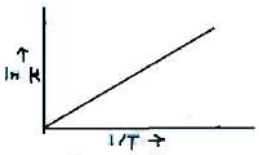
Q.4 "If the rate of the reaction $2 H_2O_2 \rightarrow 2 H_2O + O_2$ is $r = k[H_2O_2]$, what is the reaction order?"

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

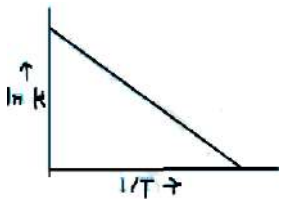
Q.5 According to Arrhenius equation rate constant k is equal to $A e^{-Ea/RT}$. Which of the following options represents the graph of ln k vs 1/T ?

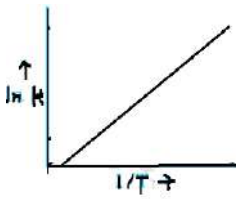
(a) (b)





(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) $\ln [R]_o$ (d) k/2.303

Q.7 A 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.8 If 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) 0 (b) 1 (c) 2 (d) 3

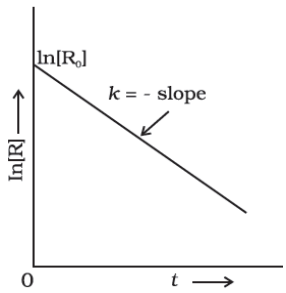
Q.9 To what order of a reaction does the following graph belong to?

(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):** Hydrolysis of methyl ethanoate is a pseudo-first-order reaction.

Reason(R): Water is present in large excess, and therefore its concentration remained constant throughout the reaction.

Q.12 **Assertion (A):** The presence of a catalyst increases the activation energy of a reaction.

Reason (R): Catalysts provide an alternative reaction pathway with a lower activation energy.

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): A bimolecular reaction becomes first order reaction when one of the reactants is in excess.

Reason(R): Rate is not significantly affected by change in concentration of the reactant present in small amount.

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

<u>Section – B (Short answer Questions) 2 marks each</u>

Q.1 A chemical reaction reduces the amount of a substance following first-order kinetics, with k=$60s^{-1}$. 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 order is different from Molecularity.

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

(Hint: Yes)

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.5 From 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.

[Hint: Put the value of E_a by this formula $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$

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

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

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

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.

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

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 $2{\cdot}418 \times 10^{-5}$ 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.

[Hint:

According to Arrhenius equation,

$$\log K = \log A - \frac{E_a}{2{\cdot}303RT}$$

so value of pre-exponential $A = \text{Antilog } 12{\cdot}5916 = 3{\cdot}9 \times 10^{12}\,s^{-1}$.

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

The data obtained is:

[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 s

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) (i) $t = \{[A]_o - [A]\}/k$; $t = 30$ sec

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

Q.3a) A reaction is first order in A and second order in B.

(i) Write the differential rate equation.

(ii) How is the rate affected when the concentrations of both A and B are doubled?

b) The half-life for radioactive decay of 14C is 5730 years. An archaeological artifact containing wood had only 80% of the 14C found in a living tree. Estimate the age of the sample.

Hint- a .i) Rate= $k[A][B]^2$ (ii) Use formula, Rate= $k[A][B]^2$

b) use first order integrated rate equation to solve the problem.

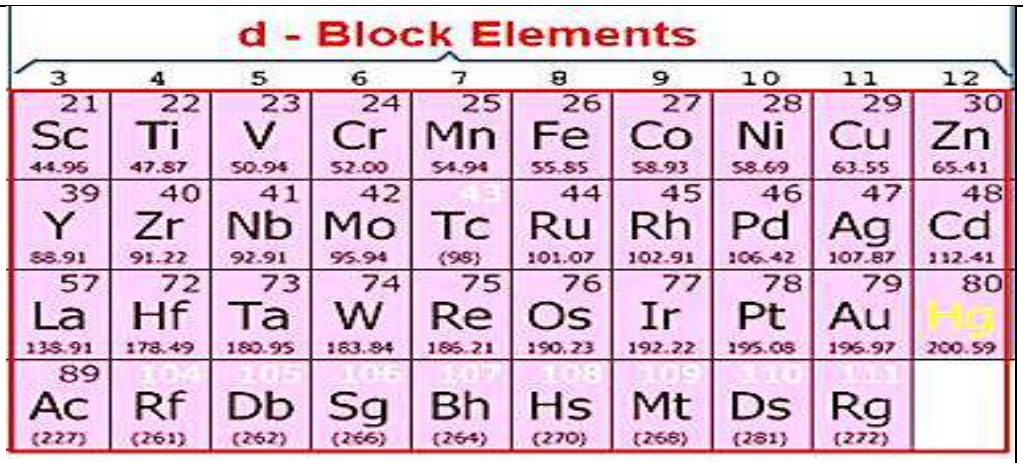
UNIT-4: d & f-BLOCK ELEMENTS (7 Marks)

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

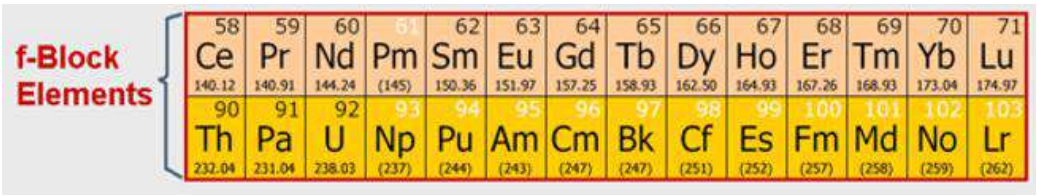
and lanthanide contraction and its consequences. Actinides - Electronic configuration, oxidation states and comparison with lanthanides

Key Concepts

s-Block



p-Block



General introduction-

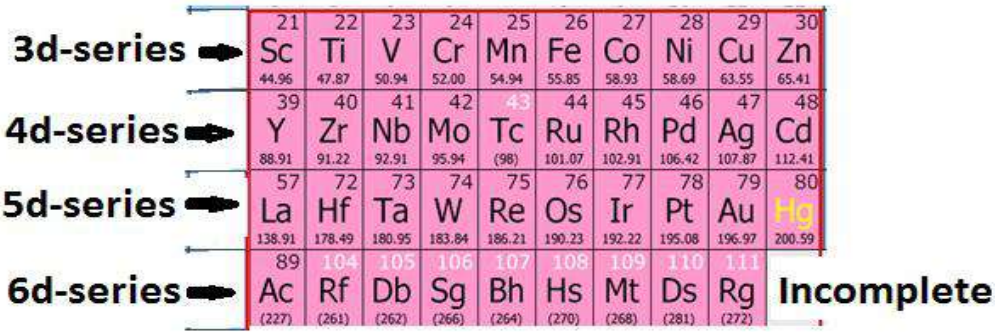
- The TRANSITION ELEMENTS are those elements which have partially filled d-sub shell in their elementary form or in their commonly occurring oxidation states.
- Zn, Cd and Hg not regarded as transition elements because they do not have partially filled d-subshell

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

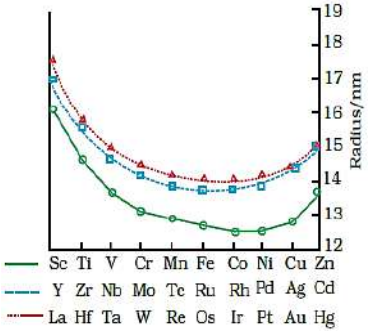
There are four transition series in d-Block of elements –

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.

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 O_2 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 MnO_2 followed by the electrolytic oxidation of manganate (VI).

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

c) In laboratory, Mn^{2+} 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:

$$5\,\begin{matrix}COO^-\\|\\COO^-\end{matrix} \longrightarrow 10CO_2 + 10e^- \qquad 5NO_2^- + 5H_2O \rightarrow 5NO_3^- + 10H^+ + 10e^-$$

$$5\,Fe^{2+} \rightarrow 5\,Fe^{3+} + 5e^- \qquad 10I^- \rightarrow 5I_2 + 10e^-$$

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:

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

f-Block Elements
Lanthanoids and Actinoids

General Comparison

Basis of Comparison	Lanthanoids	Actinoids
Position in Periodic Table	Elements from La (57) to Lu (71) involving filling of 4f orbitals	Elements from Ac (89) to Lr (103) involving filling of 5f orbitals
General Electronic Configuration	[Xe] $4f^{1-14}$ $5d^{0-1}$ $6s^2$	[Rn] $5f^{1-14}$ $6d^{0-1}$ $7s^2$

Physical Properties

Property	Lanthanoids	Actinoids
Appearance	Soft, silvery white metals	Silvery metals, mostly radioactive
Hardness	Hard but less hard than actinoids	Harder and denser
Melting and Boiling Points	High melting and boiling points	High melting and boiling points
Density	Density increases with atomic number	Generally higher densities
Radioactivity	Mostly non-radioactive except Promethium	All are radioactive
Colour of Ions	Many ions are coloured due to f-f transitions	Ions show more intense colours
Magnetic Nature	Mostly paramagnetic	Strongly paramagnetic

Chemical Properties

Property	Lanthanoids	Actinoids
Oxidation States	Mainly +3 oxidation state	Show variable oxidation states (+3 to+7)
Reactivity	React with oxygen, halogens, acids and water slowly	More reactive than lanthanoids
Formation of Compounds	Form oxides, halides and hydroxides	Form a larger variety of compounds
Complex Formation	Less tendency to form complexes	Greater tendency to form complexes
Nature of Hydroxides	Hydroxides are basic	Hydroxides are less basic
Bonding	Compounds are mainly ionic	Compounds show more covalent character

Lanthanoid Contraction and Consequences

Point	Description
Meaning	Gradual decrease in atomic and ionic radii of lanthanoids from La^{3+} to Lu^{3+}
Cause	Poor shielding effect of 4f electrons
Effect on Size	Size decreases regularly across the series
Consequences	Similarity in properties, difficulty in separation, similarity of Zr and Hf, decrease in basic strength of hydroxides

Actinoid Contraction and Consequences

Point	Description

Meaning	Gradual decrease in atomic and ionic radii from Ac^{3+} to Lr^{3+}
Cause	Poor shielding effect of 5f electrons
Effect on Size	Atomic and ionic sizes decrease gradually
Consequences	Similarity in properties, complex formation tendency, decrease in basic character, difficulty in separation

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.

Unit-4

d AND *f* BLOCK ELEMENTS

1. *d*-BLOCK ELEMENTS (Transition Elements)

1.1 General Introduction

- Elements in which the last electron enters $(n-1)d$ subshell of the outermost shell.
- Groups 3 to 12 of the Periodic Table.
- Show variable oxidation states and form coloured compounds.

1.2 Electronic Configuration

- General configuration: $(n-1)d^{1-10}ns^{0-2}$
- $(n-1)d$ subshell gets filled in these elements.

1.3 General Properties

- Metallic in nature.
- High melting and boiling points.
- Good conductors of electricity and heat.
- Form alloys.

1.4 Important Characteristics

- Variable oxidation states.
- Formation of coloured compounds.
- Paramagnetic nature.
- Tendency to form complex compounds.

1.5 Chemical Properties

- Readily react with oxygen, halogens, acids.
- Show variable oxidation states.
- Form basic oxides and hydroxides.

1.6 Important Compounds

- $KMnO_4$
- $K_2Cr_2O_7$
- MnO_2
- V_2O_5
- $Ni(CO)_4$
- $[Fe(CN)_6]^{4-}$ (Ferrocyanide)
- Pigments (Cr_2O_3)
- Batteries (Ni–Cd)

1.7 Uses

- Alloys (Stainless steel, Nichrome)
- Catalysts (V_2O_5)
- Pigments (Cr_2O_3)
- Batteries (Ni–Cd)

2. *f*-BLOCK ELEMENTS (Inner Transition Elements)

2.1 Lanthanoids (4*f*-Block Elements)

- Elements 58 to 71 (Ce to Lu)
- General electronic configuration: $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$
- Mostly show +3 oxidation state.
- Soft, silvery white metals.
- Form coloured compounds.
- Mostly non-radioactive (Except Pm).

2.2 Actinoids (5*f*-Block Elements)

- Elements 90 to 103 (Th to Lr)
- General electronic configuration: $[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$
- Show variable oxidation states (+3 to +7).
- All are radioactive.
- More reactive than lanthanoids.
- Greater tendency to form complex compounds.

2.3 Lanthanoid Contraction

- Gradual decrease in atomic and ionic radii from La^{3+} to Lu^{3+}.
- Due to poor shielding by *4f* electrons.

Consequences:

- ➢ Similarity in properties of lanthanoids.
- ➢ Difficulty in separation.
- ➢ Similarity of Zr and Hf.
- ➢ Decrease in basic strength of hydroxides from $La(OH)_3$ to $Lu(OH)_3$.

2.4 Actinoid Contraction

- Gradual decrease in atomic and ionic radii from Ac^{3+} to Lr^{3+}.
- Due to poor shielding by *5f* electrons.

Consequences:

- ➢ Similarity in properties of actinoids.
- ➢ Greater tendency to form complexes.
- ➢ Decrease in basic strength of hydroxides.
- ➢ Difficulty in separation.

3. Some Important Concepts Related to *d*-Block

3.1 Variable Oxidation States

- Small energy difference between $(n-1)d$ and ns orbitals.
- Both electrons can participate in bonding.

3.2 Colour of Compounds

- Due to *d*–d transitions.
- Absorption of light from visible region.

3.3 Magnetic Properties

- Due to unpaired electrons.
- Most are paramagnetic.

3.4 Complex Formation

- Small size, high charge and vacant *d* orbitals.
- Form complex ions with ligands.

3.5 Catalytic Activity

- Variable oxidation states.
- Provide alternate pathway.

4. Importance of *d* and *f* Block Elements

- Used in various industries, medicines, catalysts, alloys, pigments, batteries and electronic devices.
- Essential for biological processes (e.g., Fe in haemoglobin, Co in Vitamin B_{12}).
- Actinoids are important in nuclear energy.
- *f*-Block elements show unique properties due to lanthanoid and actinoid contraction.

QUESTIONS AND ANSWERS

Section A (1 MARK)

1. Manganate ion is paramagnetic due to the presence of :
(A) one unpaired electron (B) two unpaired electrons
(C) three unpaired electrons (D) fully paired electrons

2. Iron forms Fe^{2+} and Fe^{3+} ions. Which of the following is true regarding their electronic configuration?
a) Fe^{2+} : [Ar] $3d^6$, Fe^{3+} : [Ar] $3d^5$ b) Fe^{2+} : [Ar] $3d^7$, Fe^{3+} : [Ar] $3d^6$
c) Fe^{2+} : [Ar] $3d^5$, Fe^{3+} : [Ar] $3d^4$ d) Fe^{2+} : [Ar] $3d^4$, Fe^{3+} : [Ar] $3d^3$

3. Which of the following is the correct order of magnetic moment (spin-only) for the ions?
a) $Ti^{3+} < V^{3+} < Cr^{3+} < Mn^{2+}$ b) $Mn^{2+} < Cr^{3+} < V^{3+} < Ti^{3+}$
c) $Cr^{3+} < Ti^{3+} < Mn^{2+} < V^{3+}$ d) $Ti^{3+} < Cr^{3+} < Mn^{2+} < V^{3+}$

4. The electronic configuration of a transition metal ion is $[Ar]3d^5$. The ion could be:
a) Mn^{2+} b) Fe^{2+} c) Cr^{3+} d) Co^{2+}

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. Why is Zn^{2+} ion colourless?
a) It has a fully filled d-orbital b) It has unpaired electrons
c) It absorbs all visible light d) It has empty d-orbitals

7. The separation of lanthanides is difficult due to:
a) High reactivity of lanthanides
b) Similar chemical and physical properties
c) Different oxidation states of lanthanides
d) Low melting and boiling points of lanthanides

8. The stability of which ion is due to its half-filled d-orbital configuration?
a) Fe^{2+} b) Mn^{2+} c) Cu^{2+} d) Zn^{2+}

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	A	A	A	A	B	A	B	B	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 (A):** Transition metals form alloys easily.
Reason (R): Transition elements have partially filled d subshell.

3. **Assertion (A):** Lanthanides show a gradual decrease in atomic and ionic radii across the series.
Reason (R): This is due to the poor shielding effect of 4f electrons.

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	B	A	C	B

Section- C (2 Marks questions)

1. Why are Sm^{2+}, Eu^{2+}, and Yb^{2+} ions in solutions 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.

Consequences: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.

(iii) 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 √[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 , μ=√[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

UNIT- 5: COORDINATION COMPOUNDS (7 Marks)

Coordination compounds - Introduction, ligands, coordination number, colour, magnetic properties and shapes, IUPAC nomenclature of mononuclear coordination compounds. Bonding, Werner's theory, VBT, and CFT;

structure and stereoisomerism, importance of coordination compounds (in qualitative analysis, extraction of metals and biological system).

Key Concept

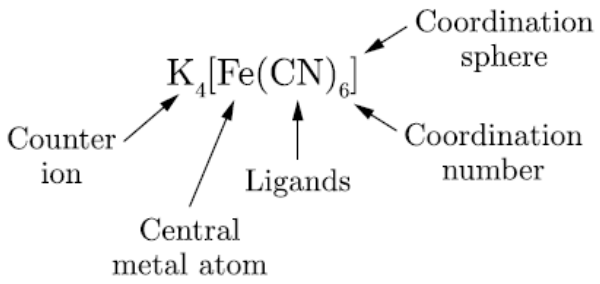
- **Coordination Compounds**

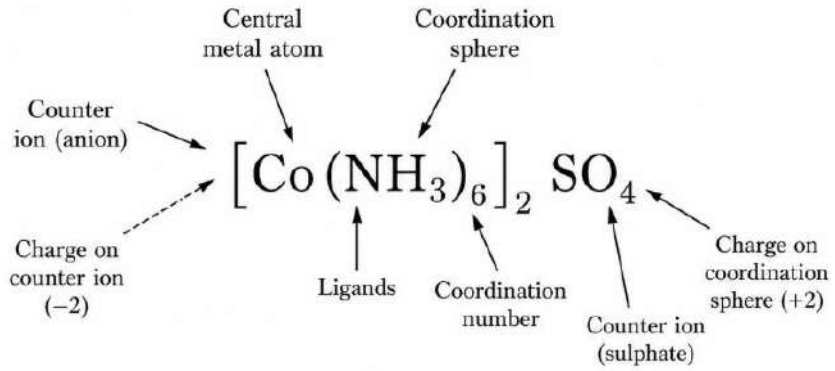
Coordination compounds are the compounds which contain complex ions. These compounds contain a central metal atom or cation which is attached with a fixed number of anions or molecules (called ligands) through coordinate bonds.

- **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, $FeSO_4.(NH_4)_2SO_4.6H_2O$ $\rightarrow Fe^{+2} + 2NH_4^+ + SO_4^{-2} + 6H2O$ Potash Alum $K_2SO_4Al_2SO_4.24H_2O$ $\rightarrow 2K^+ + 2SO_4^{-2} + 2Al^{+3} + 24H_2O$	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 COORDINATION 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-

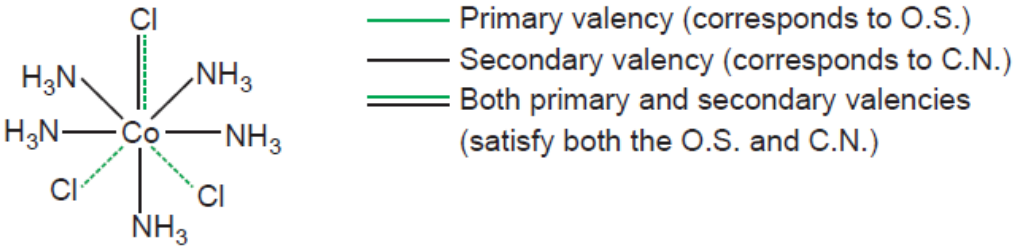
Monodentate/ Unidentate:	Ligands which Contain only one donar atom Ex-Cl^- ;H_2O, NH_3, NO_2^-.
Didentate/ Bidentate	Ligands which Contain two donor atoms. Ex-$C_2O_4^{2-}$(ox); $NH_2CH_2CH_2NH_2$(en)

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 – CNS^- and NCS^-, NO^- and ONO^-, CN^- and NC^-

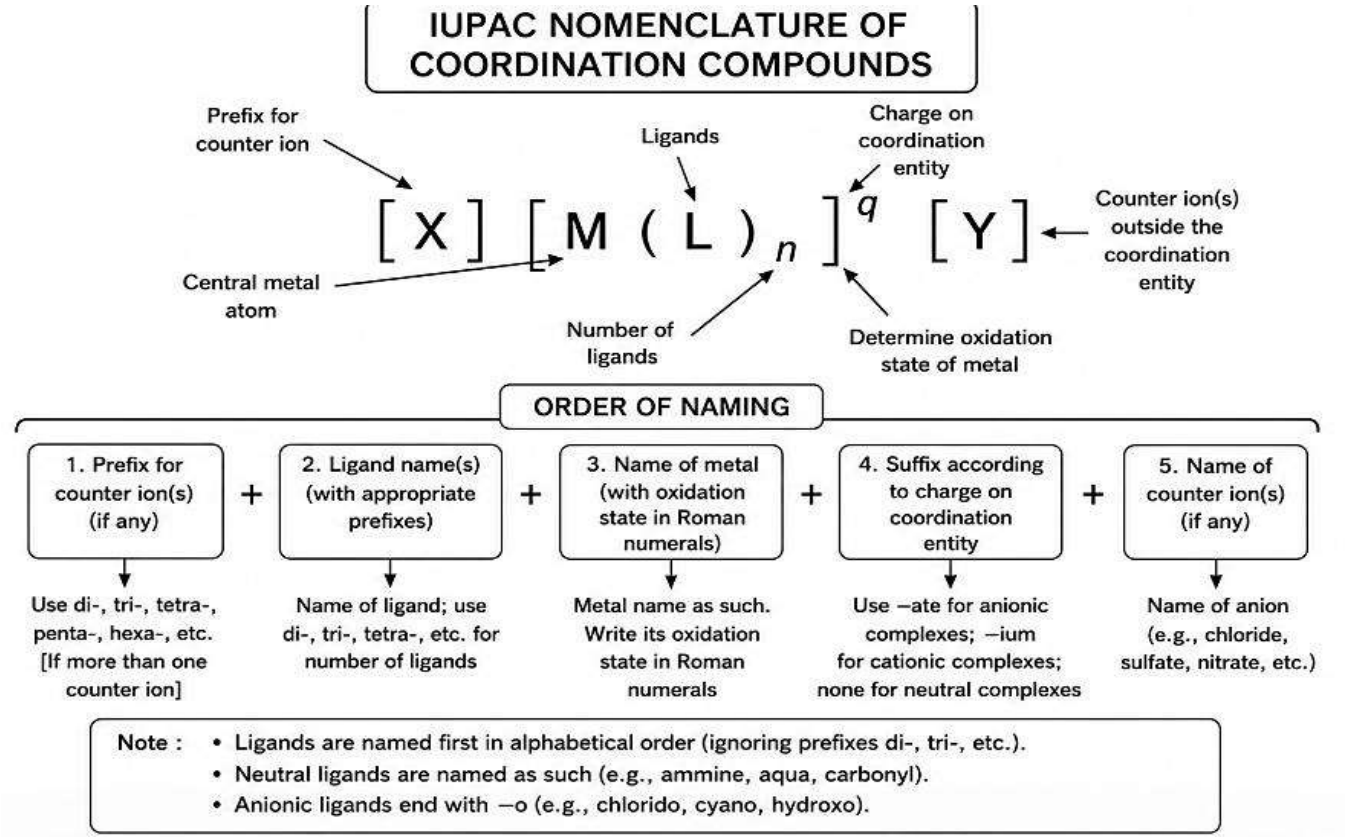
Coordination number: The number of ligand donor atoms to which the metal is directly bonded through coordinate bond. It determine the geometry of coordination complex.
Counter ions: The ionisable groups written outside the square bracket. Ex- K^+ in $K_4[Fe(CN)_6]$ OR 3 Cl^- in $[Co(NH_3)_6]Cl_3$
Coordination 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- $[Co(NH_3)_4\ Cl_2]^+$

- **<u>Werner's theory of coordination Compounds-</u>**

Developed by Alfred Werner in 1893.The main postulates of this theory are:
(*i*) In coordination compounds, metals show two types of valencies: primary and secondary.
(*ii*) The primary valencies are normally ionisable and are satisfied by negative ions.
(*iii*) The secondary valencies are non ionisable and are satisfied by neutral molecules or negative ions. The secondary valency is equal to the coordination number and is fixed for a metal.
(*iv*) The ions or groups bound by secondary linkage to the metal have characteristic spatial arrangements corresponding to different coordination number.



Example of Complex	Number and Name of Primary Valencies	Number and Name of Secondary Valencies
$[Fe(CN)_6]^{4-}$	2 primary valencies	6 secondary valencies
$[Co(NH_3)_6]Cl_3$	3 primary valencies	6 secondary valencies
$[Co(NH_3)_6][Cr(CN)_6]$	3 primary valencies each for Co and Cr	6 secondary valencies each for Co and Cr

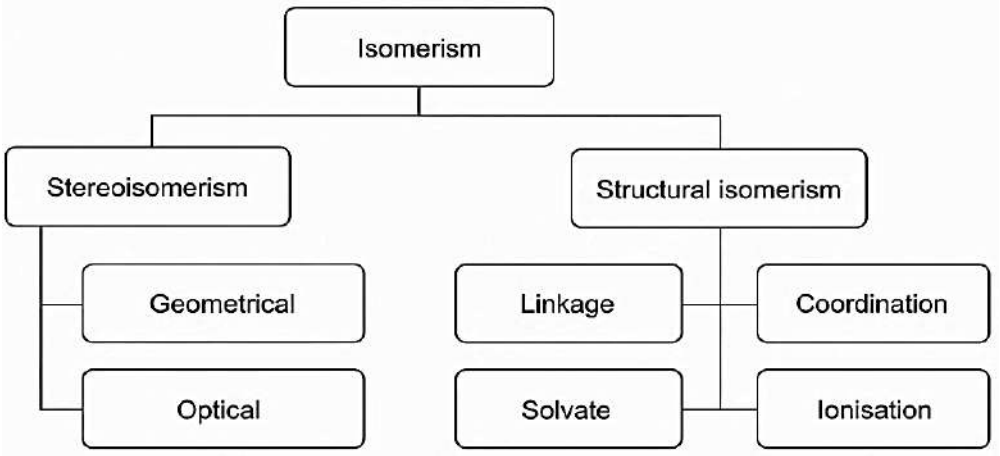


IUPAC names of some coordination compounds

S. No.	Formula	Name
(i)	$[Pt(NH_3)_2ClNO_2]$	diamminechloridonitrito–N–platinum(II)
(ii)	$[CoCl_2(en)_2]Cl$	dichloridobis(ethane-1, 2-diamine) cobalt(III) chloride
(iii)	$K_3[Fe(C_2O_4)_3]$	potassium trioxalatoferrate(III)
(iv)	$[Ag(NH_3)_2].[Ag(CN)_2]$	diammine silver(I) dicyanoargentate(I)

ISOMERISM IN COORDINATION COMPOUNDS

Compounds having same molecular formula but different structural formula or stereo-forms are called isomers and the phenomenon is said to be isomerism.

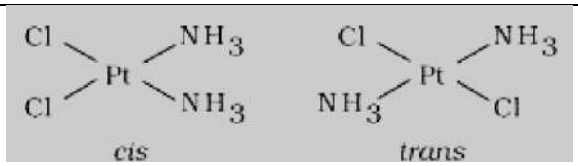
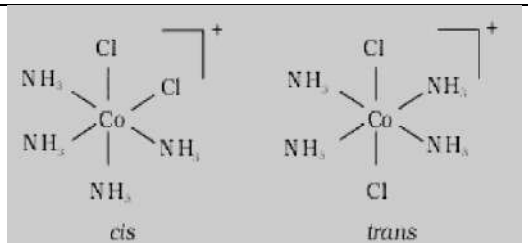
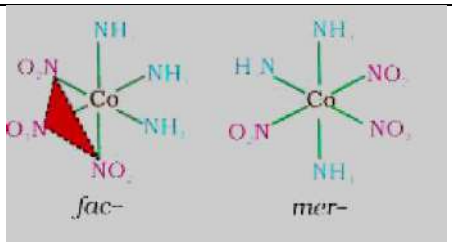


A) **Structural Isomerism**-isomerism in which coordination compounds have the same molecular formula but differ in the arrangement or connectivity of ligands, counter ions, or coordination spheres within the compound.

Sr.No.	Type	Description
1	Ionisation Isomerism	The compounds which have the same molecular formula but give different ions in solution. $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.
2	Linkage Isomerism	It occurs in compounds which having ambidentate ligands showing different modes of attachment to metal through either of the two different donar atom. (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	It arises when both the cation and anion are complexes which differ in the distribution of ligands. $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
4	Solvation Isomerism	The compounds which have the same composition but differ in the number of solvent or water molecules present as ligands $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$

B) Stereo Isomerism- Compounds are stereo-isomers when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space. They are of two types:

A. Geometrical isomerism B.Optical isomerism

<table>
<tr><td colspan="3">Geometrical Isomerism -This type of isomerism arises in heteroleptic complexes due to different possible geometric arrangements of the ligands</td></tr>
<tr><td>COORDINATION NO-4
(Square planar complexes)</td><td>$[Ma_2b_2]$ type complexes
$[Pt(NH_3)_2Cl_2]$</td><td> 
</td></tr>
<tr><td colspan="3">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</td></tr>
<tr><td rowspan="2">COORDINATION NO 6
(Octahedral Complexes</td><td>$[Ma_2b_4]$ type complexes
$[Co(NH_3)_4Cl_2]^+$</td><td> 
</td></tr>
<tr><td>$[Ma_3b_3]$ type complexes
$[Co(NH_3)_3(NO_2)_3]$</td><td> 
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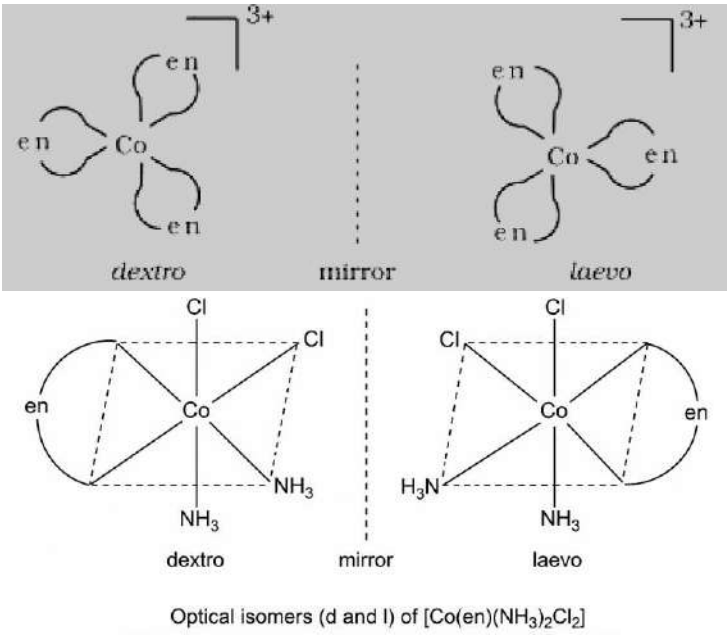
Optical Isomerism: Optical isomers are mirror images that cannot be superimposed on one another and are called as enantiomers.

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



Optical isomers (d and l) of $[Co(en)(NH_3)_2Cl_2]$

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

1. The central metal atom/ion provides empty hybrid orbitals (equivalent 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	Examples
4	sp^3	Tetrahedral	$[NiCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2	Square planar	$[PtCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$
6	sp^3d^2	Octahedral	$[CoF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$
6	d^2sp^3	Octahedral	$[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$

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.

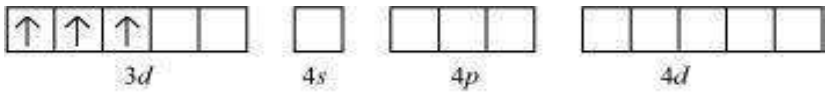
$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < CN^- < CO$

Mnemonic: "I Bought Spicy Chips, Sandwiches, Fries, Omelette, Cold Honey Noodles, Eggs, Naan, Energy Chocolates, Cookies."

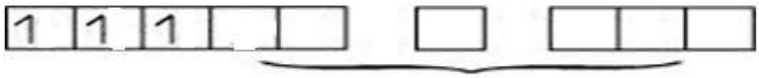
- I → I^-
- Bought → Br^-
- Spicy → SCN^-
- Chips → Cl^-
- Sandwiches → S^{2-}
- Fries → F^-
- Omelette → OH^-
- Cold → $C_2O_4^{2-}$
- Honey → H_2O
- Noodles → NCS^-
- Eggs → $EDTA^{4-}$
- Naan → NH_3
- Energy → en
- Chocolates → CN^-
- Cookies → CO

Examples (VBT in coordination Compounds): 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: **d^2sp^3** ; Geometry: **Octahedral;** Magnetic: **Paramagnetic** (due to 3 unpaired electrons)

Some more example:-

Sr.No.	**Complex**	**Oxidation State**	**Type of Ligand**	**Hybridisation**	**Geometry**	**Magnetic Nature**
1	$[Cr(NH_3)_6]^{3+}$	+3	Strong	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 (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.

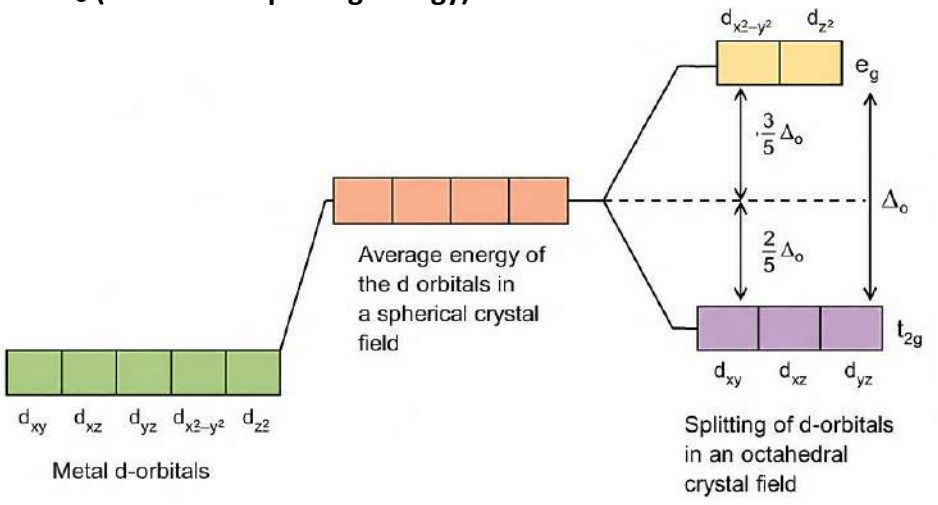
2. Degeneracy of *d*-orbitals is Lifted: In a free metal ion, the five *d*-orbitals are degenerate (have the same energy). In a complex, due to the ligand field, these orbitals split into groups with different energies.

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_o (octahedral splitting energy)**



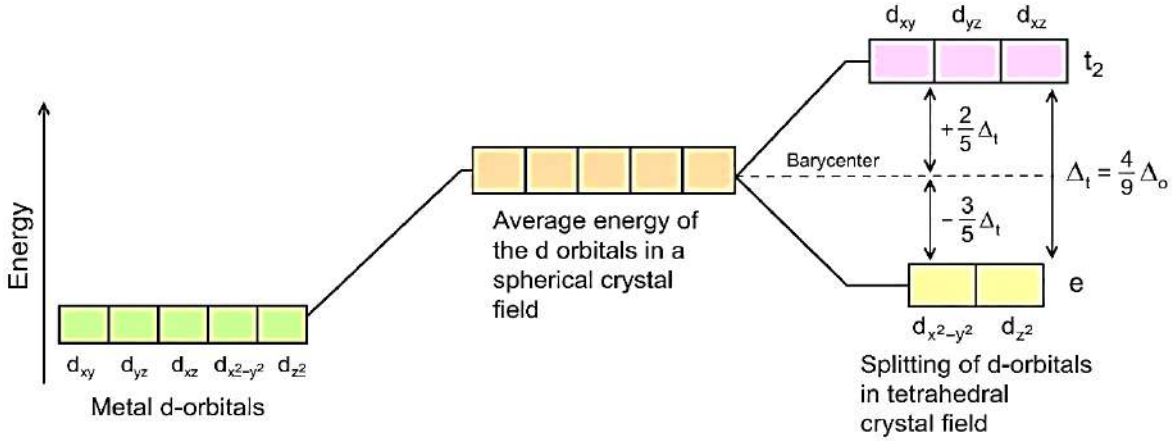
d-orbitals splitting in an octahedral crystal field

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
$\Delta_o < P$	$\Delta_o > P$
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)**



d-orbitals splitting in an tetrahedral crystal field

<u>Why Coordination Compounds are Colored-</u>

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.

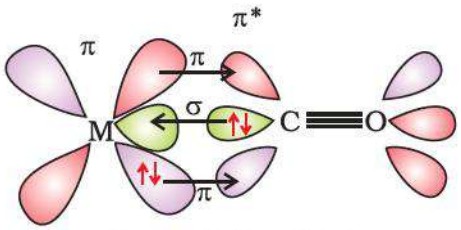
2. Charge Transfer Transitions: Electrons are transferred between the metal and ligands or vice-versa. These transitions also absorb light in the visible region, producing color.

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($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0\ e_g^1$). 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^o 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**.**



Synergic bonding

Applications of coordination compounds:

(i) Complex formation is frequently encountered in analytical chemistry. For example identification of Cu^{2+} is based on the formation of a blue complex with NH_3 :-

$CuCl_2 + 4NH_3 \rightarrow [Cu(NH_3)_4]Cl_2$

and that of Fe^{3+} on the formation of a red complex with KSCN:

$FeCl_3 + KSCN \rightarrow K_3[Fe(SCN)_6] + 3KCl$

Similarly. Ni^{+2} is estimated as red complex with dimethyl glyoxime (DMG).

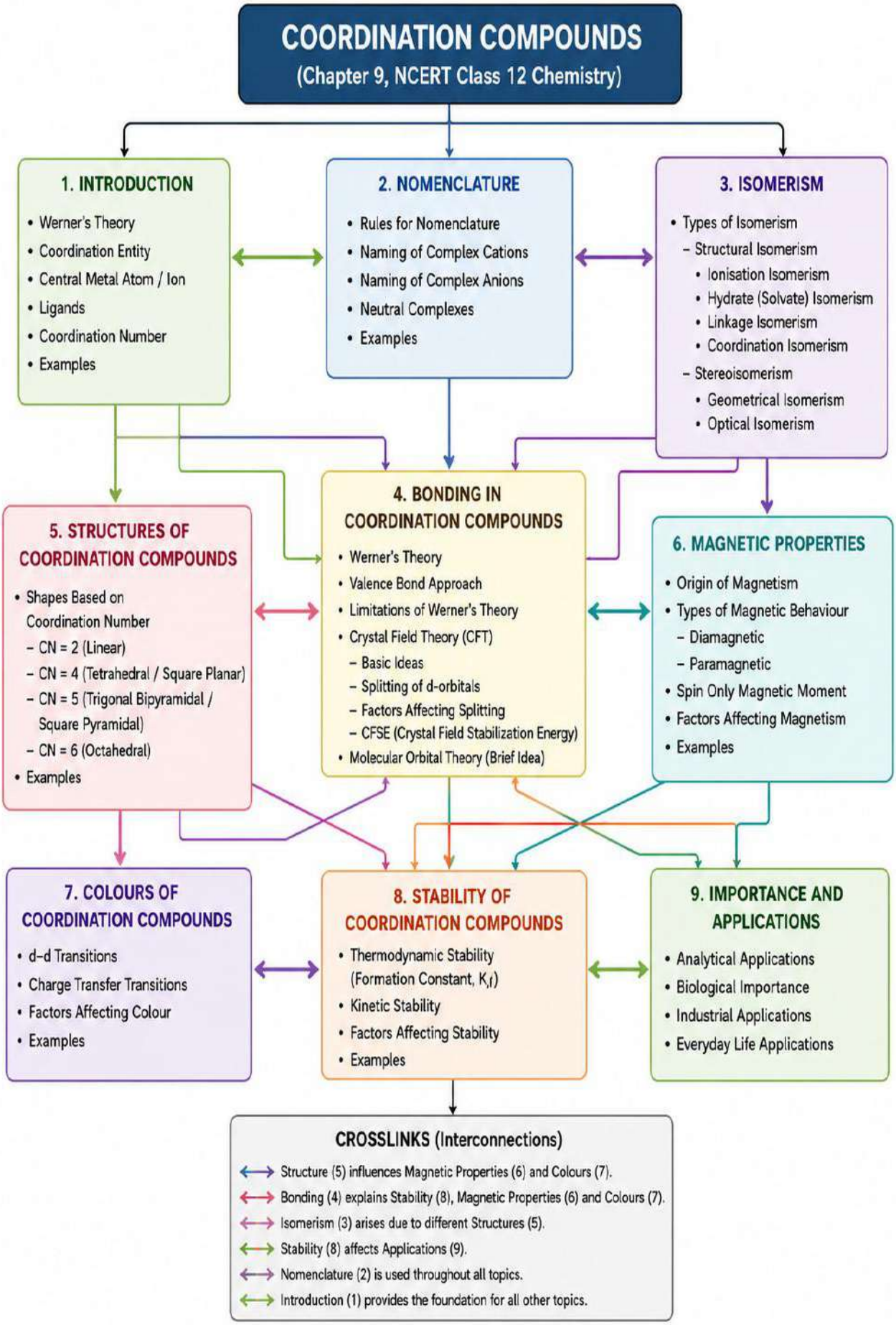
(ii) Complex formation is used in the extraction of metals from their ores. For example Ni is extracted from its ores as volatile nickel carbonyl.

$Ni + 4CO \rightarrow Ni(CO)_4 \uparrow \quad Heated \rightarrow \quad Ni + 4CO$

(iii) Metal complexes of Ag. Au, Cu, etc., are used for electroplating of these metals on the desired objects.

(iv) Many biological processes involve complex formation. For example haemoglobin, chlorophyll, vitamin B_{12} , cisplatin are complexes.

(v) Hardness of water is estimated by complexometric titration of Ca^{2+} and Mg^{2+} with ethylene diaminetetraacetic acid (EDTA).



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, $K_2[Ni(CN)_4]$, 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. The total number of possible isomers for the complex $[Co(C_2O_4)_2(NH_3)_2]$ are:

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

5. The stabilisation of coordination compounds due to chelation is called the chelate effect. Which of the following is the most stable complex species?

(a) $[Fe(CO)_5]$ (b) $[Fe(CN)_6]^{3-}$ (c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[Fe(H_2O)_6]^{3+}$

6. The colour of the coordination compounds depends on the crystal field splitting. What will be the correct order of absorption of wavelength of light in the visible region, for the complexes, $[Co(NH_3)_6]^{3+}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$?

(a) $[Co(CN)_6]^{3-} > [Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+}$

(b) $[Co(NH_3)_6]^{3+} > [Co(H_2O)_6]^{3+} > [Co(CN)_6]^{3-}$

(c) $[Co(H_2O)_6]^{3+} > [Co(NH_3)_6]^{3+} > [Co(CN)_6]^{3-}$

(d) None of the above

(Hint: Greater the crystal field splitting energy (Δ_o), smaller will be the wavelength absorbed. Use the spectrochemical series)

7. On the basis of CFT what will be the electronic configuration of d^5 in terms of t_{2g} and e_g Orbitals when $\Delta_0 > P$.

a) $t_{2g}^4 e_g^1$ b) $t_{2g}^5 e_g^0$ c)) $t_{2g}^0 e_g^5$ d)) $t_{2g}^3 e_g^2$

8. Match the coordination compounds given in Column I with their corresponding properties or applications given in Column II and choose the correct option.

Column I	Column II
(A) $[Co(NH_3)_6]Cl_3$	(1) Anticancer drug
(B) $K_4[Fe(CN)_6]$	(2) Paramagnetic complex
(C) cis-$[Pt(NH_3)_2Cl_2]$	(3) Coordination number = 6
(D) $[Cr(H_2O)_6]Cl_3$	(4) Strong field ligand complex

(a) A–3, B–4, C–1, D–2 (b) A–4, B–3, C–2, D–1

(c) A–2, B–1, C–4, D–3 (d) A–1, B–2, C–3, D–4

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. Which of the following pairs represent linkage isomers?

(a) $[Pd(PPh_3)_2(NCS)_2]$ and $[Pd(PPh_3)_2(SCN)_2]$

(b) $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$

(c) $[PtCl_2(NH_3)_4]Br_2$ and $[PtBr_2(NH_3)_4]Cl_2$

(d) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

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 chelating ligand must possess two or more lone pairs at such a distance that it may form suitable strain free rings at the metal ion.
Reason : $H_2N - NH_2$ is a chelating ligand.

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 : $[Co(NH_3)_5SO_4]Cl$ gives a white precipitate with silver nitrate solution.
Reason : The complex dissociate to give Cl^- and SO_4^{2-} ions.

ANSWERS

ANSWERS KEY :

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A	d	a	d	d	c	c	b	a	b	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(NH3)5 Br] SO4 and [CO (NH3)5 SO4] ; (b) No*

2. A, B and C are three complexes of Chromium 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 = $[Cr(H_2O)_5Cl]Cl_2 . H_2O$ As C loses 13.5% of wt. on heating which is twice the loss in the first case. C isomer exists as a dihydrate :

$[Cr(H_2O)_4Cl_2]Cl . 2H_2O$.)

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.)*

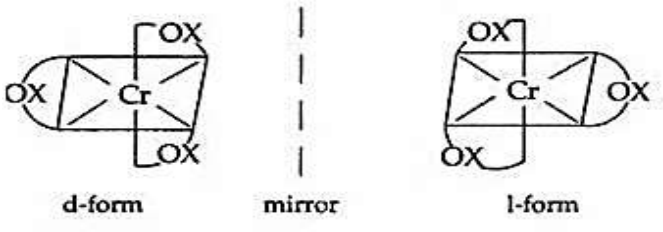
4. A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

HINT- *-In $[Ni(H_2O)_6]^{2+}$, H_2O 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.*

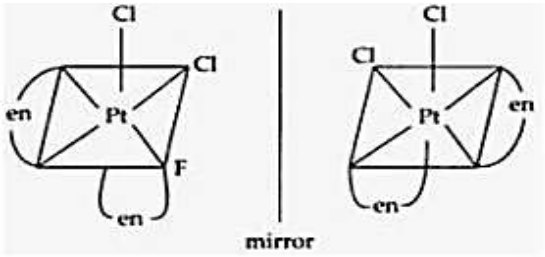
5. Draw the structures of optical isomers of each of the following complex ions:

$[Cr(C_2O_4)_3]^{3-}$, $[PtCl_2(en)_2]^{2+}$

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, e_g^2	t_{2g}^6, e_g^0

b). The orbital splitting energies, $\boldsymbol{\Delta_t}$ 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) 4

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 (Δ_o) depends upon the nature of the ligand and the charge of the metal ion. The electronic configuration of the metal ion in the complexes depends on the relative values of Δ_o and P (pairing energy). If $\Delta_o < P$, then complex will be high spin. If $\Delta_o > P$, then complex will be low spin.

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

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

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

OR

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

a) Hexaaminechromium (III) ion (At no of Chromium = 24)
b) Tetraamminezinc(II) ion (At number of Zinc =30)

HINT: *(i) Magnetic moment= √n×(n+2); Answer: μ=√24 BM*

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

OR

(iii) a) Paramagnetic. b) Diamagnetic

SECTION -E (5 MARKS):

1. (a) Draw the geometrical isomers of $[Co(en)_2Cl_2]^{2+}$. Which geometrical isomer of $[Co(en)_2Cl_2]^{2+}$ is not optically active and why?

(b) Write the hybridisation and magnetic behaviour of $[CoF_6]^{3-}$.

[Given: Atomic number of Co = 27]

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*

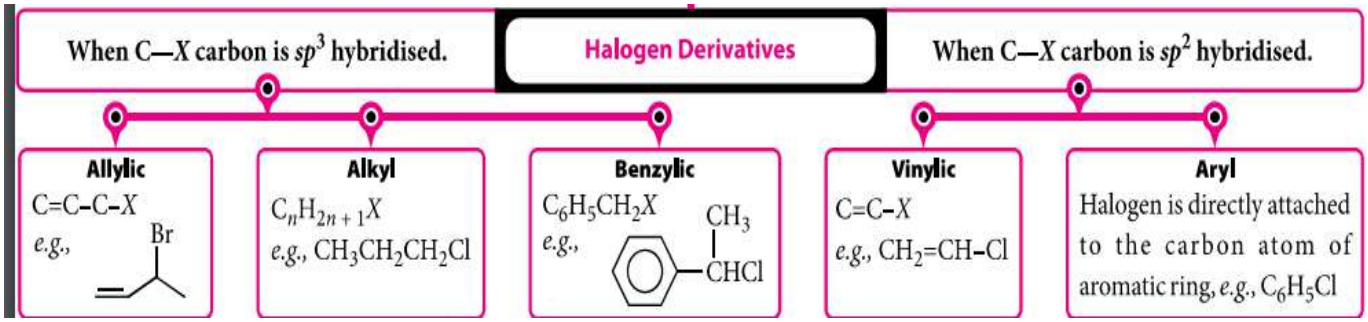
(ii) $[FeF_6]^{3-}$, F^- is a weak field ligand hence pairing doesn't occur; Answer: sp^3d^2

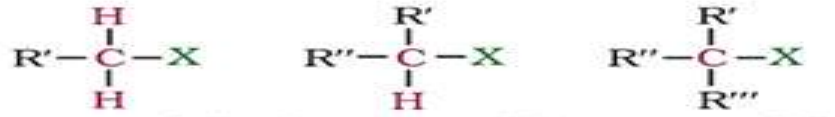
UNIT-6: HALOALKANES AND HALOARENES (6 Marks)

Haloalkanes: Nomenclature, nature of C–X bond, physical and chemical properties, optical rotation mechanism of substitution reactions. **Haloarenes**: Nature of C–X bond, substitution reactions (Directive influence of halogen in monosubstituted compounds only). Uses and environmental effects of - dichloromethane, trichloromethane, tetrachloromethane, iodoform, freons, DDT.

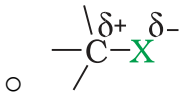
- When one or more hydrogen atoms in a hydrocarbon—either aliphatic or aromatic—are replaced by halogen atoms, the resulting compounds are known as alkyl halides (haloalkanes) and aryl halides (haloarenes), respectively.

- **CLASSIFICATION OF HALOALKANE AND HALOARENE**



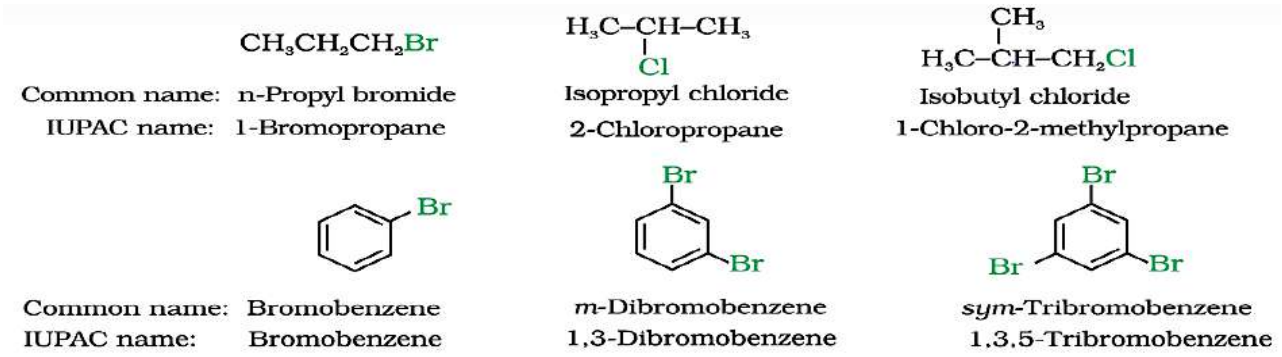
Halogen attached to sp^3 carbon	

- **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.



- **Nomenclature:**

- **Rule : Halo+ Alk+ane/ene/yne**

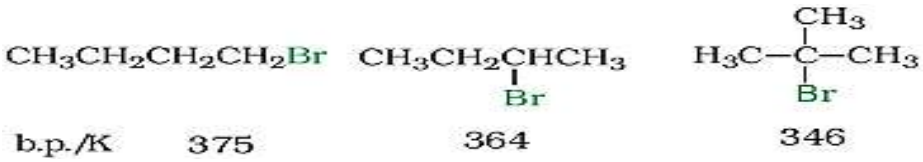


➢ Methods of Preparation for Haloalkane:

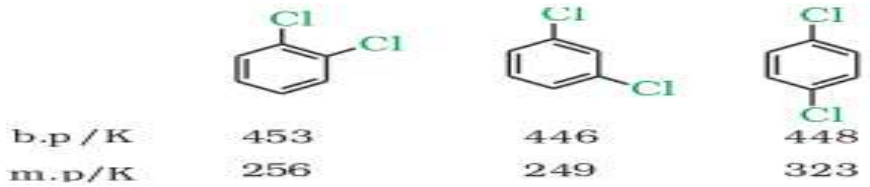
1. From Alcohol	$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$ $R\text{–}OH + NaBr + H_2SO_4 \longrightarrow R\text{–}Br + NaHSO_4 + H_2O$ $3R\text{–}OH + PX_3 \longrightarrow 3R\text{–}X + H_3PO_3 \quad (X = Cl, Br)$ $R\text{–}OH + PCl_5 \longrightarrow R\text{–}Cl + POCl_3 + HCl$ $R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red } P/X_2} R\text{–}X$ $R\text{–}OH + SOCl_2 \longrightarrow R\text{–}Cl + SO_2 + HCl$ Where R=Alkyl Group(CH_3,C_2H_5 etc)	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	$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/UV\ light} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$ $CH_3CH(CH_3)CH_2CH_3 \xrightarrow[300°C]{Cl_2}$ 2-Methylbutane → 1-Chloro-2-methylbutane + 2-Chloro-2-methylbutane + 2-Chloro-3-methylbutane + 1-Chloro-3-methylbutane	(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.
	$CH_3CH=CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$	(i) Alkene reacts with hydrogen halide (ii) Major and minor product is given by Markovnikov's rule.
	$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} BrCH_2\text{–}CH_2Br$ *vic*-Dibromide	In this reaction, brown color of bromine water disappears, indicating the presence of unsaturation (C=C or C≡C).
3. Halogen Exchange	$R\text{–}X + NaI \xrightarrow{\text{dry acetone}} R\text{–}I + NaX$ X=Cl, Br R= CH_3, C_2H_5, C_6H_5 etc	(i) Name reaction: Finkelstein Reaction (ii) NaCl or NaBr formed as side product is precipitated in dry acetone and facilitates the forward reaction.
	$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$ 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:



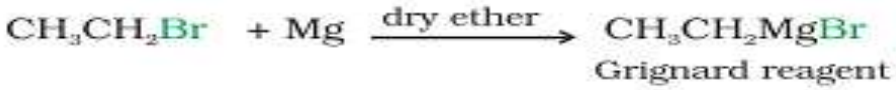
Note: Para-isomers have higher melting points than ortho- and meta-isomers due to their symmetrical structure, allowing better crystal lattice packing.

- 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**

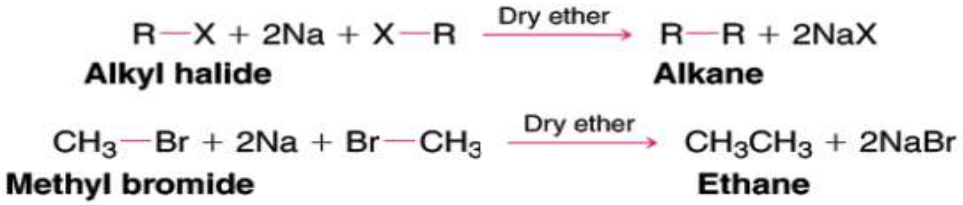
1. Reaction with Metal:

(a) Haloalkanes React with magnesium in dry ether to form RMgX, a compound known as a Grignard reagent. The reaction is given below:



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 dry ether***.

(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:



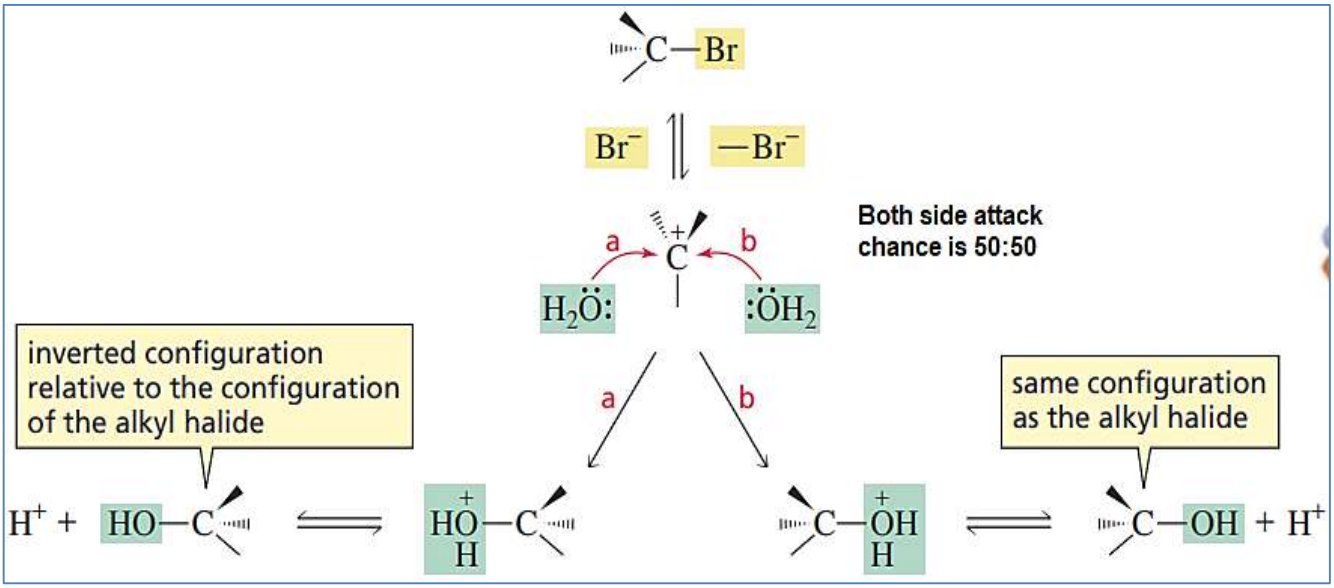
2. Nucleophilic substitution reaction:

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

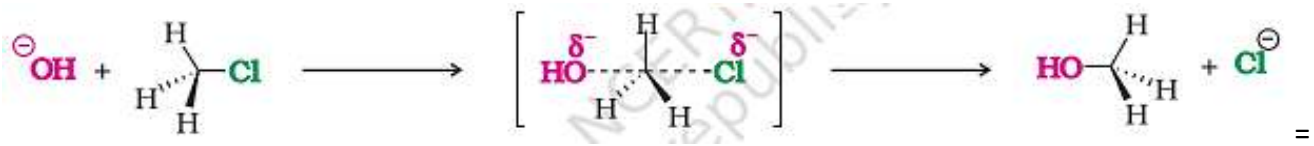
- Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. The example is given below
- (a) R-X + KCN ☮R-CN (Cyanide produce due to ionic nature of KCN)
- (b) R-X + AgCN ☮R-NC (Isocyanide produce due to covalent nature of AgCN)

<u>Substitution nucleophilic unimolecular (S_N1) and Substitution nucleophilic bimolecular (S_N2)</u>

- **<u>Mechanism:</u>**
- **S_N1 Reaction**



S_N2 Reaction



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

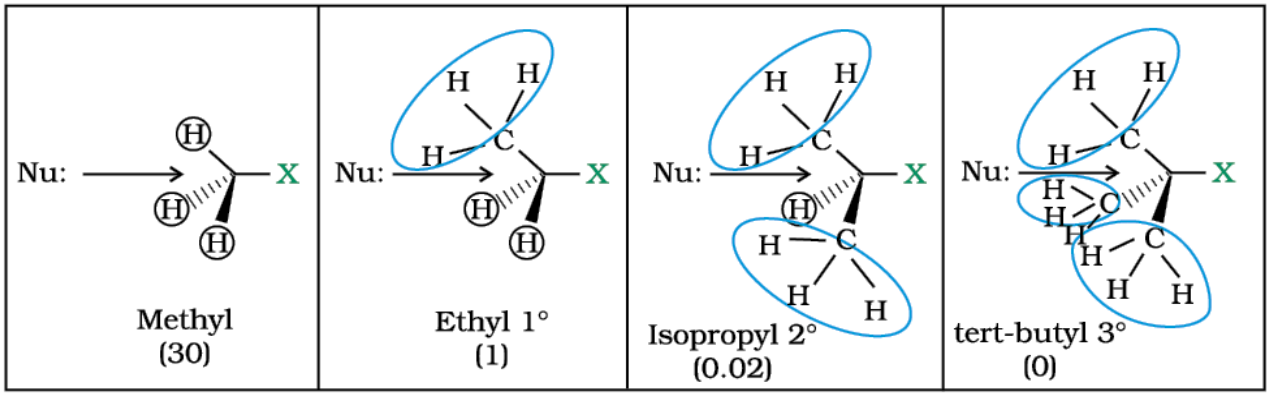
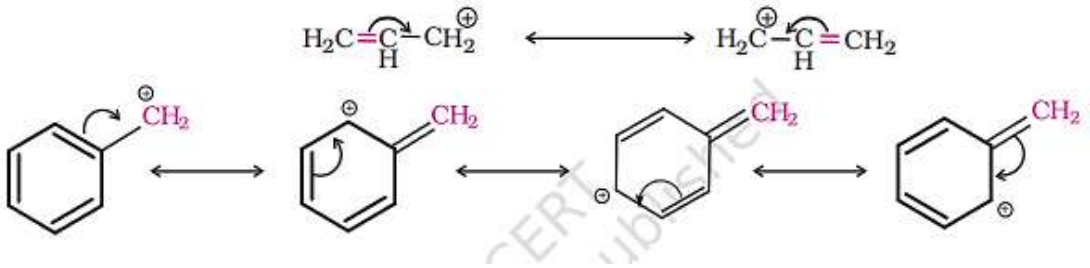


Fig.10.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

(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

For S_N2 reaction

Tertiary halide; Secondary halide; Primary halide; CH_3X

For S_N1 reaction

➢ 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.

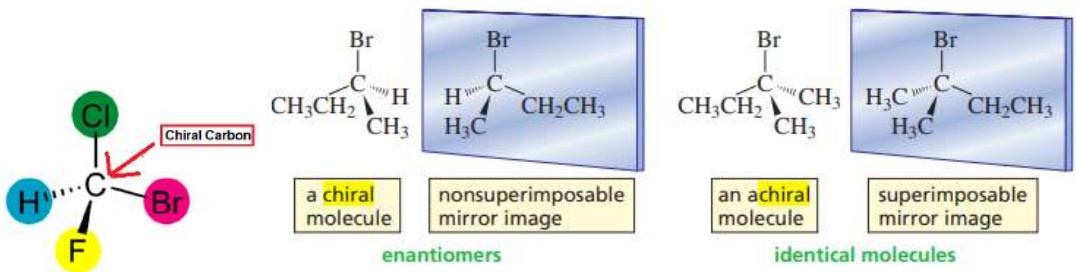
The objects or molecule which are non-superimposable on their mirror image are said to be chiral and property is known as chirality.

The objects or molecule which superimposable on their mirror images are called achiral.

Optically active

Optically inactive

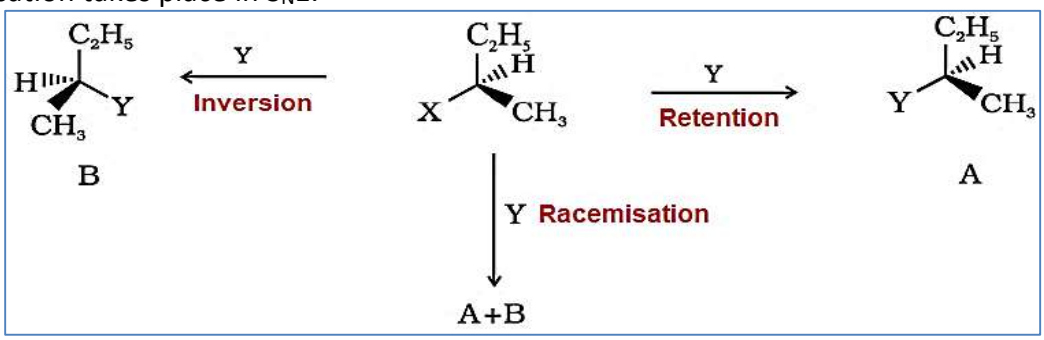
(ii) Nonsuperimposable mirror-image molecules are called **enantiomers.**



(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)**INVERSION, RETENTION AND RACEMISATION**

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

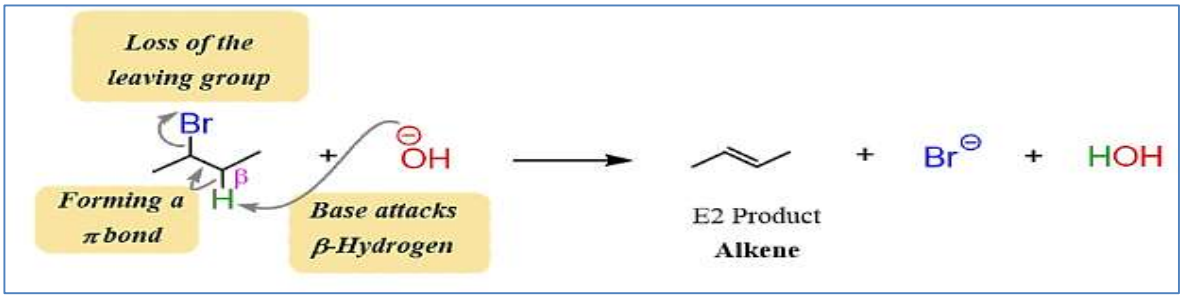


Comparison of S_N1 and S_N2

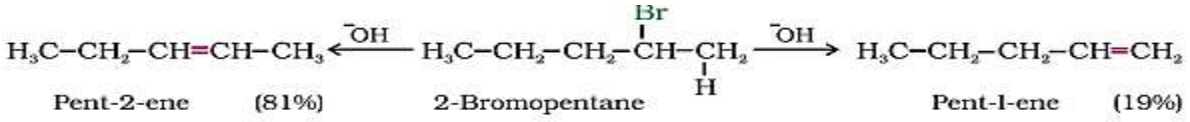
		S_N1	S_N2
A	Kinetics	1st order	2nd order
B	Rate	k[RX]	k[RX][Nu:⁻]
C	Stereochemistry	Racemisation	Inversion
D	Substrate	3 > 2 >1 > MeX	MeX > 1 > 2 >3
E	Nucleophile	Not important	Needs Strong Nu
F	Solvent	Good ionizing	Faster in aprotic
G	Leaving Group	Needs Good LG	Needs Good LG
H	Rearrangement	Possible	Not Possible

3. Elimination reaction/Dehydrohalogenation/ β-elimination

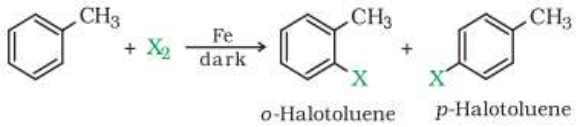
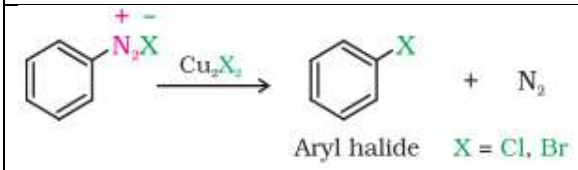
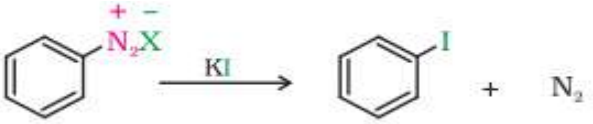
- Elimination of hydrogen atom from β -carbon and a halogen atom from the α-carbon atom simultaneously takes place in presence of strong base like alcoholic KOH is used in this reaction.
- **Mechanism:**



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:

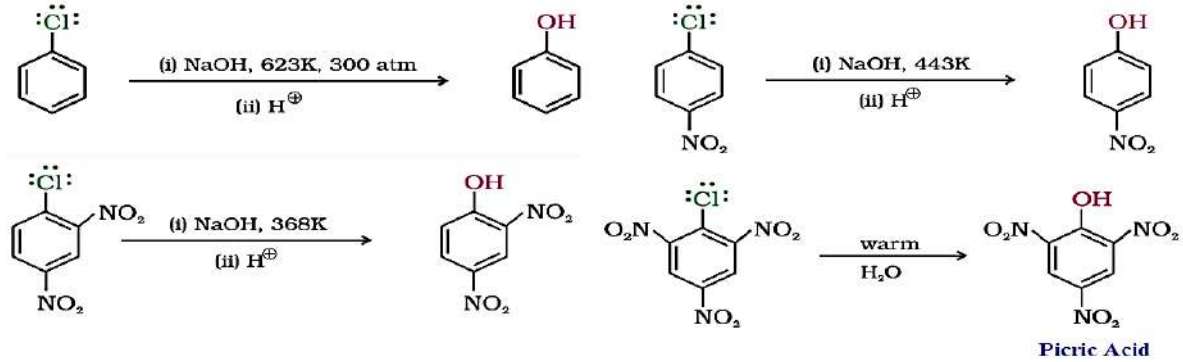


➢ PREPARATION OF HALOARENE:

 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

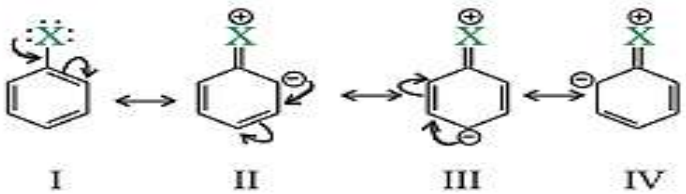
➢ CHEMICAL PROPERTIES OF HALOARENE:

1. **Nucleophilic substitution reactions** chlorobenzene reacts with aqueous NaOH at high temperature and pressure, & give 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:

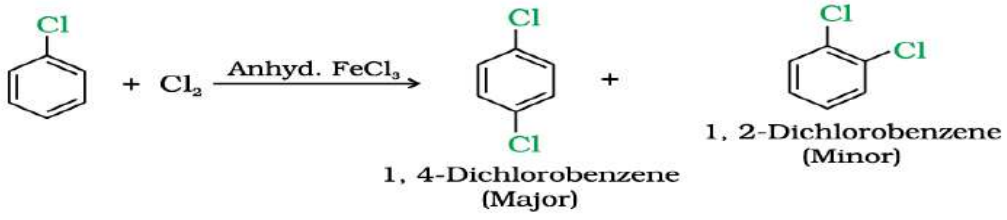


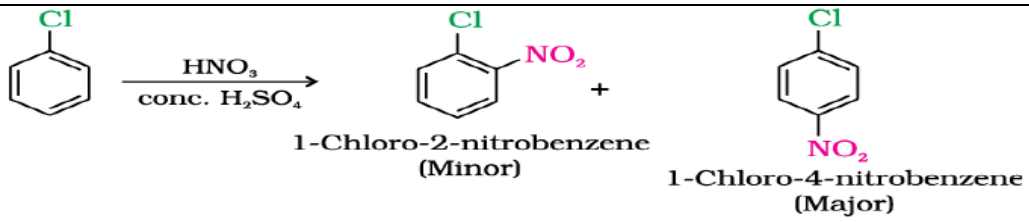
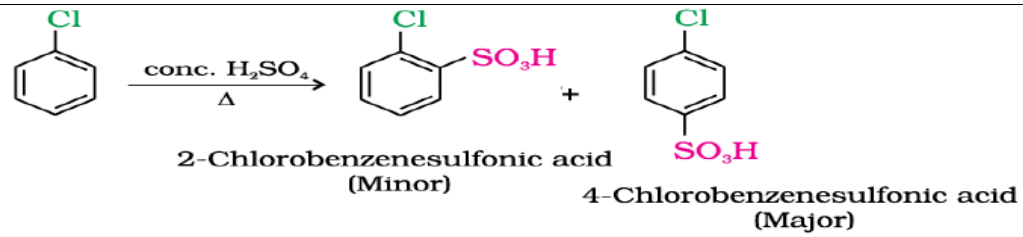
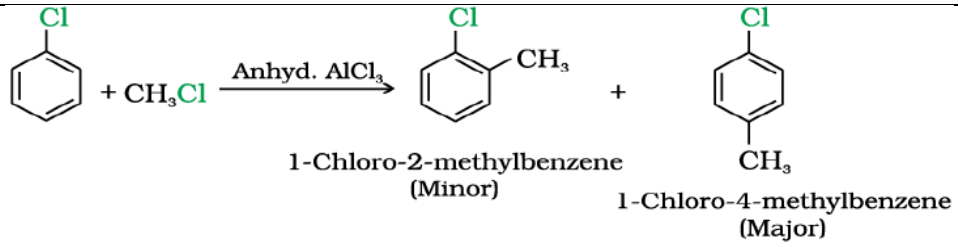
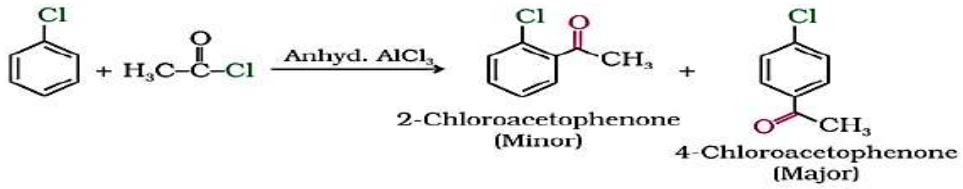
2. Electrophilic substitution reactions:

(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.

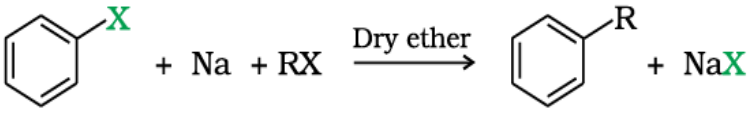
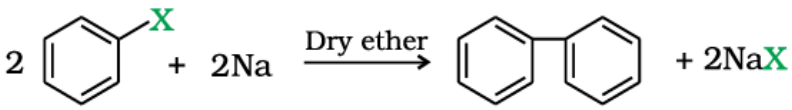


(b) The major product is the para-substituted compound, as it is favored over the ortho product.

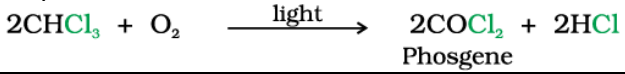
(a) Halogenation	

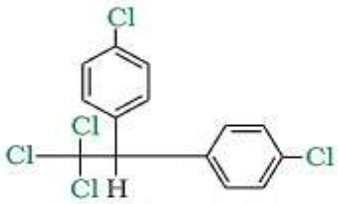
(b) Nitration	
(c) Sulphonation	
(d) Friedel-Crafts reaction (ALKYLATION)	
(d) Friedel-Crafts reaction (ACETYLATION)	

3. Reactions with Metals

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

➢ **Polyhalogen Compounds**

(a) Trichloromethane (Chloroform) **$CHCl_3$**	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. 
(b) Triiodomethane (Iodoform) **CHI_3**	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) **CCl_4**	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 Ex **Freon 12 (CCl_2F_2)**	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.	
(a) Dichloromethane (Methylene chloride) **CH_2Cl_2**	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.	
(f) p,p'Dichlorodiphenyl trichloroethane (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.	 DDT

HALOALKANES

Compounds having one or more halogen atoms bonded to sp^3 hybridised carbon of alkane.

$R-CH_2-X$

(X = F, Cl, Br, I)

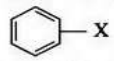
CLASS XII CHEMISTRY

HALOALKANES AND HALOARENES

Organic compounds containing halogen (F, Cl, Br, I) as the functional group.

HALOARENES

Compounds having one or more halogen atoms bonded to sp^2 hybridised carbon of aromatic ring.



(X = F, Cl, Br, I)

GENERAL POINTS

- Haloalkanes are more reactive than haloarenes.
- Reactivity order (R–X) in nucleophilic substitution: RI > RBr > RCl > RF
- Bond strength (C–X) order: R–F > R–Cl > R–Br > R–I

A. HALOALKANES (R–X)

1. PHYSICAL PROPERTIES

- Colourless compounds.
- Lower members (C_1-C_4) are gases, C_5-C_{17} are liquids and higher members are solids.
- Boiling points are higher than corresponding alkanes but lower than corresponding alcohols.
- Insoluble in water but soluble in organic solvents.
- Density greater than water.

2. CHEMICAL PROPERTIES

Undergo mainly nucleophilic substitution reactions.

$$\underset{\text{(Nucleophile)}}{\overset{Nu^-}{\underset{X}{\longrightarrow}}} R-Nu + X^-$$

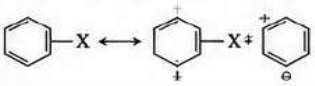
B. HALOARENES (Ar–X)

1. PHYSICAL PROPERTIES

- Generally colourless solids or liquids with characteristic odour.
- Boiling points are higher than corresponding arenes.
- Insoluble in water but soluble in organic solvents.
- Denser than water.

2. CHEMICAL PROPERTIES

Undergo mainly electrophilic aromatic substitution reactions. The C–X bond is stronger and has partial double bond character due to resonance, hence less reactive towards nucleophilic substitution.



3. IMPORTANT REACTIONS

(i) Nucleophilic Substitution Reactions

- With aqueous KOH (hydrolysis)

$$R-X + KOH\,(aq) \longrightarrow \underset{\text{(Alcohol)}}{R-OH} + KX$$

- With alcoholic KOH (dehydrohalogenation)

$$R-CH_2-CH_2-X + alc.KOH \longrightarrow \underset{\text{(Alkene)}}{R-CH=CH_2} + KX + H_2O$$

- With sodium ethoxide (Williamson synthesis)

$$R-X + C_2H_5ONa \longrightarrow \underset{\text{(Ether)}}{R-OC_2H_5} + NaX$$

- With KCN (nitrile)

$$R-X + KCN \longrightarrow \underset{\text{(Nitrile)}}{R-CN} + KX$$

- With $AgNO_3$ (precipitation)

$$R-X + AgNO_3\,(alc.) \longrightarrow R-ONO_2 + \underset{\text{(White ppt.)}}{AgX\downarrow}$$

(ii) Elimination Reaction

$$R-CH_2-CH_2-X + alc.KOH \longrightarrow \underset{\text{(Alkene)}}{R-CH=CH_2} + KX + H_2O$$

(iii) Wurtz Reaction

$$2R-X + 2Na\,(\text{dry ether}) \longrightarrow R-R + 2NaX$$

(iv) Finkelstein Reaction

$$R-Cl\,/\,R-Br + NaI\,(\text{acetone}) \longrightarrow R-I + NaCl\,/\,NaBr\downarrow$$

(v) Swarts Reaction (preparation of R–F)

$$R-Cl\,/\,R-Br + AgF\,(\text{or } Hg_2F_2) \longrightarrow R-F + AgCl\,/\,Hg_2Cl_2$$

3. IMPORTANT REACTIONS

(i) Electrophilic Substitution Reactions

- Nitration

$$Ar-X + HNO_3 \xrightarrow{\text{conc. } H_2SO_4} o\text{-, } p\text{-}NO_2-Ar-X + H_2O$$

- Sulphonation

$$Ar-X + SO_3/\text{fuming } H_2SO_4 \longrightarrow o\text{-, } p\text{-}SO_3H-Ar-X + H_2O$$

- Halogenation

$$Ar-X + X_2 \xrightarrow{FeX_3\,(cat.)} o\text{-, } p\text{-}X-Ar-X + HX$$

- Friedel–Crafts Alkylation

$$Ar-X + RCl \xrightarrow{\text{anhyd. } AlCl_3} o\text{-, } p\text{-}R-Ar-X + HCl$$

- Friedel–Crafts Acylation

$$Ar-X + RCOCl \xrightarrow{\text{anhyd. } AlCl_3} o\text{-, } p\text{-}RCO-Ar-X + HCl$$

(ii) Nucleophilic Substitution Reactions (Under drastic conditions)

- Hydrolysis (Dow process)

$$Ar-Cl + NaOH\,(aq) \xrightarrow{623\text{ K, }300\text{ atm}} \underset{\text{(Phenol)}}{Ar-OH} + NaCl$$

- With $NaNH_2$ (high temperature)

$$Ar-Cl + 2NaNH_2 \xrightarrow{623\text{ K}} \underset{\text{(Aniline)}}{Ar-NH_2} + NaCl + NH_3$$

(iii) Metalation

$$Ar-X + 2Na\,(\text{dry ether}) \longrightarrow Ar-Na + NaX$$

4. PREPARATION OF HALOALKANES

(i) From alkanes (free radical substitution)

$$RH + X_2 \xrightarrow[(X = Cl, Br)]{h\nu/\Delta} R-X + HX$$

(ii) From alcohols

$$\underset{(X = Cl, Br, I)}{R-OH} + HX \longrightarrow R-X + H_2O$$

$$R-OH + SOCl_2\,/\,PCl_5\,/\,PCl_3 \longrightarrow R-Cl + SO_2\,/\,POCl_3\,/\,HCl$$

(iii) From alkenes (addition of HX)

$$R-CH=CH_2 + HX \longrightarrow R-CHX-CH_3$$

(iv) From carboxylic acids (Hunsdiecker reaction)

$$R-COOAg + Br_2 \xrightarrow{CCl_4} R-Br + CO_2 + AgBr$$

4. PREPARATION OF HALOARENES

(i) From arenes (electrophilic halogenation)

$$Ar-H + X_2 \xrightarrow{FeX_3\,(cat.)} \underset{(X = Cl, Br)}{Ar-X} + HX$$

(ii) From diazonium salts (Sandmeyer reaction)

$$Ar-N_2^+Cl^- + CuX \longrightarrow \underset{(X = Cl, Br)}{Ar-X} + N_2 + CuCl$$

(iii) From phenols

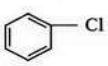
$$Ar-OH + PCl_5\,/\,SOCl_2 \longrightarrow Ar-Cl + POCl_3\,/\,SO_2 + HCl$$

USES OF HALOALKANES

- As solvents ($CHCl_3$, CCl_4).
- As refrigerants (Freons).
- As anaesthetics ($CHCl_3$).
- In fire extinguishers (CF_2Cl_2).
- As intermediates in organic synthesis.

USES OF HALOARENES

- As intermediates in dyes, drugs and pesticides.
- In manufacturing of polymers, plastics and pharmaceuticals.
- Chlorobenzene is used as solvent and in production of DDT.



KEY POINTS

- Haloalkanes: More reactive, undergo nucleophilic substitution easily.
- Haloarenes: Less reactive, undergo electrophilic substitution; C–X bond has partial double bond character.

SECTION – A (1 MARK)

1.Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as :

(**ALL INDIA 2026** *)*

(a)Mustard gas (b) Tear gas (c) Chlorine gas (d) Phosgene gas

2. Which of the following haloalkanes react with aqueous KOH most rapidly by S_N1 reaction?

(**ALL INIDA 2025)**

(A) 2-Chlorobutane (B) 1-Bromobutane

(C) 2-Bromo-2-Methylpropane (D) 2,2-Dimethyl-1-Chloropropane

3. 2 –Bromo-2-methylepropane is allowed to react with alcoholic KOH solution. The major product formed is – **(ALL INDIA 2022)**

(a) $(CH_3)_2C=CH_2$ (b) $CH_3-CH=CH-CH_3$ (c) $(CH_3)_2CH-CH_3$ (d)$CH_3-CH_2-CH_2-CH_3$

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)

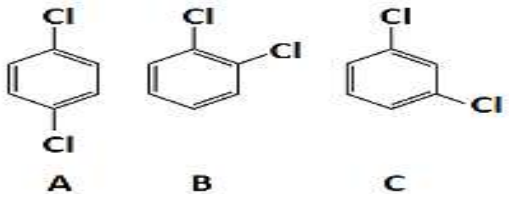
(c) (A)=(i), (B)=(ii), (C)=(iii), (D)=(iv) (d) (A)=(iii), (B)=(i), (C)=(iv), (D)=(ii)

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

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

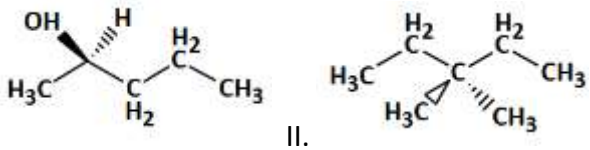
(c) $CH_3Br > CH_3Cl > CH_3F$ (d) $CH_3Br > CH_3F > CH_3Cl$

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



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

8. Consider the following compounds:



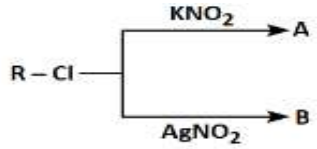
I. II.

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:

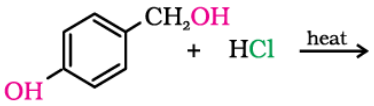


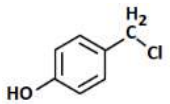
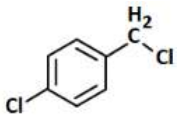
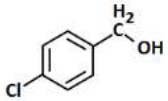
The relation between A and B are:

(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.

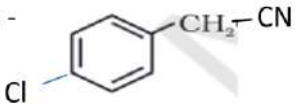
Answer Key

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

SECTION - B (2MARKS)

1. Consider the following reaction: **(ALL INDIA 2024)**

The major product to the reaction is

Ans - 

2. An alkyl halide (A) of molecular formula $C_6H_{13}Cl$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12}. Both alkenes on hydrogenation gives 2,3-dimethylbutane. Write the structures of (A) ,(B) and (C) (**ALL INDIA 2023)**

(HINT: A. ***2-chloro-2,3-dimethylbutane,B 2,3-dimethylbut-1-ene*** *, C,2,3-dimethylbut-2-ene.*

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. Draw the structures of major product(s) in each of the following reactions : *2×1=2*

(a)C_6H_5-Br + Mg (Ether)---------- ?

(b) CH_3-CH_2-Br + AgCN ----------?

(HINT (a)C_6H_5-Mg-Br

(c) CH_3-CH_2-NC + AgBr

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. Answer the following : *3×1=3* **(ALL INDIA 2026)**

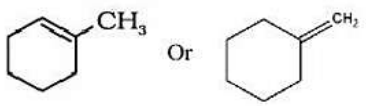
(a) Which isomer of C_4H_9Br is most reactive towards S_N1 reaction ?

(b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

Although chlorine shows strong – I effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why ?

(Hint-

(a)Tert-butyl bromide /$(CH_3)_3CBr$ /2-Bromo-2-methylpropane

(b) 

(c) Because +R effect stabilises the intermediate carbocation.

2. A compound (A) with molecular formula C_4H_9I which is a primary alkyl halide, reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HI to give (C) which is an isomer of (A). When (A) reacts with Na metal in the presence of dry ether, it gives a compound (D), C_8H_{18} which is different from the compound formed when n-butyl iodide reacts with sodium. Write the structures of (A), (B), (C) and (D). Write the chemical equation when compound (A) is reacted with alcoholic KOH. **(ALL INDIA 2025)**

(HINT ,(A,) Isobutyl iodide *(1-Iodo-2-methylpropane),(B);* ***2-methylpropene*** *(Isobutylene)*

(C): 2-iodo-2-methylpropane *(tert-butyl iodide)* ***, (D): 2,5-dimethylhexane,***

3. Explain why 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.

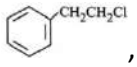
(ii) Identify the **major product** and explain **why it is formed in greater amount.**

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

$CH_3CH_2Cl + NaI \quad CH_3CH_2I + NaCl$

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

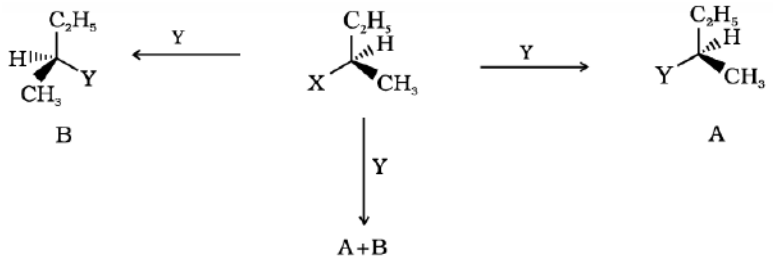
(ii) If ethyl fluoride is to be prepared, which reaction should be used?

(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:

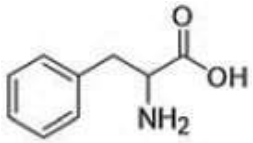


(i) In the given reaction, if compound B is the only product formed, what type of configuration change has occurred?

(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:

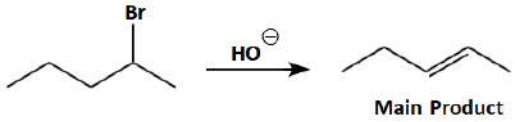
Tertiary (3°) > Secondary (2°) > Primary (1°).

If more than one β-hydrogen is available, multiple alkenes may be formed. In such cases, the **major product** follows **Zaitsev's (Saytzeff)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 $3^o > 2^o > 1^o$)

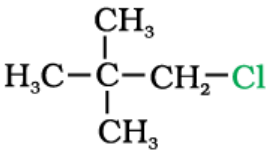
SECTION –E (5 MARKS)

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

(i). Propanenitrile; (ii). Ethyl benzene

(Hint: Halogenation, followed by nucleophilic substitution; Halogenation, followed by Friedel-Craft alkylation)

(b) Provide the IUPAC name of the given compound



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)

3. How the following conversions can be carried out?

(a) Propene to propan-1-ol

(b) Ethanol to propanenitrile

(c) Ethyl chloride to propanoic acid

(d) Aniline to chlorobenzene

UNIT- 7.ALCOHOLS PHENOLS AND ETHERS (6 Marks)

Alcohols: Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration, uses with special reference to methanol and ethanol. **Phenols**: Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.
Ethers: Nomenclature, methods of preparation, physical and chemical properties, uses

Key Concepts

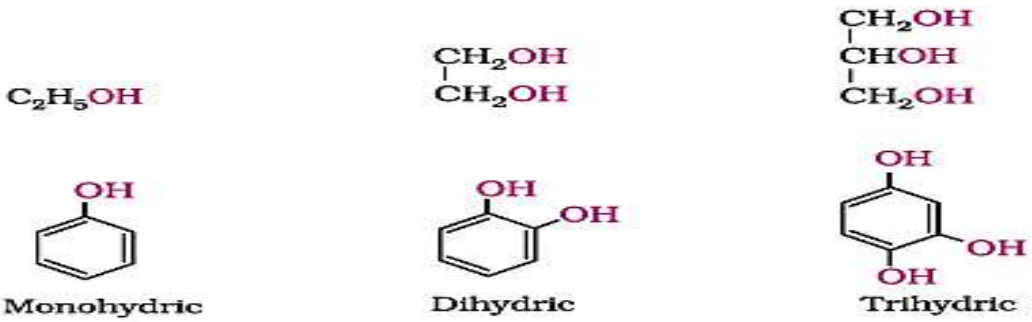
ALCOHOL- Hydroxy derivative of alkanes (R-H) such as Alkanols(R-OH)

PHENOLS - Hydroxy derivative of arene (Ar-H) such as Phenol (C_6H_5-OH)

Types of Alcohols-

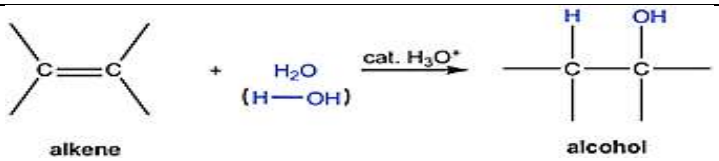
A)On the basis of Alkyl group-

B) On the basis of alcoholic(-OH) group-



PREPARATION OF ALCOHOLS-

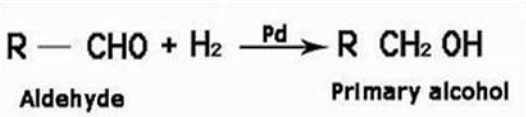
a)From Alkenes
(Acid Catalised Hydration)
2^0-Alcohols is formed-



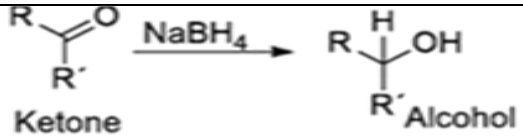
b)From Hydroboration of Alkenes-
1^0-Alcohol is formed.

R-CH = CH_2 i) BH_3 or B_2H_6 ----------> R-CH_2-CH_2-OH ii)H_2O_2/OH^-

c) FROM CARBONYL COMPOUNDS(FROM ALDEHYDES)-Besides Pd ,Pt/Ni/$NaBH_4$/$LiAiH_4$ can be used

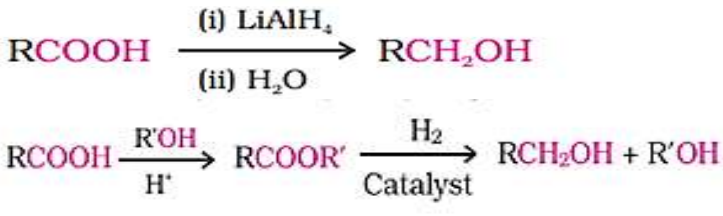


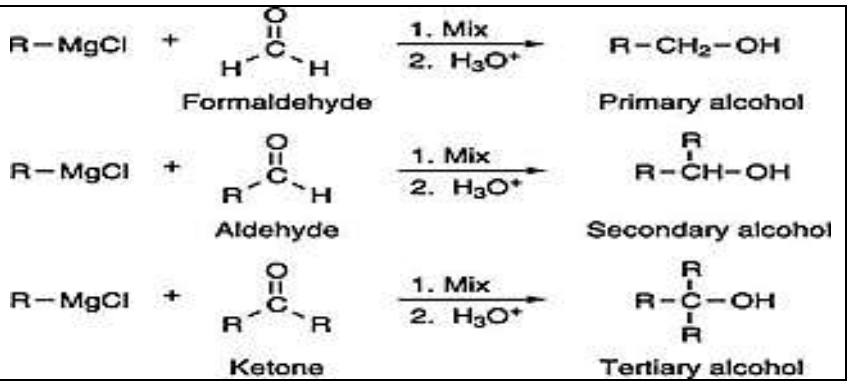
d)CARBONYL COMPOUNDS(FROM KETONES)-Besides Pd,Pt/Ni/$NaBH_4$/$LiAiH_4$ can be used



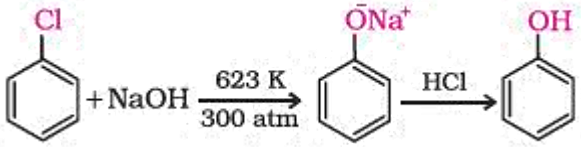
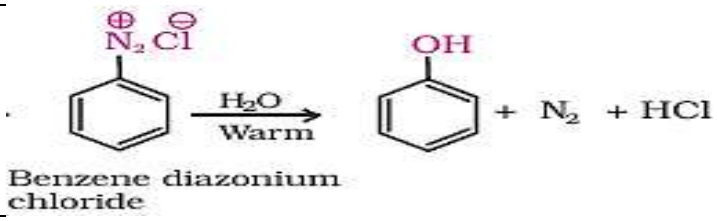
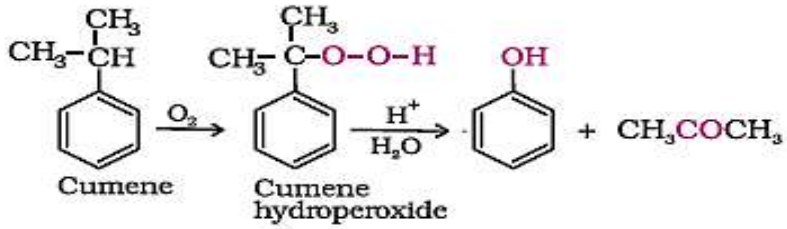
2^0-Alcohol is formed always

e) FROM REDUCTION OF CARBOXYLIC ACIDS AND ESTERS- :Only 1^0 -Alcohol is formed

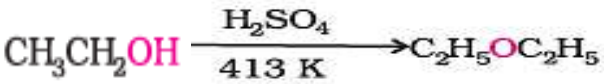
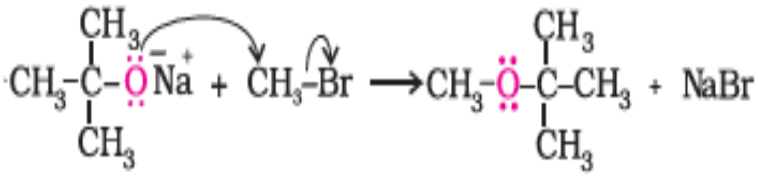


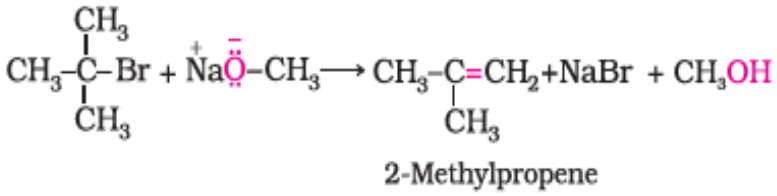
f) <u>FROM GRIGNARD REAGENTS-</u> Besides methanol other aldehydes form 2^0- alcohols ketones form 3^0- alcohols	

Preparation of Phenols

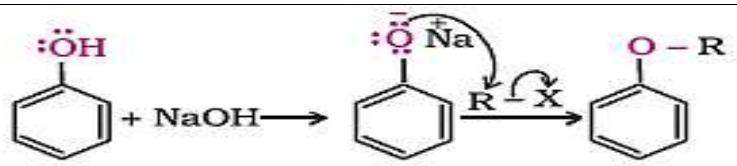
a)From Haloarenes-(Dow Process)	
b)From Benzene Sulphonic acid	
c)From Benzen Diazonium salts	
d) From Cumene(Isopropyl Benzene)-Acetone is a by product of this reaction.	

Preparation of Ethers

a)From Dehydration of Alcohol-Protic acid is used H_2SO_4/H_3PO_4	 **Ethanol** **Ethoxyethane**
b)From Willamson Synthesis-Lab Preparation of both symmetrical and unsymmetrical.	**Haloalkane**  **Sodium Alkoxide** **Ether** **It is SN^2-Reaction.So that-** **a)**  **Strong Nucleophile** **1^0-Haloalkane** **Ether** **(Weak Base)** **Here Nucleophilic reaction overcome the effect of Elemination reaction.**

	b)  2-Methylpropene **3^0-Haloalkane Weak Nuclephile (Strong Base)** **Here Alkene is formed Elemination reaction overcome the effect of Nucleophilic reaction.**

PREPARATION OF ANISOLE

From Phenol	

PHYSICAL PROPERTIES OF ALCOHOLS

> The boiling points of alcohols and phenols increase Due to--
-increase in the number of carbon atoms -Molecular mass increases
-increase in van der Waals forces -High Temprature is required to break this force

> In alcohols, the boiling points decrease with increase of branching in carbon chain. Due to-
- decrease in surface area - decrease in van der Waals forces
-decrease in intermolecular interaction - High Temprature is required to break this force.

> The boiling points of alcohols are higher than hydrocarbons, ethers, haloalkanes of comparable molecular masses Due to formation of hydrogen bonding by alcohol molecules than others.
> Increasing order of Boiling Points Propane < Methoxymethane < Ethanol .Due to formation of (INTERMOLECULAR)hydrogen bonding by ethanol only ,but not by ethers and hydrocarbons.

> Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules.
> The solubility of alcohols and phenols decreases with increase of alkyl/aryl gp. Due to
- Decreases with increase in size of alkyl/aryl groups.
-Hydro phobic nature of alkyl/aryl groups.
-Decreases capability to form hydrogen bonding.

CHEMICAL PROPERTIES OF ALCOHOLS AND PHENOLS

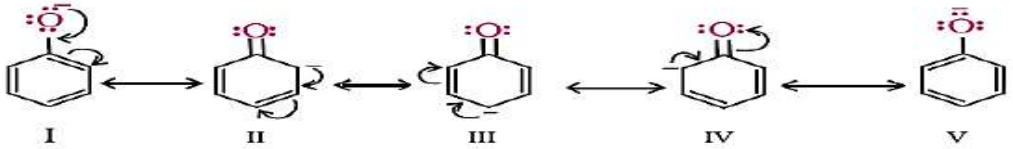
(A)ACIDIC NATURE OF ALCOHLS AND PHENOLS

>Reaction of metal with alcohols and Phenols-Pop like sound of H2 gas is produced and alkoxide is formed.This reaction is known as chemical test / functional gp test of alcohols

$2R – OH + 2Na \rightarrow 2R – ONa + H_2$

$2C_6H_5 – OH + 2Na \rightarrow 2\ C_6H_5–ONa + H_2$

- 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 more - I-effect and stabilization of phenoxide ion through resonance



- Presence of electron withdrawing groups increases the acidity of phenol by high polar nature of -OH bond,more , -I effect ,High K_a value , Low pK_a Value , Presence more & More -I effect group , Resonance effect , stabilizing the phenoxide ion.
- presence of electron releasing groups decreases the acidity of phenol by high polar nature of -OH bond, more +I effect, Low Ka value, High pK_a Value , Presence more & More +I effect group , Resonance effect , destabilizing the phenoxide ion.

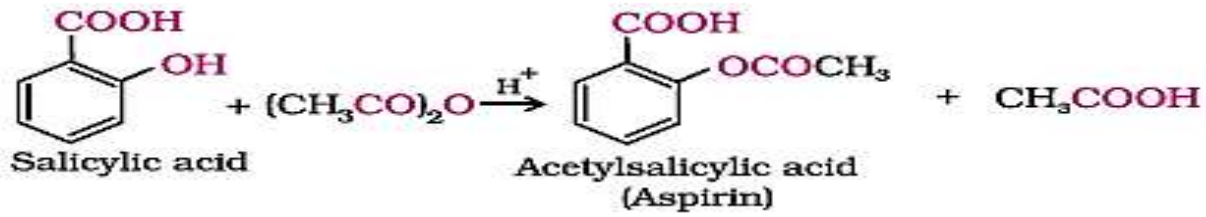
B)Esterification- The reaction of alcohols with carboxylic acid and acid anhydride is carried out in the presence of a small amount of concentrated sulphuric acid. Pleasent smell of Ester Produced.

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

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

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

<u>Acetylation of salicylic acid produces aspirin</u>.



C) <u>Reaction with hydrogen halides</u>:

- Alcohols react with hydrogen halides to form alkyl halides in anhydrous $ZnCl_2$.

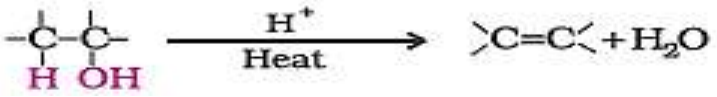
  ROH + HX →R–X + H_2O
- Reactivity of Alcohols: $3^0 > 2^0 > 1^0$
- Lucas Test: - Used to distinguish primary, secondary and tertiary alcohols
- Lucas reagent - (conc. HCl and $ZnCl_2$)
- Alcohols are soluble in Lucas reagent while Alkyl halides (RX) are immiscible and produce turbidity in solution.
- Tertiary alcohols- Immediately produce turbidity ,
- Secondary alcohols- Turbidity appears After 5 minutes,
- Primary alcohols- No turbidity at room temperature.

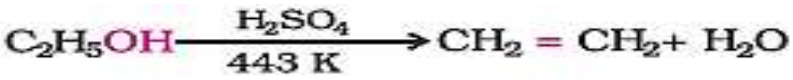
D) <u>Reaction with phosphorus halides & $SOCl_2$:</u>

CH_3CH_2-OH + PCl_3 ----------> CH_3CH_2-Cl + H_3PO_3
CH_3CH_2-OH + PCl_5 ----------> CH_3CH_2-Cl + $POCl_3$ + HCl
CH_3CH_2-OH + $SOCl_2$ ----------> CH_3CH_2-Cl + SO_2 + HCl

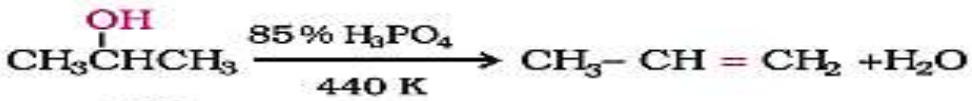
E) DEHYDRATION OF ALCOHOLS-

Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with a protic acid e.g., conc.H_2SO_4 or H_3PO_4 ,or anhydrous $ZnCl_2$ or alumina.



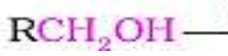


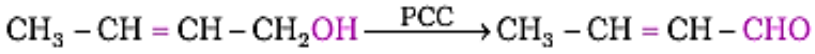
The reactivity of dehydration of alcohol – 3^0 > 2^0 > 1^0



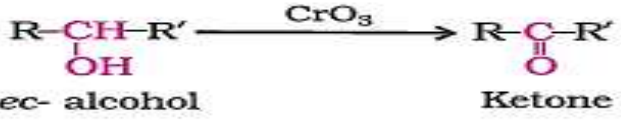
F) OXIDATION OF ALCOHOLS-

- Primary alcohol → Aldehyde → Carboxylic Acid





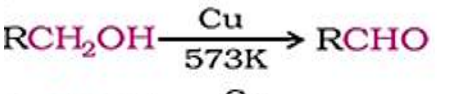
- Secndary alcohol → Ketone→ Carboxylic Acid

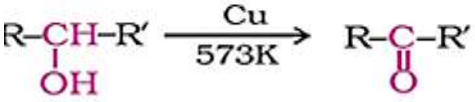


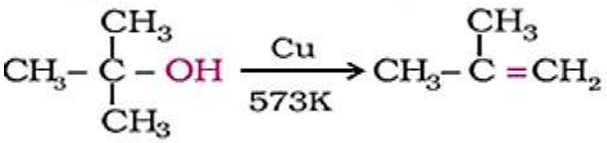
Sec- alcohol Ketone .

Tertiary alcohols do not undergo oxidation reaction. Under strong reaction conditions such as strong oxidising agents ($KMnO_4$) and elevated temperatures, a mixture of carboxylic acids containing lesser number of carbon atoms is formed

G)**Dehydrogenetion Of Alcohols-** When the vapours of a primary or a secondary alcohol are passed over heated copper at 573 K, dehydrogenation takes place,while tertiary alcohols undergo dehydration.

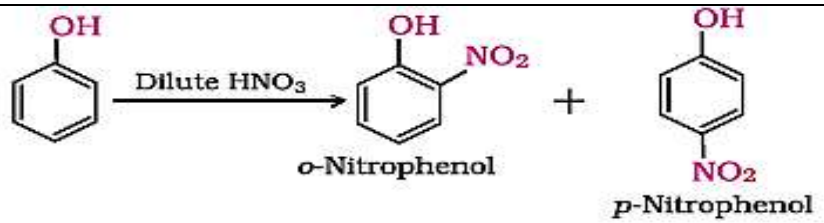
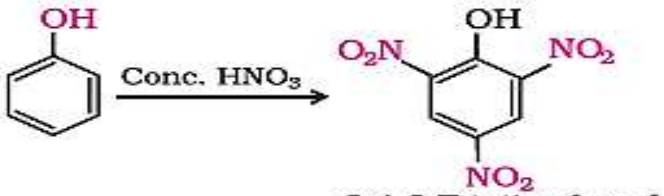
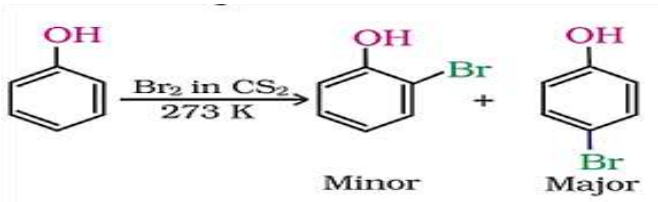
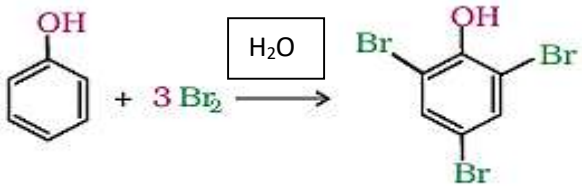
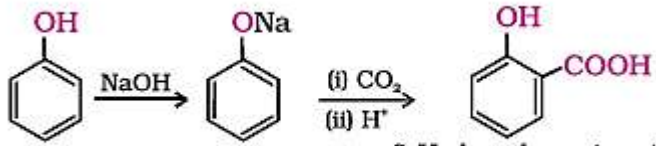
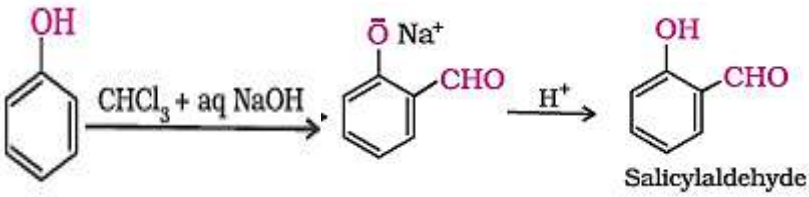
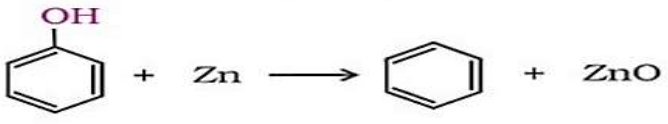
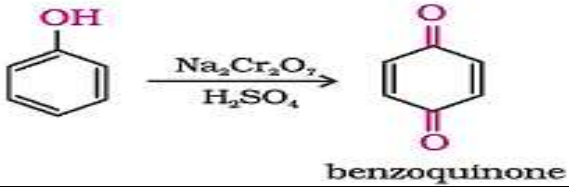






CHEMICAL PROPERTIES OF PHENOLS-

(A)Electrophilic aromatic substitution on Benzene ring of Phenol The ortho and para isomers can be separated by steam distillation.	**a)Nitration-**

o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding but p-nitrophenol dose not.	 o-Nitrophenol p-Nitrophenol  2,4,6-Trinitrophenol (Picric acid) **(yellow)**
b)Halogenation (Bromination)- When the reaction is carried out in solvents of low polarity such as $CHCl_3$ or CS_2 and at low temperature. **When phenol is treated with bromine water.**	 Minor Major  **(White PPT)** 2,4,6-Tribromophenol
c) Kolbe's reaction	 2-Hydroxybenzoic acid (Salicylic acid)
d) Reimer-Tiemann reaction	 Salicylaldehyde
e)Reaction with Zn dust-	 **Benzene**
f)Oxidation-	 benzoquinone

PHYSICAL PROPERTIES OF ETHERS-

- Ethers are polar in nature -due to polarity of C-O bond..
- The miscibility of ethers with water resembles those of alcohols of the same molecular mass. Both ethoxyethane and butan-1-ol are miscible to almost the same extent due to hydrogen bonding.
- Ethers are volatile in nature like Alcohols.

CHEMICAL REACTION OF ETHERS

A)Reaction involving Cleavage of C–O bond in ethers.

The order of reactivity of **HX- HI > HBr > HCl.**

The cleavage of ethers takes place with concentrated HI or HBr at high temperature.

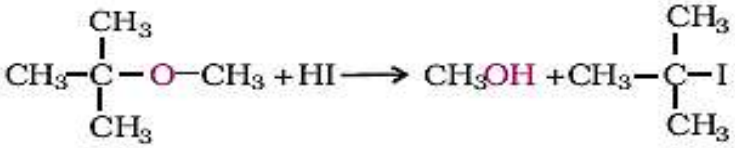
$$R\text{–}O\text{–}R + HX \longrightarrow RX + R\text{–}OH$$

$$R\text{–}OH + HX \longrightarrow R\text{–}X + H_2O$$

When primary or secondary both alkyl gp are present .Then the lower alkyl gp forms alkyl Halide (S_N2-Reaction**)**

$$R\text{–}O\text{–}R' + HX \longrightarrow R\text{–}X + R'\text{–}OH$$

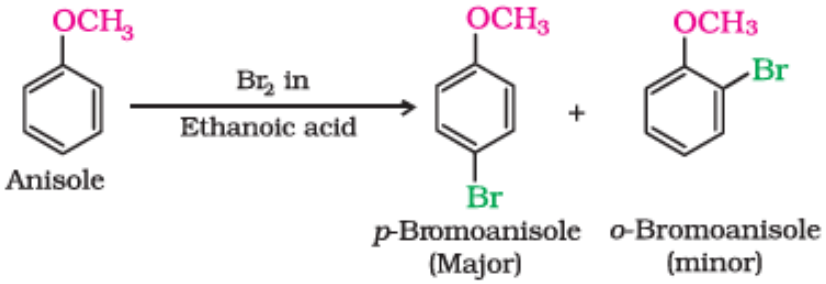
when one of the alkyl group is a tertiary group, the halide formed is a tertiary halide.

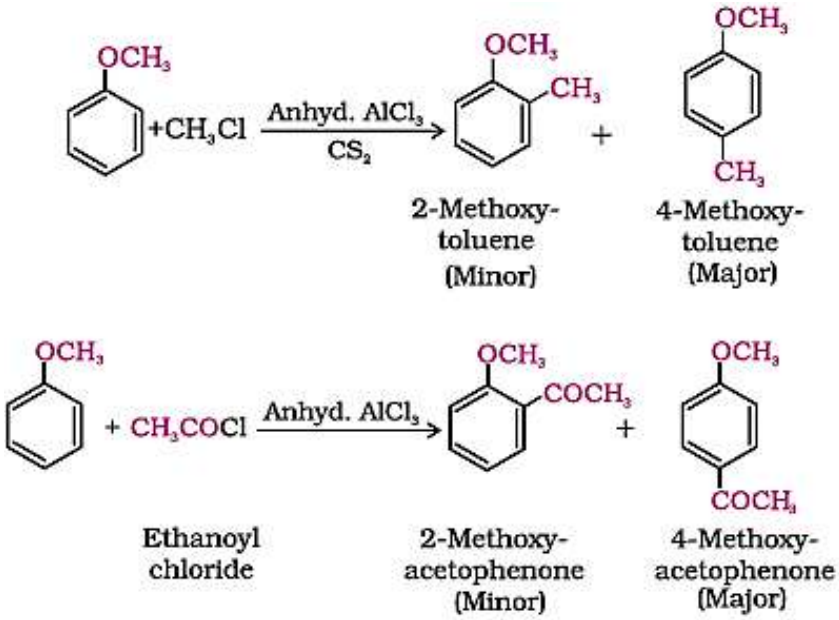


It is because in step 2 of the reaction, the departure of leaving group (HO–CH_3) creates a more stable 3^0 - carbocation [(CH_3)$_3$ C^+], and the reaction S_N1 mechanism.

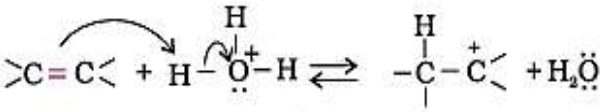
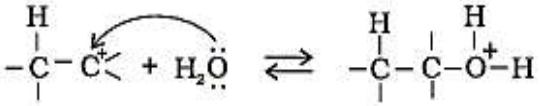
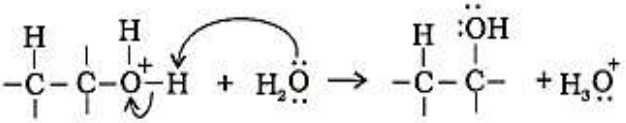
B)Reactions of Anisole.

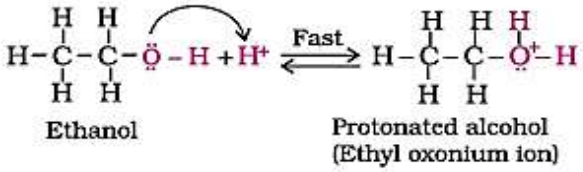
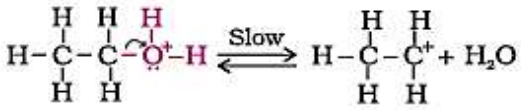
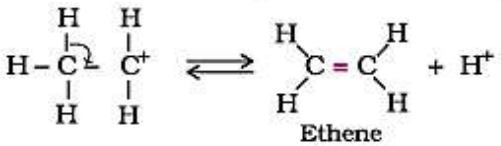
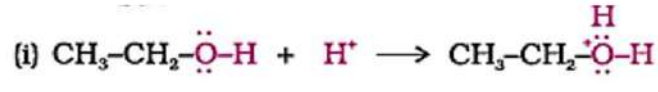
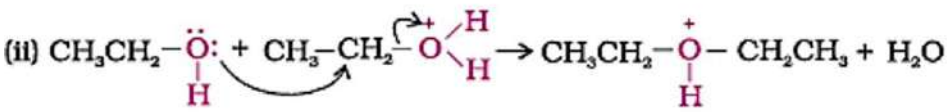
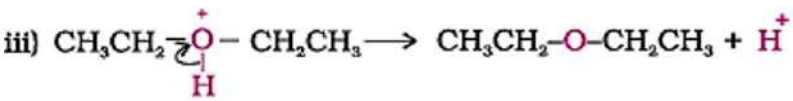
a) Halogenation



b) Friedel-Crafts reaction--Both Alkylation and Acylation	
c)Nitration-	

Mechanism of Chemical Reactions

A)Hydration of Alkenes-	Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+. $H_2O + H^+ \rightarrow H_3O^+$  Step 2: Nucleophilic attack of water on carbocation.  Step 3: Deprotonation to form an alcohol. 

B)Dehydration ofAlcohols at 443K.	*Step 1:* Formation of protonated alcohol.  Ethanol — Protonated alcohol (Ethyl oxonium ion) *Step 2:* Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.  *Step 3:* Formation of ethene by elimination of a proton.  Ethene
C)Dehydration ofAlcohols at 413K. (in excess of Alcohol)	  

ALCOHOLS, PHENOL AND ETHERS

Unit-7

IMPORTANCE
- Useful solvents
- Starting materials for organic synthesis
- Antiseptics, disinfectants
- Polymers, perfumes, medicines, dyes, etc.

GENERAL TREND IN PHYSICAL PROPERTIES
With increase in molecular mass (for the same homologous series)
Boiling point ↑
Solubility in water ↓

ALCOHOLS (R–OH)

CLASSIFICATION
(i) 1° Alcohols : $R-CH_2-OH$
(ii) 2° Alcohols : R_2CH-OH
(iii) 3° Alcohols : R_3C-OH

PREPARATION
(i) From Alkenes (Hydration)
$RCH=CH_2 \xrightarrow{H_2O/H^+} RCH_2-CH_2OH$
(ii) From Haloalkanes (Hydrolysis)
$R-X \xrightarrow{aq.\ KOH} R-OH$
(iii) From Carbonyl Compounds
$R-CHO \xrightarrow{H_2/Ni} R-CH_2OH$
$R-CO-R' \xrightarrow{H_2/Ni} R-CHOH-R'$

CHEMICAL PROPERTIES
(i) With Active Metals
$2ROH + 2Na \rightarrow 2RONa + H_2\uparrow$
(ii) With Hydrogen Halides
$ROH + HX \rightarrow RX + H_2O$
(iii) With Phosphorus Halides
$3ROH + PCl_3 \rightarrow 3RCl + H_3PO_3$
$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$
(iv) Esterification
$RCOOH + R'OH \xrightarrow{conc.\ H_2SO_4} RCOOR' + H_2O$
(v) Dehydration
Intramolecular (conc. H_2SO_4, 443 K)
$R-CH_2-CH_2-OH \rightarrow R-CH=CH_2 + H_2O$
Intermolecular (conc. H_2SO_4, 413 K)
$2ROH \rightarrow R-O-R + H_2O$
(vi) Oxidation
1° Alcohol → Aldehyde → Carboxylic acid
2° Alcohol → Ketone
3° Alcohol → No reaction (under usual conditions)

TESTS TO DISTINGUISH
(i) 1°, 2°, 3° Alcohols : Lucas test
(Conc. HCl + anhyd. $ZnCl_2$)
(1°: no turbidity; 2°: turbidity in 5–10 min; 3°: immediate turbidity)
(ii) 1° Alcohols : Iodoform test
$CH_3-CH(OH)-R \xrightarrow{I_2/NaOH} CHI_3$ (yellow ppt.) + $RCOONa + H_2O$

USES
- As solvents
- Antiseptics (e.g., ethanol, 70%)
- In pharmaceuticals, perfumery
- As fuel (ethanol)
- Manufacture of esters, polymers, etc.

PHENOL (Ar–OH)

PREPARATION
(i) From Haloarenes (Dow's process)
$C_6H_5-Cl \xrightarrow{aq.\ NaOH,\ 623\ K,\ 300\ atm} C_6H_5-ONa$
$C_6H_5-ONa + HCl \rightarrow C_6H_5-OH + NaCl$
(ii) From Benzene Sulphonic Acid
$C_6H_5-SO_3H \xrightarrow{NaOH\ fusion,\ 623\ K} C_6H_5-ONa$
$C_6H_5-ONa + HCl \rightarrow C_6H_5-OH + NaCl$
(iii) From Cumene (Cumene process)
$C(CH_3)_2$ (cumene) $\xrightarrow{O_2}$ $C(CH_3)_2OOH$ (cumene hydroperoxide) $\xrightarrow{H^+} C_6H_5-OH + (CH_3)_2CO$

CHEMICAL PROPERTIES
(i) Acidic Nature (weaker than carboxylic acids)
$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$
(No reaction with Na_2CO_3)
(ii) Electrophilic Substitution (activating; o, p-directing)
a. Bromination : $C_6H_5OH + 3Br_2 \rightarrow$ 2,4,6-tribromophenol (white ppt.) + 3HBr
b. Nitration : $C_6H_5OH + HNO_{3(dil.)} \rightarrow$ o-nitrophenol + p-nitrophenol + H_2O
c. Sulphonation : $C_6H_5OH + H_2SO_{4(conc.)} \rightarrow$ o- and p-hydroxybenzenesulphonic acids
(iii) With Neutral $FeCl_3$ Solution
Gives violet colour (characteristic test)

DIFFERENCE BETWEEN PHENOL AND ALCOHOL

Property	Phenol	Alcohol
Acidic nature	Acidic (forms salts with NaOH)	Neutral (no salt with NaOH)
Reaction with Na_2CO_3	No reaction	No reaction
Bromination	With Br_2 water, white ppt. of 2,4,6-tribromophenol	No ppt.
$FeCl_3$ test	Violet colour	No colour
Iodoform test	Negative	Positive for $CH_3-CH(OH)-R$

USES OF PHENOL
- As antiseptic and disinfectant
- In the manufacture of phenolic resins (Bakelite)
- In dyes, drugs, pesticides, explosives
- In preparation of salicylic acid, picric acid, etc.

ETHERS (R–O–R')

PREPARATION
(i) Williamson Synthesis
$R-ONa + R'-X \rightarrow R-O-R' + NaX$
(ii) Intermolecular Dehydration of Alcohols
$2ROH \xrightarrow{conc.\ H_2SO_4,\ 413\ K} R-O-R + H_2O$

PROPERTIES
- Ethers are neutral compounds.
- Lower ethers are soluble in water.
- Boiling points are lower than isomeric alcohols due to absence of H-bonding.

CHEMICAL PROPERTIES
(i) Cleavage by Hydrogen Halides
$R-O-R' + HX \rightarrow R-X + R'-OH$ (excess HX)
(ii) Cleavage by HI (heat)
$R-O-R' + HI \rightarrow R-I + R'-OH$
(iii) Peroxidation
$R-O-R' \xrightarrow{excess\ O_2,\ light} R-O-O-R'$
(Peroxides may be explosive)

DIFFERENCE BETWEEN ETHERS AND ALCOHOLS

Property	Ethers	Alcohols
Functional group	R–O–R'	R–OH
H-bonding	No	Yes
Boiling point	Lower	Higher
Cleavage by HI	Cleaved	Not cleaved
Reaction with active metals	No reaction	Reacts to give alkoxide + H_2

USES OF ETHERS
- As solvents (diethyl ether, THF, dioxane)
- As anaesthetics (historically: diethyl ether)
- In organic synthesis as intermediates
- In perfumes and flavouring agents

INTERRELATIONSHIP
- Alcohols on dehydration give ethers.
- Phenol can be converted to ethers (Williamson synthesis) by forming phenoxide ion.
- All three classes contain oxygen and show different reactivities due to difference in structure.

QUESTION BANK

SECTION - A (1 MARK)

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

(a) 1M acetic acid + 1M ethyl alcohol (b) 1M ethyl alcohol + 1M methyl alcohol

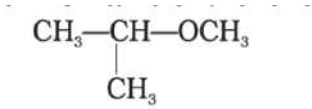
(c) 2M ethyl alcohol (d) 1M of 2-butanol

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



(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 ?

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

(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. Denatured alcohol (ethanol) is prepared by addition with-

(a)Methanol,$CuSO_4$ and Pyridine (b) Ethers, $CuSO_4$ and Pyridine

(c) Acetone, $CuSO_4$ and Pyridine (d)Benzene and Pyridine

Q7.Which alcohol known as 'wood spirit', was produced by destructive distillation of wood.

(a)Ethanol (b)Propanol (c)Methanol (d)iso Propyl Alcohols

Q8. Arrange the following compounds in increasing order of boiling point. Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

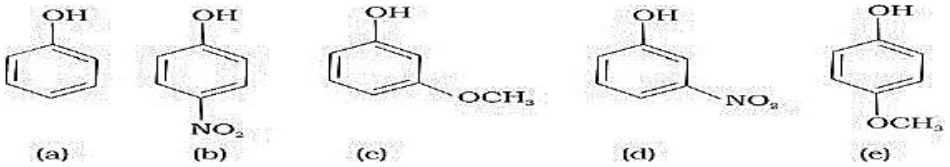
(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol

(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 1mol 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 (A); The boiling point of ethanol is higher than that of dimethyl ether.

Reason (R): Ethanol molecules are associated through hydrogen bonding whereas in dimethyl ether, it is not possible.

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

VERY SHORT ANSWER TYPE QUESTIONS (2 MARKS)

Q1.Arrange each set of compounds in the decreasing order of property indicated

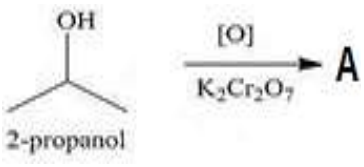
a) Ethanol, isopropanol, tertiary butyl alcohol (reactivity towards Lucas reagent)

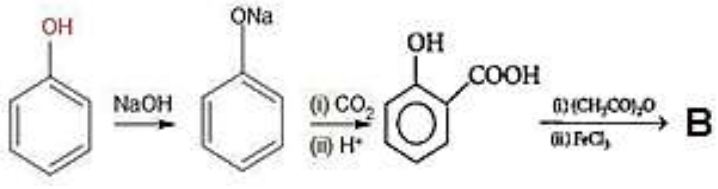
Hint- reactivity order -Tertiary > secondary > primary

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.

i)Neutral $FeCl_3$ Test –Phenol produces violet colour with neutral $FeCl_3$ only but not Benzoic acid

ii) Iodoform Test-Ethanol Produces yellow colour with Iodine and KOH but not Methanol.

Q5 Alcohol reacts with sodium metal whereas ether do not.

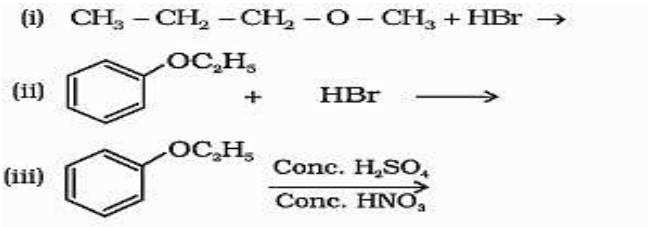
Hint-presence of active hydrogen.

b) Write the equations involved in the following reaction- Reimer - Tiemann reaction.

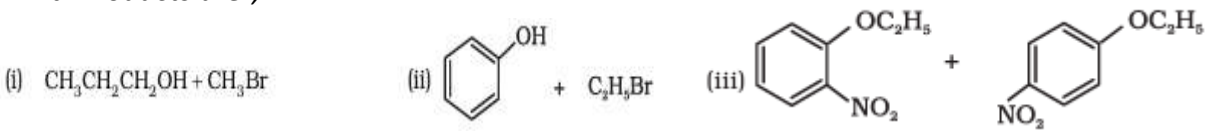
Hint-refer chemical reactions of phenol (name reaction)

SHORT ANSWER TYPE QUESTIONS (3 MARKS)

Q1- Predict the products of the following reactions:



Hint- Products are-;



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 and,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.

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.)*

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 6.9×10^{-8} whereas o-nitro hydroxybenzene is 6.0×10^{-8}

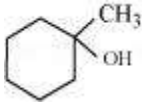
Hint-hydrogen bonding between the -OH group and the nitro group.

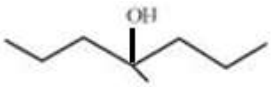
Q2 How would you obtain

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

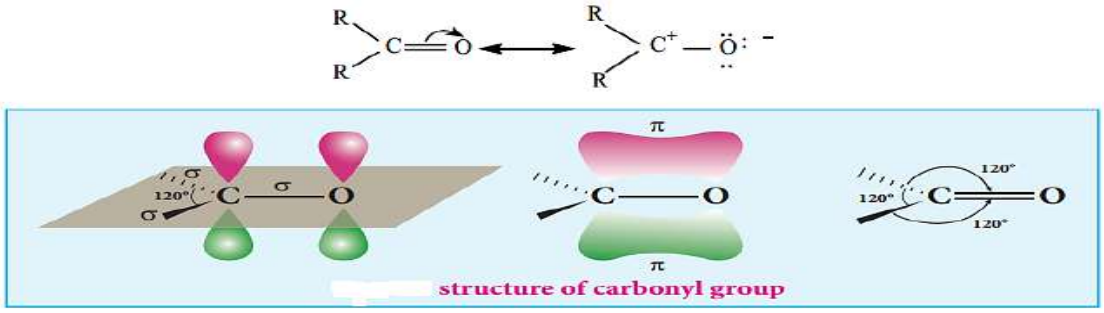
UNIT-8: ALDEHYDES, KETONES AND CARBOXYLIC ACIDS (8 Marks)

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

Key Concepts

➢ **Nature of Carbonyl Group**

- 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 .



➢ **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 ..

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.

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

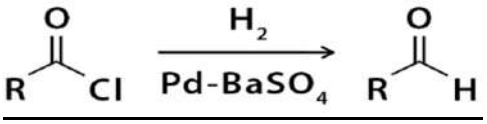
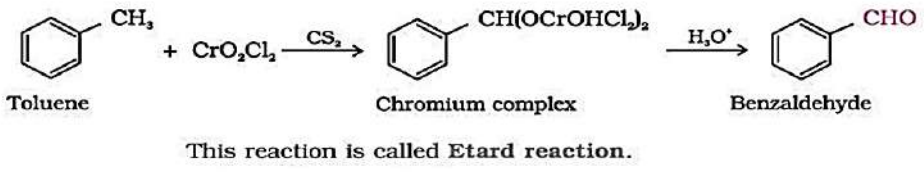
- **Preparation of Ketones** :

a. oxidation of secondary alcohols b. Hydration of alkenes
c. Reaction acyl chlorides with dialkylcadmium d. By friedel crafts reaction

- **Preparation of Carboxylic acids :**

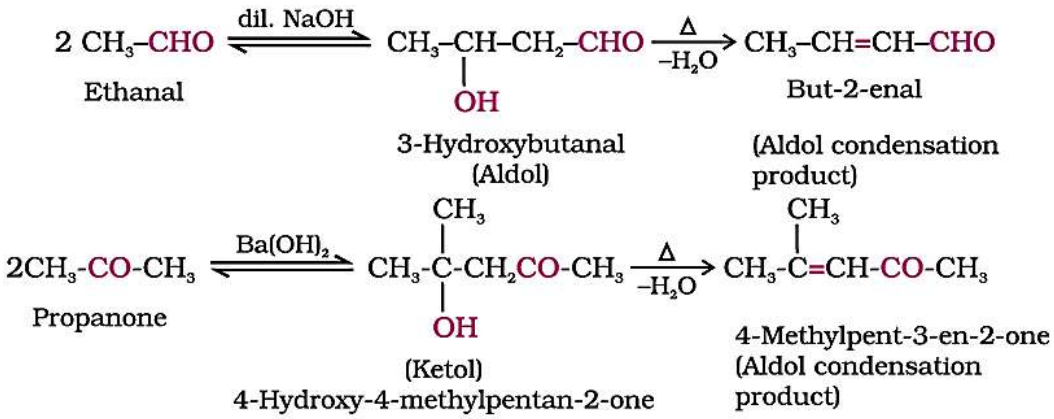
a. oxidation of primary alcohols, aldehydes and alkenes b. hydrolysis of nitriles
c. Treatment of grignard reagent with carbon dioxide.

- **IMPORTANT NAMED REACTIONS**

ROSENMUND REDUCTION:	
2. STEPHEN REACTION	**RCN + $SnCl_2$ + HCl RCH=NH** $H_3O^+ \rightarrow$ **RCHO**
3. ETARD REACTION:	 This reaction is called Etard reaction.
4. CLEMMENSEN REDUCTION	>C=O Zn-Hg/HC >CH2 + H2O
5. WOLFF-KISHNER REDUCTION	NH >C=O >C=NNH2 KOH/ethylene glycol /H2O >CH2 + N2

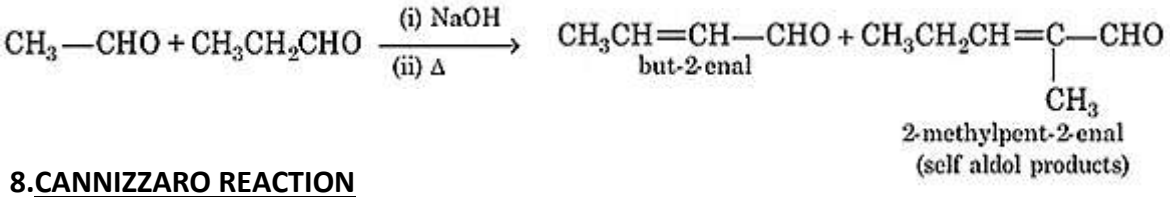
6. ALDOL CONDENSATION

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:



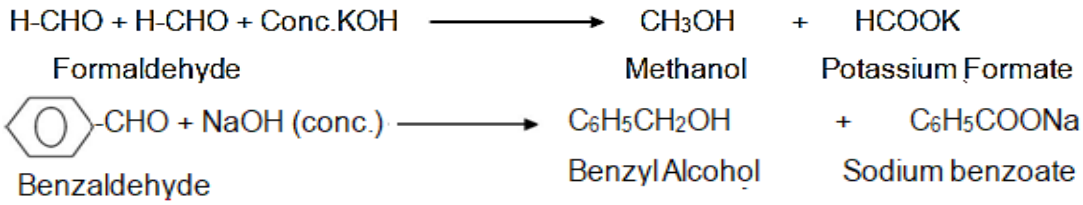
7. <u>CROSS- ALDOL CONDENSATION</u>

When aldol condensation is carried out between two different aldehydes and / or ketones, a mixture of self and cross-aldol products are obtained.

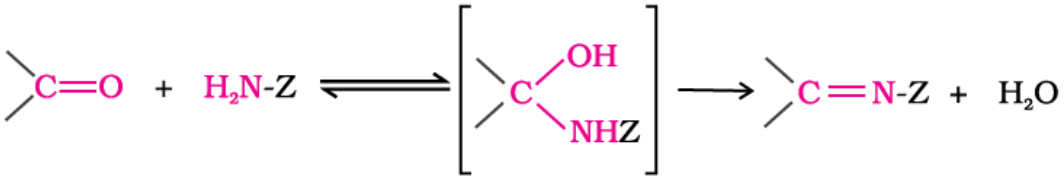


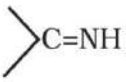
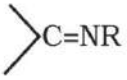
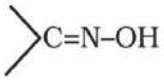
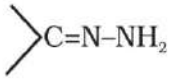
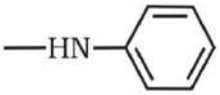
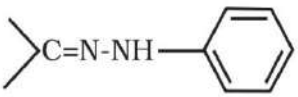
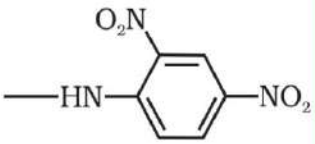
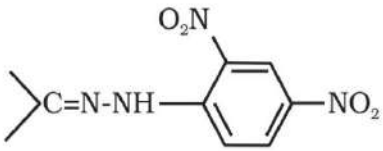
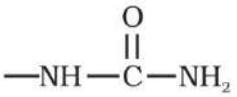
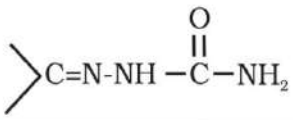
8.<u>CANNIZZARO REACTION</u>

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.



<u>ADDITION OF AMMONIA AND ITS DERIVATIVES</u>:



Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia		Imine
-R	Amine		Substituted imine (Schiff's base)
—OH	Hydroxylamine		Oxime
—NH_2	Hydrazine		Hydrazone
	Phenylhydrazine		Phenylhydrazone
	2,4-Dinitrophenyl-hydrazine		2,4 Dinitrophenyl-hydrazone
	Semicarbazide		Semicarbazone

CARBOXYLIC ACID: (R-COOH)

Acidic Nature of Carboxylic Acids

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.

FACTORS AFFECTING ACIDIC STRENGTH OF CARBOXYLIC ACIDS

ACIDIC NATURE

Carboxylic acids donate a proton (H^+) to form a resonance stabilised carboxylate ion.

$$R-COOH \rightleftharpoons R-COO^- + H^+$$

$$R-C(=O)-O^- \longleftrightarrow R-C(-O^-)=O$$

The acidic strength of carboxylic acids depends on the **stability of the carboxylate ion ($RCOO^-$)**.

1. INDUCTIVE EFFECT (–I and +I Effect)

–I Electron withdrawing groups (–I) increase acidity by stabilising the carboxylate ion.

TREND

$CCl_3COOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

+I Electron releasing groups (+I) decrease acidity by destabilising the carboxylate ion.

TREND

$HCOOH > CH_3COOH > C_2H_5COOH > (CH_3)_3CCOOH$

2. RESONANCE EFFECT (–R and +R Effect)

–R Electron withdrawing groups (–R) increase acidity by delocalising the negative charge through resonance.

TREND

$p\text{-}NO_2C_6H_4COOH > C_6H_5COOH > p\text{-}CH_3C_6H_4COOH$

+R Electron donating groups (+R) decrease acidity by increasing electron density on $-COO^-$ group.

TREND

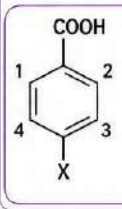
$p\text{-}OCH_3C_6H_4COOH < C_6H_5COOH$

3. POSITION OF SUBSTITUENT

The nearer the electron withdrawing group to –COOH group, the stronger is the acid.

TREND

$CH_2ClCOOH > CH_2ClCH_2COOH > CH_2ClCH_2CH_2COOH$



o-Substituted > *m*-Substituted > *p*-Substituted

4. NUMBER OF ELECTRON WITHDRAWING GROUPS

The more the number of electron withdrawing groups, the stronger is the acid.

TREND

$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

More –I groups ⇒ more stability of carboxylate ion ⇒ higher acidity

KEY POINT

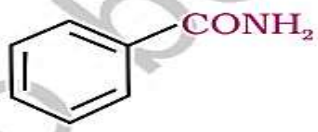
Stability of the carboxylate ion ($RCOO^-$) increases ⇒ acidity increases.
Any factor that stabilises $RCOO^-$ increases acidity, and vice versa.

PREPRATION OF CARBOXYLIC ACID

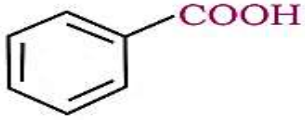
$$R\text{-}CN \xrightarrow[H_2O]{H^+ \text{ or } \bar{O}H} R-C(=O)-NH_2 \xrightarrow[\Delta]{H^+ \text{ or } \bar{O}H} RCOOH$$

$$CH_3CONH_2 \xrightarrow[\Delta]{H_3O^+} CH_3COOH + NH_3$$

Ethanamide → Ethanoic acid



$\xrightarrow[\Delta]{H_3O^+}$



$+ NH_3$

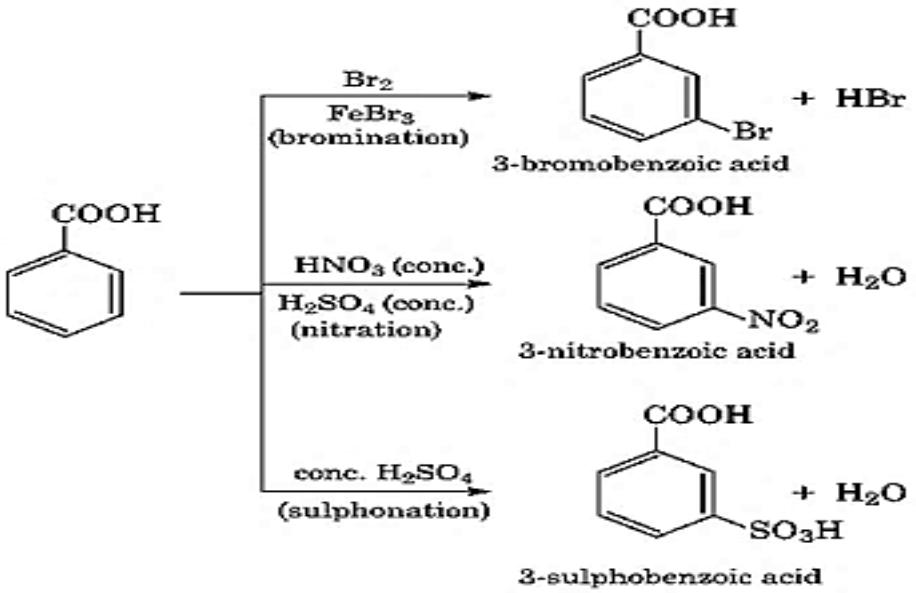
Benzamide → Benzoic acid

REACTIONS OF CARBOXYLIC ACID:

1. HELL-VOLHARD-ZELINSKY REACTION (HVZ)	$R\text{-}CH_2\text{-}COOH \xrightarrow[(ii)\ H_2O]{(i)\ X_2/\text{Red phosphorus}} R\text{-}\underset{\displaystyle X}{\underset{\vert}{CH}}\text{-}COOH$ X = Cl, Br α – Halocarboxylic acid
2. ESTERIFICATION	RCOOH + R'OH $\xrightarrow{H^+}$ RCOOR + H_2O Carboxylic acid alcohol

3. DECARBOXYLATION	$R\text{-}COONa \xrightarrow[Heat]{NaOH\ \&\ CaO} R\text{-}H + Na_2CO_3$ 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

Unit-8
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

ALDEHYDES
(R–CHO)

–CHO group attached to at least one H atom.

NOMENCLATURE
IUPAC: Replace –e of alkane with –al.

Common: Formyl derivatives
R–CHO → Alkyl/aryl + aldehyde

PREPARATION
1. **From Alkanes**
   – Controlled oxidation
2. **From Alkenes**
   – Ozonolysis (reductive)
3. **From Alcohols**
   – 1° alcohols → Aldehydes (PCC/ Cu/573 K or mild oxidising)
4. **From Acyl Chlorides**
   – Rosenmund reduction
5. **From Esters**
   – DIBAL–H reduction

NATURE OF CARBONYL GROUP
$>C=O$

Polar due to difference in electronegativity. Carbonyl carbon is electrophilic.

KETONES
(R–CO–R′)

–CO– group attached to two carbon atoms.

NOMENCLATURE
IUPAC: Replace –e of alkane with –one.

Common: Named as alkyl/aryl ketones R–CO–R′

PREPARATION
1. **From Alkenes**
   – Ozonolysis (oxidative)
2. **From Alcohols**
   – 2° alcohols → Ketones (CrO_3/H^+ or PCC)
3. **From Acyl Chlorides**
   – With Gilman reagent (R_2CuLi)
4. **From Esters**
   – With Grignard reagent (RMgX)
5. **From Nitriles**
   – RCN + RMgX → Ketone

PHYSICAL PROPERTIES
- Lower members are soluble in water (due to H-bonding with water). Solubility decreases with increase in molecular mass.
- Boiling points higher than hydrocarbons but lower than corresponding alcohols.
- Both are colourless, have characteristic odour.

CHEMICAL PROPERTIES
Due to polar carbonyl (>C=O) group.

REACTIONS OF ALDEHYDES
1. **Nucleophilic Addition**
   – HCN → Cyanohydrin
   – $NaHSO_3$ → Addition compound
   – Alcohols (H^+) → Hemiacetal → Acetal
   – NH_3 and 1° amines → Imine (Schiff base)
2. **Oxidation**
   – Mild oxidising agents: RCHO → RCOOH (Tollens', Fehling's, Benedict's)
   – Strong oxidising agents: RCHO → RCOOH ($KMnO_4$, $K_2Cr_2O_7$, HNO_3)
3. **Reduction**
   – H_2/Ni or $NaBH_4$ → RCH_2OH
   – Clemmensen reduction
   – Wolff–Kishner reduction → RCH_3
4. **Condensation Reactions**
   – With 1° amines → Schiff bases
   – Aldol condensation (self/with other)
   – Cannizzaro reaction (no α–H atom)
5. **Haloform Reaction**
   – With I_2/NaOH → CHI_3 + Carboxylate (for CH_3CHO and compounds having $CH_3CO–$ group)

INTERCONVERSION
1° Alcohol —Oxidation→ Aldehyde

2° Alcohol —Oxidation→ Ketone

Aldehyde —Oxidation→ Carboxylic Acid

Carboxylic Acid —Reduction→ 1° Alcohol

Acyl Chloride / Ester / Nitrile (via reduction) → Carboxylic Acid

REACTIONS OF KETONES
1. **Nucleophilic Addition**
   – HCN → Cyanohydrin
   – $NaHSO_3$ → Addition compound
   – Alcohols (H^+) → Ketal
   – NH_3 and 1° amines → Imine
2. **Reduction**
   – H_2/Ni or $NaBH_4$ → 2° Alcohol
   – Clemmensen reduction
   – Wolff–Kishner reduction → Alkane
3. (No oxidation with mild oxidising agents) Under strong conditions, C–C bond cleavage may occur.
4. **Haloform Reaction**
   – With I_2/NaOH → CHI_3 + Carboxylate (for methyl ketones R–CO–CH_3)
5. **Condensation Reactions**
   – Aldol condensation (self/with other)
   – Claisen–Schmidt condensation (with aromatic aldehydes)

Aldehydes (oxidation) → **CARBOXYLIC ACIDS (R–COOH)** ← Ketones (methyl ketones) (oxidation)

Obtained by oxidation of aldehydes and some ketones.

PREPARATION
1. Oxidation of 1° alcohols, aldehydes
2. Hydrolysis of nitriles
3. Hydrolysis of esters
4. Carboxylation of Grignard reagents
5. By Kolbe's electrolytic method (for ethanoic acid)

PROPERTIES
- **Physical:** Higher members are insoluble in water, have high b.p., acidic in nature.
- **Acidic Nature:** React with metals, bases, carbonates, hydrogencarbonates.
- Formation of esters, amides, acid chlorides, anhydrides.

IMPORTANT REACTIONS
1. Esterification
2. Formation of Acid Chlorides ($SOCl_2/PCl_5$)
3. Formation of Amides (NH_3)
4. Reduction → 1° Alcohols ($LiAlH_4$)
5. Decarboxylation (Soda lime)
6. HVZ Reaction (α–halogenation)

USES
- **Aldehydes:** Formaldehyde (disinfectant, resins), Benzaldehyde (flavouring agent), Acetaldehyde (manufacture of acetic acid, perfumes).
- **Ketones:** Acetone (solvent), Methyl ethyl ketone (solvent), Used in manufacture of drugs, perfumes, polymers.

→ Main flow ⇢ Interconversion / interrelation

R = Alkyl group
R′ = Alkyl/Aryl group

PCC = Pyridinium chlorochromate
DIBAL–H = Diisobutylaluminium hydride

SECTION –A (1 MARK)

1 In the reaction of NaOBr with amide, the carbonyl carbon is lost as :

(A)HCO_3^- B) CO_3^{2-} (C) CO_2 (D) CO

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) $C_6H_5CH(OH)CN$ (b) $C_6H_5CH(OH)COC_6H_5$

(c) $C_6H_5CH(OH)COOH$ (d) $C_6H_5CH(OH)CHOHC_6H_5$

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) $KMnO_4$ 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) (i), (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

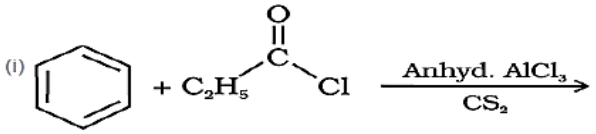
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
c	c	a	a	d	c	b	c	c	d	a	a	b	a	c

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]

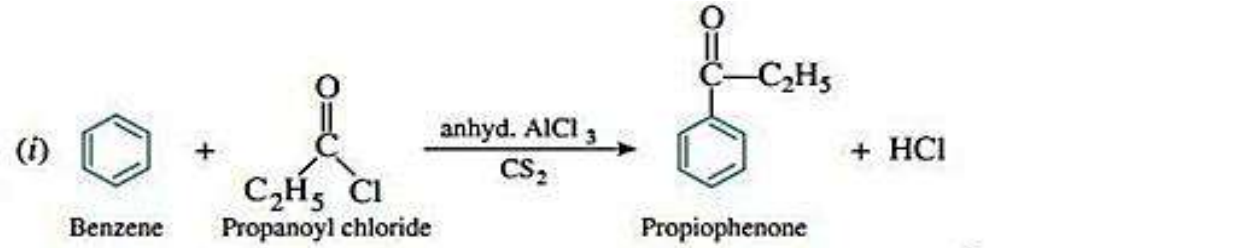
3 . Give the IUPAC names of the following compounds: (i) $PhCH_2CH_2COOH$
(ii) $(CH_3)_2C=CHCOOH$
[Hint: (i) 3-Phenylpropanoic acid (ii) 3-Methylbut-2-enoic acid]

4. Predict the product of the following reactions::

(i) 

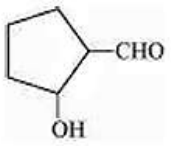
(ii) $(C_6H_5CH_2)_2Cd + 2\ CH_3COCl \rightarrow$

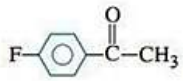
Hint:



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:

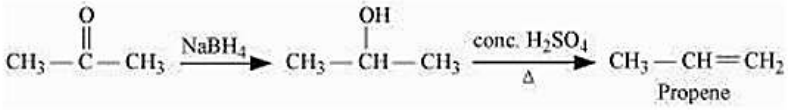
(i) Butane-1,3-diol (ii) But-2-enal (iii) But-2-enoic acid

[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]

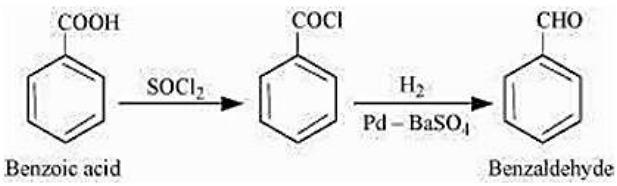
Note: try to draw the structure of all the compounds involved in these reactions

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

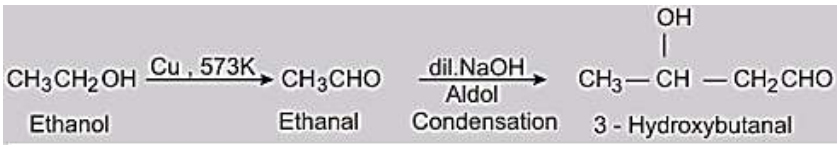
[Hint: (i)



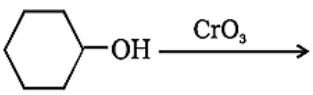
(ii)

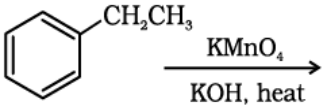


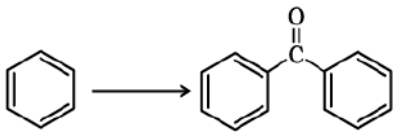
(iii)



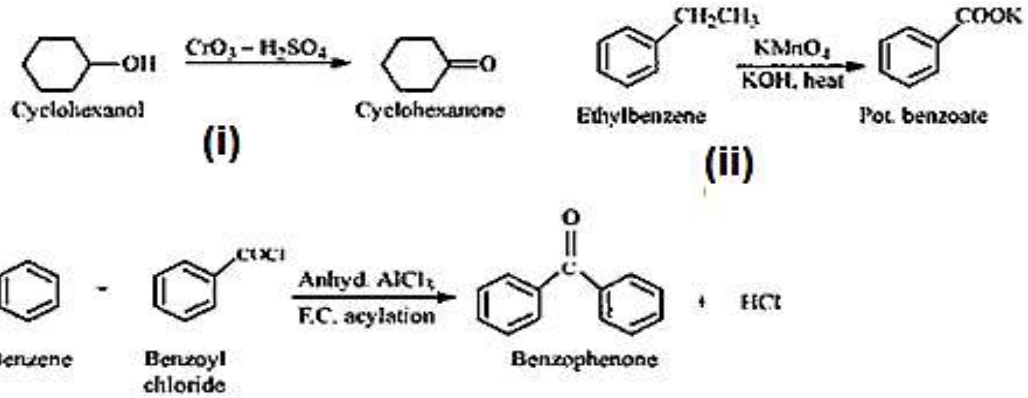
4. Complete each synthesis by giving missing starting material, reagent or products:

(i) 

; (ii) 

; (iii) 

Hint:



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.(a) How will you bring about the following conversions : **2026**

(I)Bromobenzene to 1-phenylethanol

(II)Benzene to m-nitroacetophenone

(III)An organic compound with the molecular formula C8H8O forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation with acidic or alkaline KMnO4 it gives Benzene-1,2-dicarboxylic acid. Identify the compound and write the products when it undergoes Cannizzaro reaction.

(IV)Arrange the following compounds in increasing order of their acid strength :

C6H5COOH, O2N – CH2 – COOH, CF3 – COOH, HCOOH 2+2+1=5

OR

(b) (i) Write the products formed when benzaldehyde reacts with the following reagents :

(I)2,4-Dinitrophenylhydrazine

(II) Acetophenone in the presence of dilute NaOH followed by heating

(ii) Give reasons for the following :

(I)Benzoic acid does not undergo Friedel-Crafts reaction.

(II) Carboxylic acids have higher boiling point than alcohols of comparable molecular mass.

(iii)Write simple chemical test to distinguish between propanal and propanone. 2+2+1=5

ANS. *(a) Conversions*

(I) Bromobenzene to 1-Phenylethanol

C_6H5Br --(Mg/ether)--> C_6H_5MgBr --(CH_3CHO)--> $C_6H_5CH(OMgBr)CH_3$ --(H_3O^+)--> $C_6H_5CH(OH)CH_3$
(II) Benzene to m-Nitroacetophenone
C_6H_6 --($CH_3COCl/AlCl_3$)--> $C_6H5COCH_3$ --(conc. HNO_3/H_2SO_4)--> m-$NO_2C_6H_4COCH_3$
(III) Identification of compound
Given:
• *Molecular formula = C_8H_8O , Gives 2,4-DNP test, Reduces Tollens' reagent, Undergoes Cannizzaro reaction, Oxidation gives benzene-1,2-dicarboxylic acid*
Compound: o-Methyl benzaldehyde (2-methylbenzaldehyde)

2. 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) $CH_3COCH_3 + 3I_2 + 4NaOH \rightarrow CH_3COO - Na + CHI_3 + 3NaI + 3H_2O$

2022 TERM I(ONLY DESCRIPTIVE TYPE QUESTIONS DUE TO COVID -19)

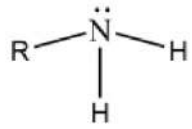
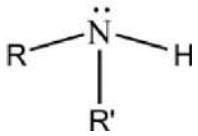
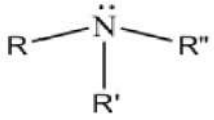
Q1. Predict the reagent for carrying out the following transformations (Any Two)
(i) Benzoyl chloride to Benzaldehyde
Reagent: H2 / Pd-BaSO4 (Rosenmund Reduction)
(ii) Ethanal to 3-hydroxybutanal
Reagent: Dilute NaOH (Aldol condensation)
(iii) Ethanoic acid to 2-chloroethanoic acid
Reagent: Cl2 / Red phosphorus (HVZ Reaction)
(a) What happens when:
(i) Propanone is treated with CH3MgBr and then hydrolysed?
Reaction:
CH3COCH3 + CH3MgBr → (Hydrolysis) → (CH3)3COH
Product formed: tert-Butyl alcohol (2-methylpropan-2-ol)
(ii) Ethanal is treated with excess ethanol and acid?
Reaction: CH3CHO + 2C2H5OH → CH3CH(OC2H5)2 + H2O
Product formed: Acetal (1,1-diethoxyethane)
(iii) Methanal undergoes Cannizzaro reaction?
Reaction:
2HCHO + NaOH → CH3OH + HCOONa
Products formed:
• *Methanol*
• *Sodium formate*
OR
(b) Write the main product in the following reactions:
(i) 2CH3COCl + (CH3)2Cd → CH3COCH3 (*Product: Propanone (Acetone)*
(ii) CH3CH2CHO --(Zn(Hg)/conc. HCl)--> CH3CH2CH3
Product: Propane
(iii) C6H13COONa + NaOH/CaO, Heat → C6H14 (*Hexane)*

UNIT- 9 : AMINES (6 Marks)

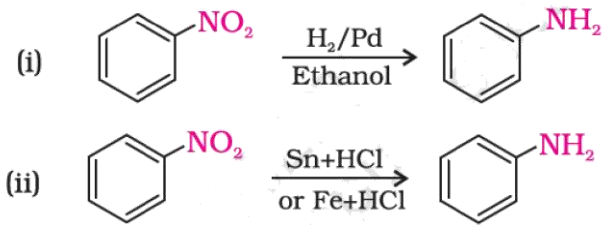
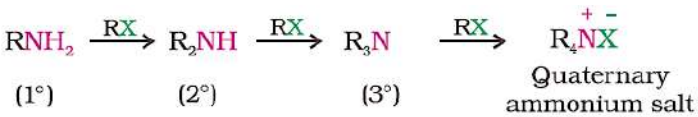
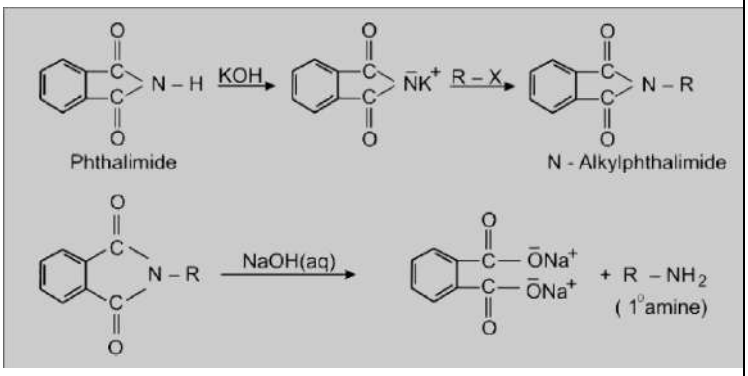
Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.
Diazonium salts: Preparation, chemical reactions and importance in synthetic organic chemistry.

Key Concepts

1. Amines are alkyl / aryl derivatives of ammonia. In amines nitrogen atom is sp^3 hybridized and contains one lone pair.
2. Amines can be classified as 1°, 2° and 3° based on the number of hydrogen atom present on nitrogen.

1^0 Amine	2^0 Amine	3^0 Amine
 CH_3-NH_2 = Methanamine CH_3-CH-CH_3 NH_2 Propan-2-amine	 CH_3-NH- CH_3 N-methylmethanamine	 $(CH_3)_3N$ N,N-dimethylmethanamine

➢ PREPRATION OF AMINES

1. **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	
2. **Ammonolysis of alkyl halides**: - Reagent: Ethanolic solution of ammonia. ***If Alkyl hailde is in excess the major product is 4° ammonium salt, if ammonia is in excess primary amine is major product.***	 Disadvantage: Mixture of 1°,2° & 3° amines formed
3. **Reduction of nitriles** Reducing agents: - ***$LiAlH_4$, H_2/Ni, Na/C_2H_5OH***	R – CN $(H_2/Ni\ or\ Na(Hg)/C_2H_5OH \rightarrow$ R–CH_2NH_2
4. **By the reduction of amides**	CH_3CONH_2 +($LiAlH_4$ +H_2O) → $CH_3CH_2NH_2$
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 → R – NH_2 + Na_2CO_3 + 2NaBr + $2H_2O$ C_6H_5-$CONH_2$ $Br2 + OH- \rightarrow$ C_6H_5-NH_2
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)
  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$
- $2^0 > 1^0 > 3^0 > NH_3$(Basic nature of Methyl substituted amines in aqueous phase)
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Aniline is weaker base than ammonia (Its pK_b value is large, lone pair of electrons are involved in resonance)

2. **Acetylation:** Replacement of H-atom from $–NH_2$ or >NH by Acid chloride, anhydride and esters to give **N-substituted amide.** **$(C_2H_5)_2NH + CH_3COCl$** **$CH_3CON(C_2H_5)_2 + HCl$**

3. **Reaction with Nitrous acid:** Forms aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and alcohols after reacting with water

R-NH_2 + HNO_2 ($NaNO_2$+ HCl) [R-$N_2^+Cl^-$] $\xrightarrow{H2O}$ **R-OH** +N_2 + HCl

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

R-NH_2 + C_6H_5-SO_2Cl $\xrightarrow{-HCl}$ ***$C_6H_5SO_2$-NH-R*** $\xrightarrow{NaOH}$ ***[$C_6H_5SO_2$-NR]$^-Na^+$*** *(water soluble)*

b. 2^0 amine forms a salt which is insoluble in alkali

R_2NH + C_6H_5-SO_2Cl $\xrightarrow{-HCl}$ ***C_6H_5-SO_2-NR*** $\xrightarrow{NaOH}$ ***No Reaction*** *(water insoluble)*

c. 3^0amine do not react with Hinsberg reagent

R_2NH + C_6H_5-SO_2Cl No Reaction

5. **Carbylamine reaction: (i)** ***Primary aliphatic and aromatic amine*** reacts with chloroform and KOH to form **alkyl/aryl isocyanides**(***foul smell compound).***

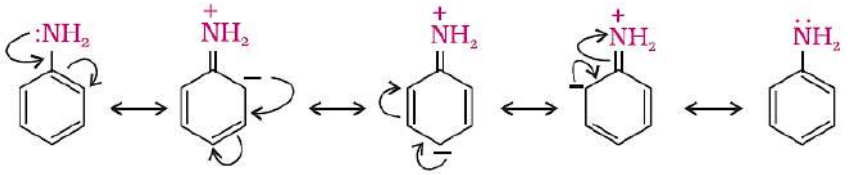
R-NH_2 + $CHCl_3$+3KOH R-NC + 3KCl + $3H_2O$

*Used as distinguish test for primary amine from secondary and tertiary amine

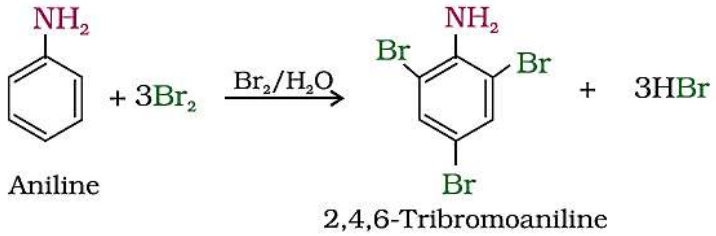
6. **REACTIONS OF ANILINE**

Electrophilic Substitution:

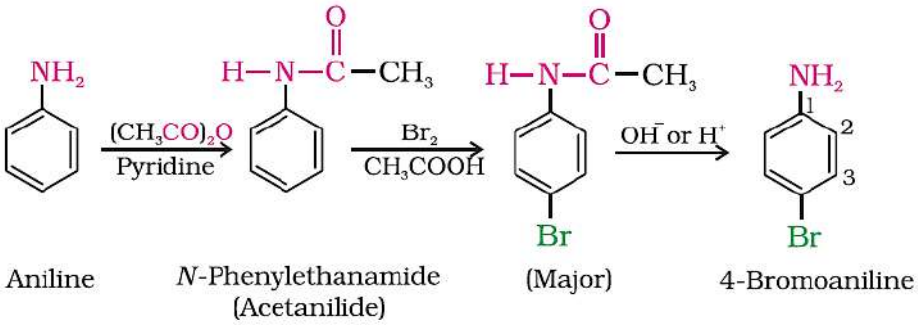
$–NH_2$ group is ***ortho and para directing*** and a powerful ***activating*** group.



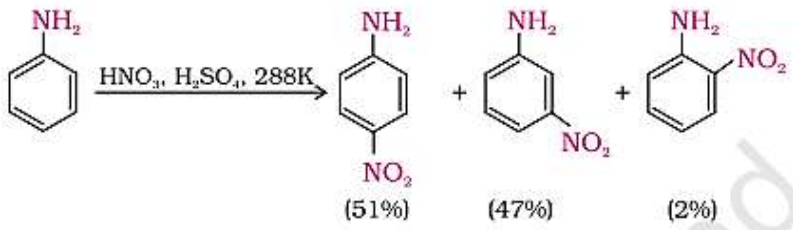
Bromination: Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



To prepare mono- substituted aniline derivative, the ***activating effect of –NH₂ group is controlled by protecting the -NH₂ group by acetylation with acetic anhydride****, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.*

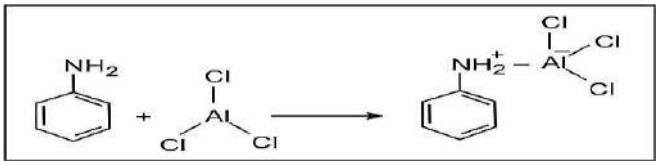


Nitration- Direct nitration of aniline yields tarry oxidation products in addition to the nitro derivatives.

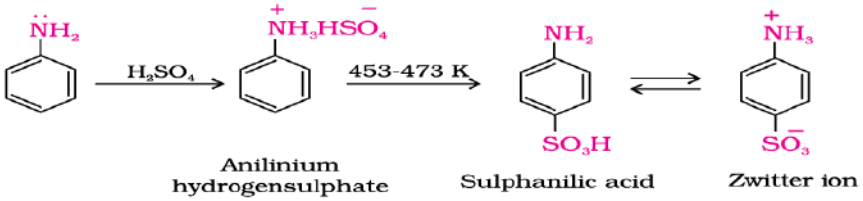


Note-In presence of HNO₃ & H₂SO₄ acids, most of aniline gets protonated to form anilinium ion. The —NH₂ group in aniline is o, p-directing and activating while the —NH₃⁺ group in anilinium ion is m-directing and deactivating.

- Aniline do not undergo Friedel craft reaction as it forms salt with the catalyst $AlCl_3$

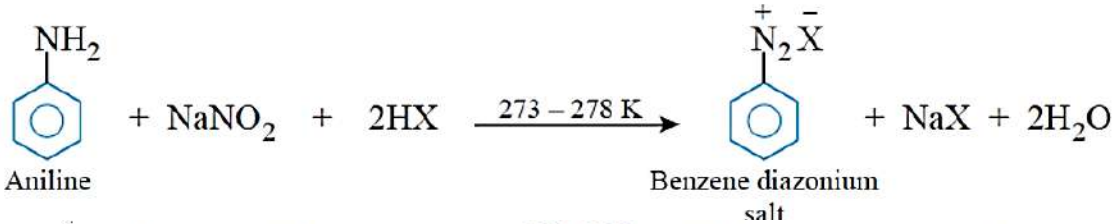


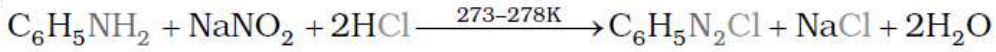
Sulphonation: Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate, which on heating at 453–473 K yields p-aminobenzene sulphonic acid (sulphanilic acid) as the major product.



BENZENE DIAZONIUM SALT $C_6H_5N_2^+X^-$ (X may be Cl, Br, NO_3, SO_4 etc.)

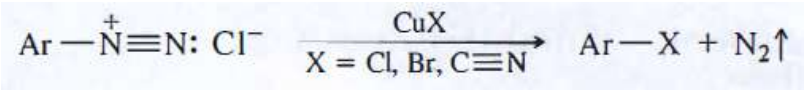
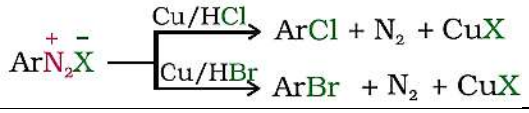
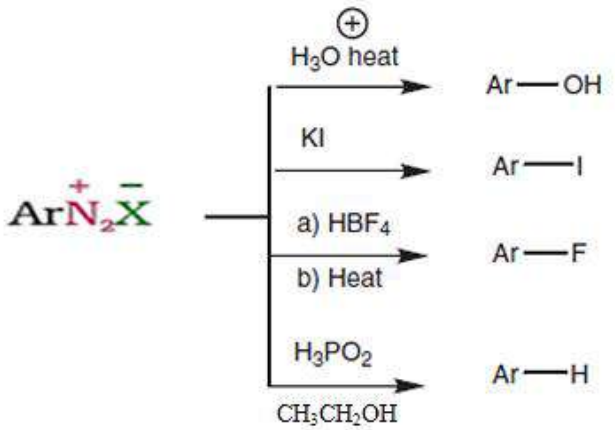
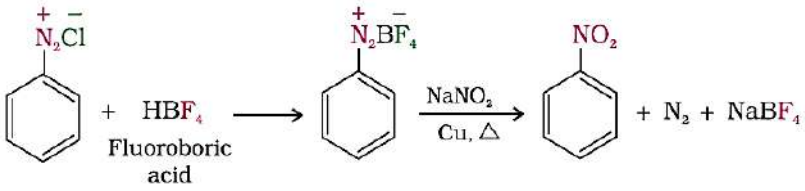
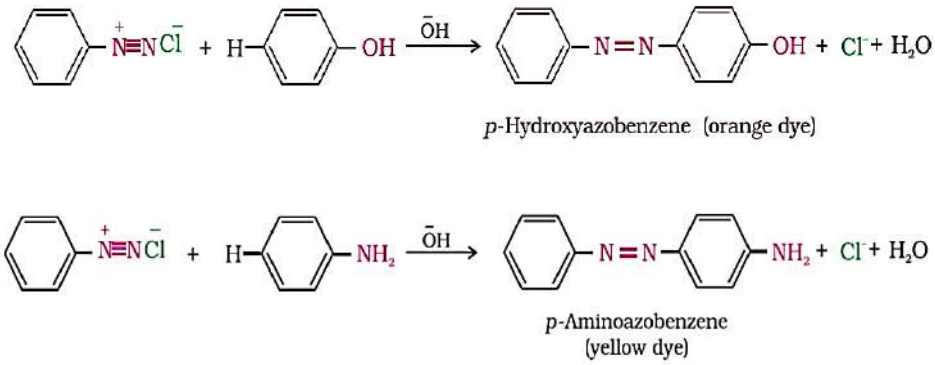
Prepration : Diazotisation of aniline using $NaNO_2$ & HX (HCl/H_2SO_4 etc.)



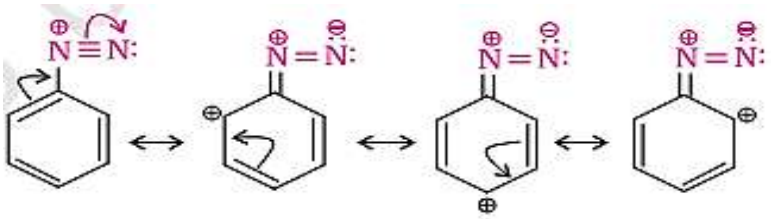


e.g.

REACTIONS OF BENZENE DIAZONIUM SALT

1.Sandmayer Reaction- (*Replacement of N_2 by halide or cyanide ion)*	
2.Gatterman reaction:	
3. Replacement of N_2 by OH /I / F and H	
4.Replacement of N_2 by – NO_2 group:	
5.Coupling Reactions Reaction of diazonium salts with phenols and aromatic amines to form azo compounds of the general formula, Ar—N—N—Ar is called coupling reaction.	

Note:Diazonium salt of alkyl amines are highly unstable but Primary aromatic amines form arenediazonium salts which are stable for a short time in solution at low temperatures (0 -5 ^{o}C). The stability of arenediazonium ion is explained on the basis of resonance.



Unit-9
Amines

Amines are organic derivatives of ammonia (NH_3) in which one or more hydrogen atoms are replaced by alkyl or aryl groups.

GENERAL STRUCTURE

$R-NH_2$, R_2NH , R_3N

(Where R = alkyl or aryl group)

1. CLASSIFICATION

(A) On the basis of nature of alkyl/aryl group attached to nitrogen

- 1° (Primary) $R-NH_2$ — One alkyl/aryl group
- 2° (Secondary) R_2NH — Two alkyl/aryl groups
- 3° (Tertiary) R_3N — Three alkyl/aryl groups

(B) On the basis of nature of hydrocarbon group

- Aliphatic amines (Alkyl amines)
- Aromatic amines (Aryl amines)

2. PREPARATION

(i) By ammonolysis of alkyl halides

$R-X + NH_3$ (alc.) $\rightarrow R-NH_2$

(Excess NH_3 gives 1° amine, limited gives 2° & 3° amines and quaternary ammonium salts)

(ii) By reduction of nitro compounds

$R-NO_2 \xrightarrow{[H]\ /\ Sn,\ HCl} R-NH_2$

(iii) By reduction of nitriles

$R-C\equiv N \xrightarrow{[H]/LiAlH_4} R-CH_2NH_2$

(iv) By Gabriel phthalimide synthesis

Phthalimide salt + $R-X$ $\rightarrow$ N-alkyl phthalimide $\rightarrow$ (hydrolysis) $\rightarrow$ $R-NH_2$

(v) By Hofmann Bromamide reaction

$R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

3. PROPERTIES OF AMINES

(A) PHYSICAL PROPERTIES

- Lower members are gases, middle members are liquids and higher members are solids.
- Lower aliphatic amines are soluble in water (H–bonding) and have fishy smell.
- Boiling points: 1° > 2° > 3° amines (due to intermolecular H–bonding).
- Aromatic amines have higher boiling points than aliphatic amines.

(B) BASIC NATURE

- Due to lone pair of electrons on N.
- Basic strength in aqueous solution: Aliphatic amines > Ammonia > Aromatic amines
- Order in aqueous solution: 2° > 1° > 3° amines
- Basicity decreases in aniline due to resonance of lone pair with benzene ring.

(C) CARBYLAMINE TEST (Only 1° amines)

1° amines on heating with $CHCl_3$ and alcoholic KOH give foul smelling isocyanides (carbylamines).

$R-NH_2 + CHCl_3 + 3KOH$ (alc.) $\rightarrow R-NC + 3KCl + 3H_2O$

4. CHEMICAL REACTIONS

(i) Alkylation

$R-NH_2 + R-X \rightarrow R-NHR + HX$

Further alkylation gives 2°, 3° amines and quaternary ammonium salts.

(ii) Acylation

$R-NH_2 + R'COCl \rightarrow R-NHCO-R' + HCl$

(Forms amides)

(iii) Reaction with nitrous acid (HNO_2)

1° aliphatic: $R-NH_2 + HNO_2 \rightarrow ROH + N_2\uparrow + H_2O$

1° aromatic: $Ar-NH_2 + HNO_2$ (Azo: 278–4) $\rightarrow Ar-N_2^+Cl^- + 2H_2O$ (Diazonium salt)

2° amines: $R_2NH + HNO_2 \rightarrow R_2N-NO + H_2O$ (N–nitrosamine)

3° amines: No reaction with HNO_2 (forms salts with it).

(iv) Azo coupling

(Diazonium salt + aromatic compound)

$Ar-N_2^+Cl^- + Ar'-H + OH^- \rightarrow Ar-N=N-Ar' + H_2O$

(Azo dye)

(v) With acids

(Amines are basic)

$R-NH_2 + HCl \rightarrow [R-NH_3]^+Cl^-$

(Forms ammonium salts)

(vi) Oxidation

1° & 2° amines on strong oxidation give corresponding nitro compounds.

3° amines $\rightarrow$ N-oxides.

(vii) REACTIONS OF BENZENE DIAZONIUM SALT ($Ar-N_2^+Cl^-$)

Preparation: $C_6H_5NH_2 + NaNO_2 + 2HCl$ (273–278 K) $\rightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$

1. **Replacement by Cl (Sandmeyer reaction)**
   $C_6H_5N_2^+Cl^- \xrightarrow{CuCl/HCl} C_6H_5Cl + N_2\uparrow$
2. **Replacement by Br (Sandmeyer reaction)**
   $C_6H_5N_2^+Cl^- \xrightarrow{CuBr/HBr} C_6H_5Br + N_2\uparrow$
3. **Replacement by I**
   $C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + KCl + N_2\uparrow$
4. **Replacement by F (Schiemann reaction)**
   $C_6H_5N_2^+BF_4^- \xrightarrow{\Delta} C_6H_5F + BF_3 + N_2\uparrow$
5. **Replacement by CN**
   $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} C_6H_5CN + N_2\uparrow$
6. **Replacement by OH**
   $C_6H_5N_2^+Cl^- + H_2O \xrightarrow{(warm)} C_6H_5OH + HCl + N_2\uparrow$
7. **Reduction to benzene**
   $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6 + H_3PO_3 + HCl + N_2\uparrow$
8. **Azo coupling (with phenol)**
   $C_6H_5N_2^+Cl^- + C_6H_5OH + OH^- \rightarrow p\text{-}HO-C_6H_4-N=N-C_6H_5 + H_2O$

5. IMPORTANCE / APPLICATIONS

- (i) Aniline is used in the manufacture of aniline dyes, polymers (m–phenylene diamine for nylon–6,6), agrochemicals and pharmaceuticals.
- (ii) Used in the preparation of medicines, rubber chemicals, photographic chemicals and corrosion inhibitors.
- (iii) Quaternary ammonium compounds are used as phase transfer catalysts, disinfectants and fabric softeners.
- (iv) Many natural products containing amines are biologically important (eg. alkaloids, amino acids, etc.).

SUMMARY FLOW

Classification ↓ Preparation ↓ Properties (Physical, Basicity, Carbylamine test) ↓ Chemical Reactions (including Diazonium reactions) ↓ Applications

SECTION – A (1 Mark)

Q1. The correct order of decreasing basicities of $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ in aqueous solution is :

(A) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$ (B) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N$

(C) $C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (D) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$

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 Which of the following compounds will dissolve in an alkali solution after it undergoes reaction with Hinsberg's reagent?

(a) $(CH_3)_3$ N (b) CH_3NH_2 (c) $(C_2H5)_2NH$ (d) $C_6H_5NHC_6H_5$

Q5.The correct IUPAC for $CH_3CH_2CH_2N(CH_3)C_2H_5$ 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. Anilinium hydrogen sulphate on heating at 453-473 K produces which of the following as a major product?

(A) 2-aminobenzene sulphonic acid (B) benzene sulphonic acid

(C) 2-aminobenzoic acid (D) sulphanilic acid

Q7. An amine 'X' reacts with Hinsberg reagent and the product obtained is insoluble in alkali. The amine 'X' is:

(A) $(CH_3)_2NH$ (B) $(CH_3)_3$ N (C) CH_3-CH_2-NH_2 (D) C_6H_5-NH_2

Q8. Which of the following amines does not give foul smell of isocyanide on heating with chloroform and ethanolic KOH?

(A) CH_3-CH_2-NH_2 (B) $(CH_3)_3CH$-CH_2-NH_2

(C) $(CH_3$-$CH_2)_3N$ (D) C_6H_5-NH_2

Q9. When alkyl iodide is treated with large excess of ammonia, the major product obtained is:

(A) Tertiary amine (B) Quaternary ammonium salt

(C) Secondary amine (D) Primary amine

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): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

REASON(R): Diazonium salts of aliphatic amines undergo resonance.

Q12. ASSERTION (A): Aniline undergoes Friedel-Crafts reaction.

REASON (R): Aniline forms salt with $AlCl_3$ The Lewis acid in Friedel-Craft reaction..

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 easily.

Q14. ASSERTION(A):): Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.

REASON(R): Acetylation decrease the activation effect of the amino group.

Q15. ASSERTION(A): Nitration of aniline in strongly acidic medium give m-nitro aniline as major product.

REASON(R): -NH_2 group in aniline is ortho-para directing .

ANSWERS KEY:

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

SECTION - B (2 marks)

Q1. a)Arrange the following in increasing order of their basic strength:

$C_2H_5NH_2$, $C_6H_5NH_2$, NH3, $C_6H_5CH_2NH_2$, $(C_2H_5)_2NH$

b) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. Give reason.

Hint: Greater stability for ammonium cation of dimethyl amine than ammonium cation of trimethyl amine.

Q2. The -NH_2 group in aniline is acetylated before nitration, cite possible reason for it.

[Hint: Direct nitration of aniline gives tarry oxidation product]

Q3. Account for the following:

(i) pK_b of aniline is more than that of methylamine.

Hint: aniline is a weaker base than methylamine as lone pair of electron in aniline is delocalized over the benzene ring and less available for protonation.

(ii) Although trimethylamine and n-propylamine have the same molecular weight, but the former boils at a lower temperature (276 K) than the latter (322 K). Explain.

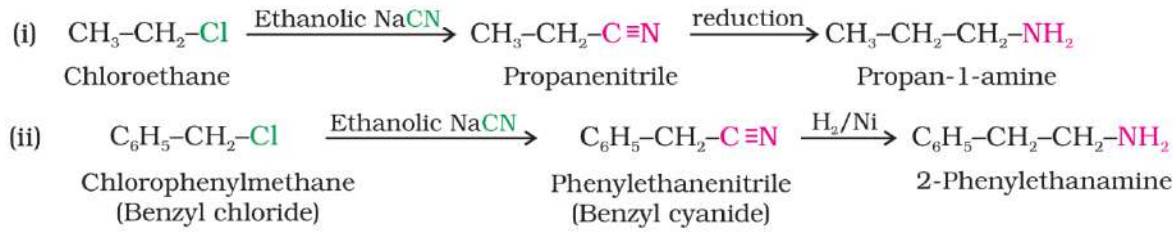
Hint: $(CH_3)N$, is a tertiary amine does not have any H-atom on the N-atom & thus it does not undergo H-bonding.

Q4. Write chemical equations for the following conversions:

(i) $CH_3–CH_2–Cl$ into $CH_3–CH_2–CH_2–NH_2$

(ii) $C_6H_5–CH_2–Cl$ into $C_6H_5–CH_2–CH_2–NH_2$

Hint:



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 :

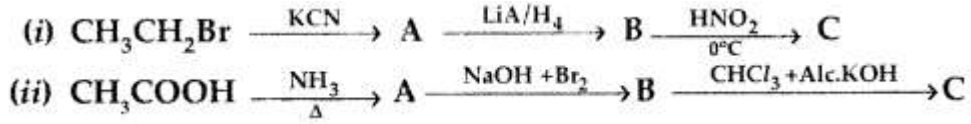
(i) Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(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:



[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. Complete & give names to the following reactions:

(a) $C_6HN_2Cl + CuCl + H^+$

(b) $CH_3CH_3NH_2 + CHCl_3 + KOH$

(c) $C_6H_5CONH_2 + Br_2 + KOH$

[Hint: a- Sandmeyers reaction, b- Carbylamine reaction c- Hoffmann bromamidereaction]

SECTION D Case Based Questions (4 Marks)

Q1. Read the following passage carefully and give answers of following questions:

Amines are usually formed from amides, imides, halides, nitro compounds, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing. steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. Amines being basic in nature, react with acids to form salts. Aryldiazonium salts, undergo replacement of the diazonium group with a variety of nucleophiles to produce aryl halides, cyanides, phenols and arenes.

Answer the following questions:

(a) How can you convert the following?

(i) Ethanoic acid to methanamine (ii) Propanenitrile to 1-aminopropane

[Hint: i) Heat with NH_3 followed by Hoffmann bromamide reaction

ii) reduce with suitable reducing agent)]

(b) Why do primary amines have higher boiling point than tertiary amines?

[Hint: 1^o amines have intermolecular H-bonding but 3^o do not.]

(c) (1) Arrange the following in increasing order of their basic strength in aqueous solution:

CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

OR

(2) Give the structures of A and B in the following reaction:

$C_6H_5NO_2$ ----------> A ----------> B (Fe/HCl; HNO_2/ 273K) [Hint: A= $C_6H_5NH_2$, B= $C_6H_5N_2X$]

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

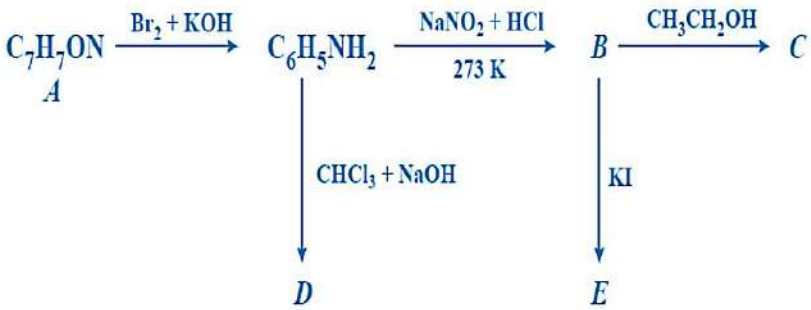
(a) $NH_3 > C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (b) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(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. An aromatic compound 'A' of molecular formula C7H7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:



[Hint : A = C_6H_5-$CONH_2$ B = $C_6H_5N_2$ Cl C= C_6H_6 D= C_6H_5NC E = C_6H_5I]

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.(i)Ammonolysis of alkyl halides in not a good method to prepare pure primary amines.

(ii) Aniline does not give Friedel Craft reaction.

[Hint : ref. summary]

UNIT-10: BIOMOLECULES (7 Marks)

Carbohydrates. Proteins, Enzymes, Vitamins Nucleic Acids, Hormones

- **Monosaccharide** : Cannot be hydrolyzed further to simpler molecules. Example: Glucose, fructose, Ribose etc.

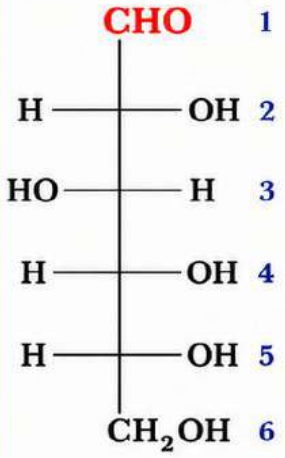
REACTIONS OF GLUCOSE

CBSE Class XII

(Open Chain Structure)

Glucose is an aldohexose. In open chain form, it contains an aldehyde group (– CHO) at C-1 and five hydroxyl groups (–OH). Hence, it shows the following reactions.

Open Chain Structure of Glucose

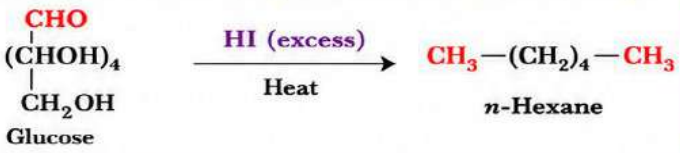


D-Glucose
(An aldohexose)

Key Points

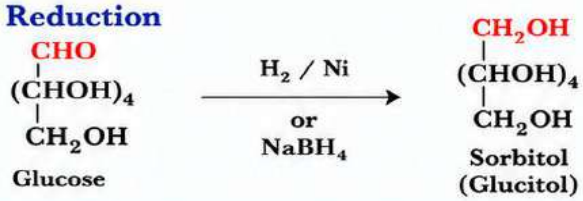
- Aldehyde group at C-1 gives typical reactions of –CHO.
- –OH groups give reactions of alcohols.
- On oxidation, glucose forms gluconic acid (mild) or saccharic acid (strong).
- Glucose reduces mild oxidising agents (Tollens', Fehling's) but not bromine water.

1 Reaction with HI (Formation of n-hexane)



Aldehyde group and all –OH groups are replaced by hydrogen to give *n*-hexane.

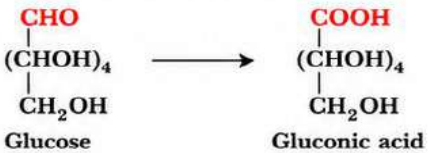
2 Reduction



Aldehyde group (–CHO) is reduced to primary alcohol ($-CH_2OH$).

3 Oxidation

(i) Mild oxidation
Br_2 water
or
Tollens' reagent
or
Fehling's solution



Aldehyde group oxidised to carboxylic acid (–COOH).

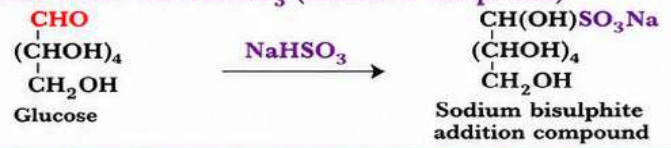
(ii) Strong oxidation
HNO_3 (conc.)

Both –CHO (C-1) and $-CH_2OH$ (C-6) oxidised to –COOH.

4 Reaction with HCN (Cyanohydrin formation)

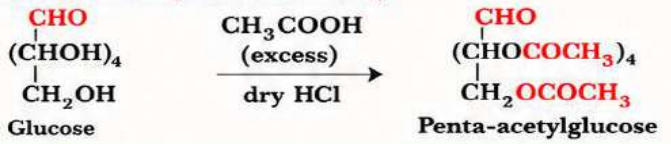
Alddtion of HCN to aldehyde group forms cyanohydrin.

5 Reaction with $NaHSO_3$ (Addition compound)



Aldehyde group adds $NaHSO_3$ to give addition compound.

6 Esterification (with Acetic acid)



–OH groups are esterified with acetic acid to give penta-acetylglucose.

☆ These reactions show that glucose behaves like an aldehyde as well as a polyhydric alcohol.

➢ **Reactions of glucose (Open Chain structure):**

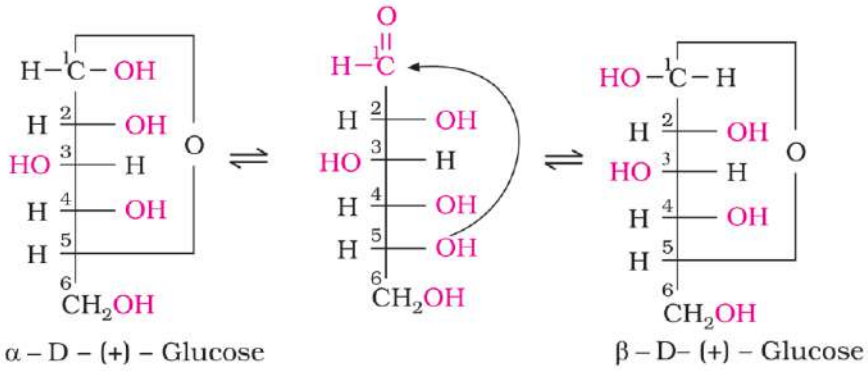
➢ **Reactions of glucose could not be explained by open chain structure.**

1. Glucose does not give Schiff's test and it does not form the hydrogensulphite.
2. The pent acetate 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**
Aldehydes/ kenotic 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.

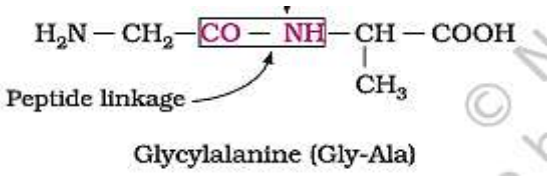
Amino Acids: Amino acids contain amino (–NH2) and carboxyl (–COOH) functional groups. Depending upon the relative position of amino group with respect to carboxyl group, the amino acids can be classified as α, β, γ, δ and so on.

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

Peptide linkage: peptide linkage is an amide formed between –COOH group and NH_2 group of two successive amino acids in peptide chain.



Structure of Proteins.

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 1º 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.

VITAMINS – AN ESSENTIAL GUIDE

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.

VITAMIN	CHEMICAL NAME (Other names)	FUNCTIONS (Important for)	DEFICIENCY DISEASES (Important)
VITAMIN A	Retinol (Alcohol form) Also: Retinal (Aldehyde form) Retinoic acid (Acid form)	• Essential for vision (especially night vision). • Maintains healthy epithelial tissues, skin and mucous membranes. • Important for growth and immunity.	**Xerophthalmia** (hardening of cornea of eye) **Night blindness**
VITAMIN B_1 (Thiamine)	Thiamine (Also called Aneurin)	• Coenzyme in carbohydrate metabolism. • Essential for normal growth and functioning of nerves.	**Beriberi** (Peripheral neuritis, weakness, oedema)
VITAMIN B_2 (Riboflavin)	Riboflavin (Lactoflavin)	• Component of coenzymes (FMN, FAD). • Important for growth, skin, eye and mucous membranes.	**Cheilosis** (cracking at the corners of mouth), sore throat, dermatitis
VITAMIN B_6 (Pyridoxine)	Pyridoxine (Pyridoxal, Pyridoxamine are active forms)	• Coenzyme in amino acid metabolism. • Necessary for synthesis of neurotransmitters and haemoglobin.	**Convulsions, irritability, dermatitis, anaemia**
VITAMIN B_{12} (Cobalamin)	Cyanocobalamin (Coenzyme form)	• Necessary for RBC formation. • Important for nervous tissue and DNA synthesis.	**Pernicious anaemia** (Decrease in RBCs, weakness, fatigue)
VITAMIN C (Ascorbic acid)	Ascorbic acid	• Essential for formation of collagen. • Heals wounds and increases resistance to infections.	**Scurvy** (bleeding gums, loose teeth, poor wound healing)
VITAMIN D (Cholecalciferol)	Cholecalciferol (Vitamin D_3)	• Helps in absorption of Ca and P. • Essential for healthy bones and teeth.	**Rickets in children** (bone deformities), **Osteomalacia in adults** (bone pain and weakness)
VITAMIN E (Tocopherol)	α-Tocopherol (most active form)	• Powerful antioxidant. • Necessary for reproduction and healthy muscles.	**Fragility of RBCs (haemolytic anaemia), muscular weakness, reproductive problems**
VITAMIN K (Phylloquinone)	Phylloquinone (Vitamin K_1)	• Essential for synthesis of prothrombin. • Required for normal blood clotting.	**Increased blood clotting time (haemorrhage)**

IMPORTANT POINTS

- Vitamins are required in very small amounts.
- They do not provide energy but regulate metabolic processes.
- Deficiency of vitamins causes specific deficiency diseases.
- Balanced diet with fruits, vegetables, whole grains, milk, egg and nuts ensures adequate supply of vitamins.

FAT SOLUBLE vs WATER SOLUBLE VITAMINS

Fat Soluble Vitamins (A, D, E, K)	Water Soluble Vitamins (B-complex, C)
• Absorbed with fats. • Stored in body. • Excess intake may cause toxicity.	• Absorbed in water. • Not stored (except B_{12}). • Excess is excreted in urine.

☆ **A balanced diet is the key to good health. Vitamins are vital micronutrients that keep our body healthy and active by performing various life-sustaining functions.**

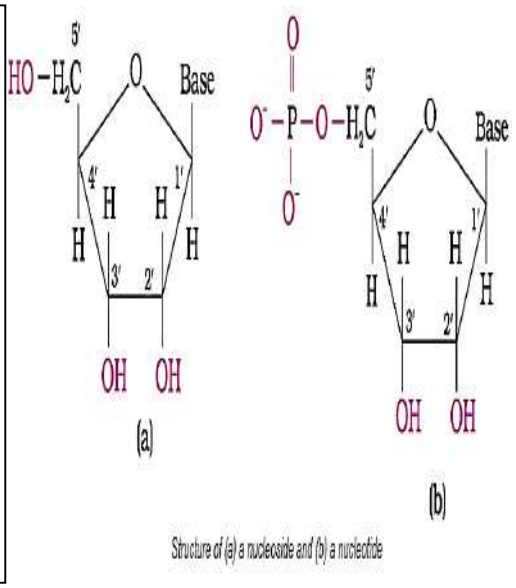
Nucleic acid

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'-

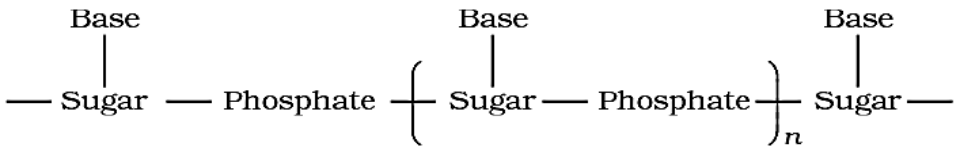


Structure of (a) a nucleoside and (b) a nucleotide

DNA	RNA
Structural difference	
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.
Functional diffrence	
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.



Hormones

Hormones are chemical substances produced by ductless glands (endocrine glands) in the body. They act as intercellular messengers and regulate various physiological activities.

Ex.1. Protein/Polypeptide Hormones **Insulin** – Secreted by pancreas; controls blood sugar level 2. . **Thyroxine** – Secreted by thyroid gland; regulates metabolism	2. Steroid Hormones • **Estrogen** (Oestrogen) – Responsible for female sexual development. • **Progesterone** – Regulates menstrual cycle. • **Testosterone** – Primary male sex hormone.

Unit-10 BIOMOLECULES

1. CARBOHYDRATES

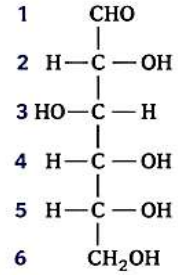
Definition:
Polyhydroxy aldehydes or ketones or substances that on hydrolysis give such compounds.

Classification

Monosaccharides	Disaccharides	Polysaccharides
(One unit)	(Two units)	(Many units)
e.g., Glucose, Fructose	e.g., Sucrose, Maltose, Lactose	e.g., Starch, Cellulose, Glycogen

Important Monosaccharide: Glucose (Aldohexose)

Open Chain Structure of D-Glucose



IMPORTANT REACTIONS OF GLUCOSE

1.	Reduction (To sugar alcohol)	Glucose	H_2/Ni or $NaBH_4$ →	Sorbitol (Glucitol)
2.	Mild oxidation	Br_2 water / Tollens' reagent / Fehling's solution	→	Gluconic acid
3.	Strong oxidation	(Conc. HNO_3)	→	Saccharic acid (Glucaric acid)
4.	Cyanohydrin formation	HCN	→	Glucose cyanohydrin
5.	Addition of $NaHSO_3$	$NaHSO_3$	→	Sodium bisulphite addition compound
6.	Esterification	Excess CH_3COOH / dry HCl	→	Penta-acetyl glucose
7.	Formation of osazone	Phenylhydrazine	→	Glucosazone
8.	Deoxygenation (HI)	HI (excess)	→	*n*-Hexane
9.	Fermentation (Yeast)	Zymase	→	Ethanol + CO_2
10.	Formation of glycosides	ROH / dry HCl	→	Glucosides

2. VITAMINS

Definition:
Organic compounds required in small amounts in diet for normal growth and health.

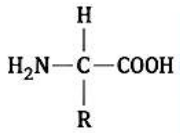
DEFICIENCY DISEASES

Vitamin	Deficiency Disease
Vitamin A	Xerophthalmia (hardening of cornea of eye), Night blindness
Vitamin B_1 (Thiamine)	Beriberi
Vitamin B_2 (Riboflavin)	Cheilosis
Vitamin B_6 (Pyridoxine)	Convulsions
Vitamin B_{12} (Cobalamin)	Pernicious anaemia
Vitamin C (Ascorbic acid)	Scurvy (bleeding gums)
Vitamin D (Calciferol)	Rickets, Osteomalacia
Vitamin E (Tocopherol)	Fragility of RBCs and muscular weakness
Vitamin K (Phylloquinone)	Increased blood clotting time

3. PROTEINS

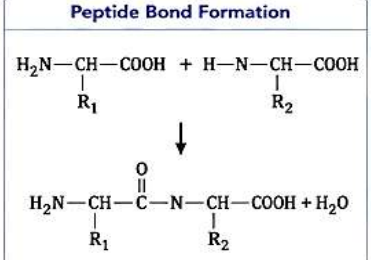
Definition: High molecular weight natural polymers of α-amino acids linked by peptide bonds.

Amino Acid (General Structure)



R = Side chain

Peptide Bond Formation



(—CO—NH— Peptide bond)

Levels of Protein Structure

- **Primary** (Linear sequence of amino acids)
- **Secondary** (α-helix / β-sheet stabilized by H-bonds)
- **Tertiary** (Overall 3D shape due to R-group interactions)
- **Quaternary** (Association of two or more polypeptide chains)

Types of Bonding / Interactions in Proteins

1. Peptide Bond	2. Hydrogen Bond	3. Disulphide Bond	4. Ionic Bond	5. Hydrophobic Interactions	6. Van der Waals Forces
(—CO—NH—) Primary structure	Between —C=O and —N—H (Stabilizes 2° str.)	(—S—S—) Between cysteine residues	Between opposite charged R-groups	Between nonpolar R-groups	(Weak interactions)

Functions of Proteins: Structural support, Enzymes (catalysts), Transport, Hormones, Immunity, Movement, Storage.

4. HORMONES

Definition: Chemical messengers produced by endocrine glands; act on specific target organs.

1. Protein / Polypeptide Hormones

- **Insulin** – Secreted by pancreas; controls blood sugar levels.
- **Glucagon** – Secreted by pancreas; increases blood sugar levels.
- **Pituitary Hormones** – e.g., Growth Hormone (GH), Vasopressin.

2. Steroid Hormones

- **Oestrogen (Estrogen)** – Responsible for female sexual development.
- **Progesterone** – Regulates menstrual cycle.
- **Testosterone** – Primary male sex hormone.
- **Cortisol** – Adrenal cortex hormone involved in stress response.

3. Amino Acid Derivatives

- **Adrenaline (Epinephrine)** – Secreted by adrenal gland; "Fight or Flight" hormone.
- **Thyroxine** – Secreted by thyroid gland; regulates metabolism.

5. NUCLEIC ACIDS

Definition: Biopolymers of nucleotides; store and transmit genetic information.

Nucleotide = Nitrogenous base + Pentose sugar + Phosphate

Types

DNA (Deoxyribonucleic acid)	RNA (Ribonucleic acid)
Sugar: Deoxyribose	Sugar: Ribose
Bases: A, T, G, C	Bases: A, U, G, C
Structure: Double helix (Watson-Crick model)	Structure: Generally single stranded

Important Points

- Besides glucose, carbohydrates include:
  Monosaccharides: Glucose, Fructose, Galactose
  Disaccharides: Sucrose, Maltose, Lactose
  Polysaccharides: Starch (storage in plants), Glycogen (storage in animals), Cellulose (structural)
- General formula (monosaccharides): $(CH_2O)_n$
- Reducing sugars have free –CHO or –CO– group.
- Glycosidic linkage joins monosaccharides.

Functions of Carbohydrates

- Primary source of energy
- Storage (Starch, Glycogen)
- Structural (Cellulose, Chitin)

SECTION - A (1 MARKS)

Q.1 Which of the following is a water-soluble vitamin ? **(2026)**
(A)Vitamin K (B) Vitamin A (C) Vitamin B (D) Vitamin D

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 a-helix structure refers to:
(A) primary structure of protein (B) secondary structure of protein **(2025)**
(C) tertiary structure of protein (D) quaternary structure of protein

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 (A): Maltose is a reducing sugar.
Reason (R): One of the two glucose units can open to expose free aldehydic group in solution. .

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
C	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 protein; ii)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.

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

Q5 i) 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?

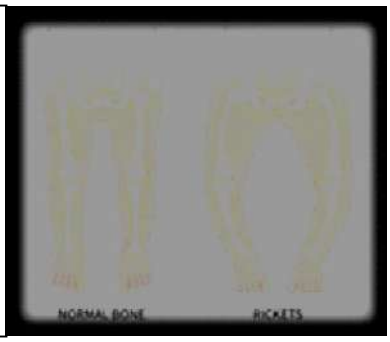
Hint-i)glucose's aldehyde group is involved in the ring structure

ii)Fructose contains a free aldehyde group

Case Based Questions (4 Marks)

Q1.

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) Id

(ii) Is

(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*

Q2.Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, liquids, etc. Carbohydrates are optically active polyhydroxy aldihydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups – monosaccharides,oligosaccharide, and polysaccharide. Monosaccharides are held together by glycosidic linkages to form diasaccharides like sucrose, maltose, or polysaccharides like starch and cellulose.

Another biomolecule: proteins are polymers of alpha-amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. Structure and shape of protein can be studied at four different levels i.e. primary, secondary, tertiary and quaternary, each level being more complex than the previous one. . **(2023)**

Answer the following questions:

(i) What is the difference between a glycosidic linkage and peptide linkange?

(ii) Which amino acids are called essential amino acids?

(iii) What are the common types of secondary structures of proteins?
Write any two forces which stabilize the secondary and tertiary structures of protein.

OR

(iii)Define denaturation of protein with an example. During denaturation which structure of protein lose their biological activity?

(Hints: ref. to theory)

LONG ANSWER TYPE QUESTIONS (5 MARKS)

1. Questions: Give the Product of the Following Reactions of Open Chain Glucose

1. D-(+)-Glucose + HI (excess), heat →
2. D-(+)-Glucose + Br_2 water ⟶
3. D-(+)-Glucose + conc. HNO_3 ⟶
4. D-(+)-Glucose + HCN →
5. D-(+)-Glucose + excess CH_3COOH / dry HCl ⟶

Hint. Refer theory

Q2. A. Write two differences between Amylose and Amylopectin components of starch. (2+3)(**2025)**

Feature	Amylose	Amylopectin
1. Structure	Linear polymer	Branched polymer
2. Glycosidic linkage	α-1,4 linkage only	α-1,4 and α-1,6 linkages(branches)
3. Solubility	Less soluble in water	More soluble due to branching

B. Differentiate between:

(a) Essential amino acids and Non-essential amino acids

(b)Peptide linkage and Glycosidic linkage

(e) Fibrous protein and Globular protein

Hints. Peptide vs Glycosidic linkage
Peptide: Protein, CO–NH bond
Glycosidic: Sugar, C–O–C bond
Tip: "Peptide = Protein link, Glyco = Glucose link"

(c) Fibrous vs Globular protein
Fibrous: Thread-like, insoluble, structural → e.g., keratin, collagen
Globular: Spherical, soluble, functional → e.g., enzymes, hemoglobin
Mnemonic: "Fibrous = Frame, Globular = Go-function"

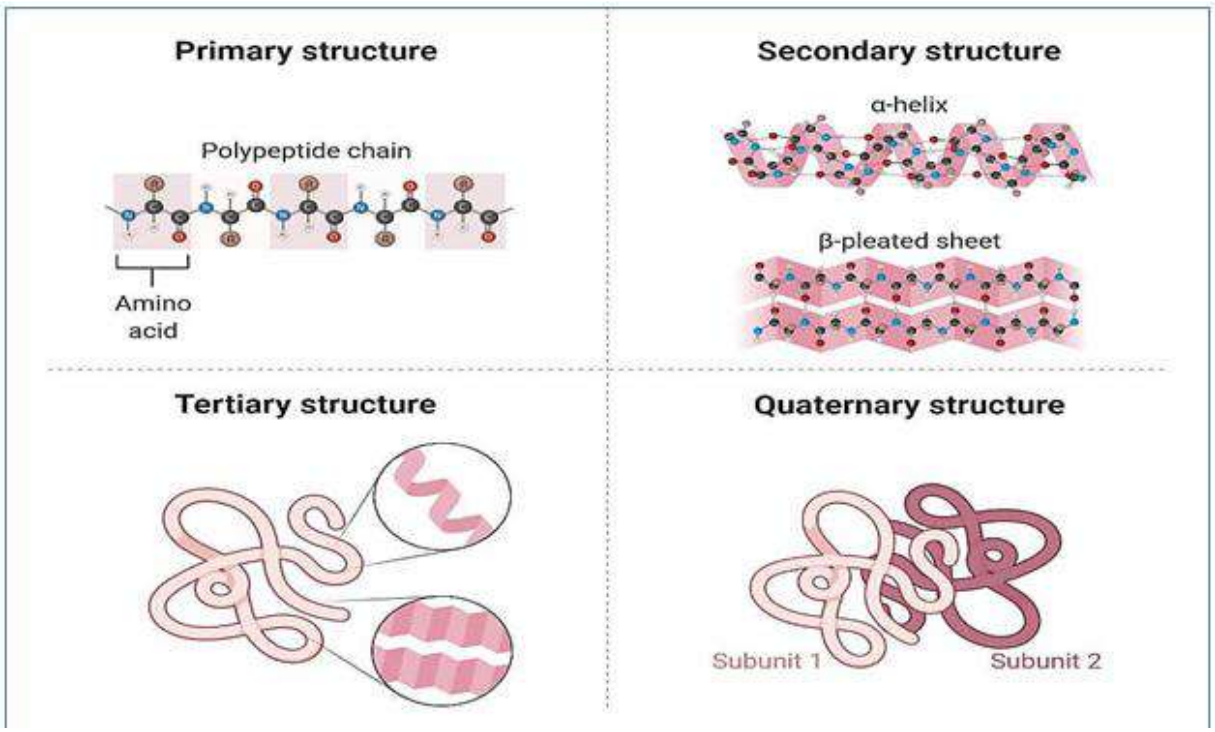
Q3 a. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be :

(A)primary structure of proteins (B) secondary structure of proteins
(C)tertiary structure of proteins (D)quaternary structure of proteins

b. What is the effect of denaturation on the structure of proteins ? What are the common types of secondary structures of proteins ?

Hints. The specific sequence of amino acids in a polypeptide chain is called the primary structure of proteins.
Correct Answer: (A) Primary structure of proteins
b.Effect of denaturation on proteins:
Denaturation disturbs the natural shape of proteins due to heat, chemicals, change in pH, etc. It destroys the secondary and tertiary structures, causing loss of biological activity, but the primary structure usually remains unchanged.

Common types of secondary structures of proteins:
α-Helix
β-Pleated sheet



Link For Quiz & Extra Practice Questions

Quiz/ Multiple Choice Practice Questions		
Name of Chapers	**Google Form Link**	**QR Code**

1. Solutions	https://docs.google.com/forms/d/e/1FAIpQLScPYcZbrJBZebvLIpSakw7WomnUNcggk6PXTNLAxYyZwu5Mcg/viewform?usp=header	
2. Electrochemistry	https://docs.google.com/forms/d/e/1FAIpQLSfsZqlsfMof6cUNImYtTr0sS2kEXFnm7LnlpA2OZOCX7Owl6Q/viewform?usp=header	
3. Chemical Kinetic	https://docs.google.com/forms/d/e/1FAIpQLSfrE9to6FcOIlmNH8gS9TrZdXw8CkZeSveGGqq0Du-b21401w/viewform?usp=header	
4. The d and f Block Elements	https://docs.google.com/forms/d/e/1FAIpQLSd7a9nZys-JEEdUeLEoPmEMxzHIKJ10-XcqZNt4nd-9z6t02g/viewform?usp=dialog	
5. Coordination Compound	https://docs.google.com/forms/d/e/1FAIpQLSf_lNDsqcYTiz8LwIdwyMLe6BI-ObRgJD-BoRcWenggeZTFzQ/viewform?usp=dialog	
6. Haloalkane and Haloarene	https://docs.google.com/forms/d/e/1FAIpQLScFjtQC1dU-hMF66NAl8VeYVOSXOYiFsZx07WPckvvZOJI2rA/viewform?usp=header	
7. Alcohols, Phenols, and Ethers	https://docs.google.com/forms/d/e/1FAIpQLSfUhf-_ph9h_al8ORZmBR3dH_hxIxsRh6_I5DUwSKvQNjGjEQ/viewform?usp=header	
8. Aldehydes, Ketones and Carboxylic Acids	https://docs.google.com/forms/d/e/1FAIpQLSd32d3stJd5X3j9nBsBp030dE7kVAa--dBGyKJBKR0lZaUoNA/viewform?usp=publish-editor	

9. Amines	https://docs.google.com/forms/d/e/1FAIpQLSdRUQHIdo9vGgf_2oN-pSbQ1POnw_m5XAN3sNSb6JWqZX9WCQ/viewform?usp=header	
10. Biomolecules	https://docs.google.com/forms/d/e/1FAIpQLScFqDwBsLo_KJ6it5Pq0bmvH_JnCdOc1Ma3eO5h8Zo5R4E0Bg/viewform?usp=publish-editor	

Extra Practice Questions		
Name of Chapers	**Question Bank Link**	**QR Code**
1. Solutions	https://docs.google.com/document/d/1wfPFlj7L3KfCYUeFM2UCqyZE1Zd0mvqu/edit?usp=drive_link&ouid=107228232524760083604&rtpof=true&sd=true	
2. Electrochemistry	https://docs.google.com/document/d/1puAIiLkN7kIRW85xX4F9_m2Hv6ik_vrv/edit?usp=sharing&ouid=110109177899496866646&rtpof=true&sd=true	
3. Chemical Kinetic	https://docs.google.com/document/d/1rVBlTs20Xn5zSyOWFnLUuwKSzYmqnHhK/edit?usp=drive_link&ouid=110109177899496866646&rtpof=true&sd=true	
4. The d and f Block Elements	https://docs.google.com/document/d/1lZXGAWHWhtlPfrJwC1y4YiJvb03Ll_Nh/edit?usp=drive_link&ouid=116175101467491393246&rtpof=true&sd=true	
5. Coordination Compound	https://docs.google.com/document/d/1HBBLAP97MamqPHRlBISyGwp9WEiobHOg/edit?usp=sharing&ouid=110109177899496866646&rtpof=true&sd=true	

6. Haloalkane and Haloarene	https://docs.google.com/document/d/1Hgr5AeTyvN3moDkFudXEFUP5pvyC9VSL/edit?usp=drive_link&ouid=116175101467491393246&rtpof=true&sd=true	
7. Alcohols, Phenols, and Ethers	https://docs.google.com/document/d/1kooGAicx8_nsb2XNXLw_l7NNEYbmu21Y/edit?usp=drive_link&ouid=116175101467491393246&rtpof=true&sd=true	
8. Aldehydes, Ketones and Carboxylic Acids	https://docs.google.com/document/d/1lgB1whZmlibF8WbQNZlYmq9g_bkltqPT/edit?usp=drive_link&ouid=114906486254430890313&rtpof=true&sd=true	
9. Amines	https://docs.google.com/document/d/1EqL2nfaUNfTJKjvKJaJwpvmuYb7P4fbL/edit?usp=sharing&ouid=110109177899496866646&rtpof=true&sd=true	
10. Biomolecules	https://docs.google.com/document/d/1ylpTemeGvNhLNv33YztQnB5FHYtbawVb/edit?usp=sharing&ouid=114906486254430890313&rtpof=true&sd=true	

Max. Marks:70 **Time: 3 hours**

GENERAL INSTRUCTIONS:

Read the following instructions carefully.

(a) There are 33 questions in this question paper with internal choice.
(b) SECTION A consists of 16 multiple-choice questions carrying I 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 of3 long answer questions carrying 5 marks cach.
(g) All questions are compulsory.
(h) Use of log tables & calculator is not allowed.

SECTION A

*Questions no. **1** to **16** are Multiple Choice type Questions, carrying **1** mark each.* *16X1=16*

1. Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as :

(A) Mustard gas (B) Tear gas
(C) Chlorine gas (D) Phosgene gas

2. Lucas reagent produces cloudiness immediately with :

(A) 2-methyl-1-propanol (B) Butan-2-ol
(C) 2-methyl-2-propanol (D) Butan-1-ol

3. Which of the following d-orbitals experience more repulsion in the crystal field splitting of octahedral complex ?

(A) d_{xy} , d_{yz} , d_{xz} (B) $d_{x^2-y^2}$, d_{z^2}
(C) d_{xy} , $d_{x^2-y^2}$ (D) d_{xz} , d_{z^2}

4. The chelating ligand used for the treatment of lead poisoning is :

(A) Ethane-1,2-diamine (B) Oxalate ion
(C) Dimethylglyoxime (D) EDTA

5. Manganate ion is paramagnetic due to the presence of :

(A) one unpaired electron (B) two unpaired electrons
(C) three unpaired electrons (D) fully paired electrons

6. The correct order of decreasing basicities of $C_2H_5NH_2$, $(C_2H_5)_2NH$ and $(C_2H_5)_3N$ in aqueous solution is :

(A) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$ (B) $(C_2H_5)_2NH > C_2H_5NH_2 > (C_2H_5)_3N$
(C) $C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$ (D) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$

7. The boiling point of one molal NaCl solution, assuming NaCl to be completely dissociated in water is : (K_b for water = 0·52 K kg mol^{-1})

(A) 100·52ºC (B) 101·04ºC
(C) 100·04ºC (D) 101·52ºC

8. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased :

(A) vapour pressure of the solution increases (B) heating occurs
(C) cooling occurs (D)equilibrium remains unaffected

9. Consider the following cell at 298 K :

Mg (s) | Mg^{2+} (1·0 M) || Cu^{2+} (1·0 M) | Cu (s)

How can we increase the emf of the cell using the same substances ?

(A) By decreasing only the [Mg^{2+}] to 0·1 M

(B) By decreasing only the $[Cu^{2+}]$ to 0·1 M

(C) By increasing both $[Mg^{2+}]$ and $[Cu^{2+}]$ to 2·0 M

(D) By increasing only the $[Mg^{2+}]$ to 2·0 M

10. The rate of a first order reaction is $5{\cdot}6 \times 10^{-4}$ mol L^{-1} s^{-1}, when the concentration of reactant is 0·2 mol L^{-1}. The rate constant 'k' is :

(A) $5{\cdot}6 \times 10^{-3}\ s^{-1}$ (B) $2{\cdot}8 \times 10^{-4}\ s^{-1}$

(C) $2{\cdot}8 \times 10^{-5}\ s^{-1}$ (D) $2{\cdot}8 \times 10^{-3}\ s^{-1}$

11. Nucleic acids are polymers of :

(A) amino acids (B) nucleosides

(C) nucleotides (D) pentose sugar

12. In the reaction of NaOBr with amide, the carbonyl carbon is lost as :

(A) HCO_3^- B) CO_3^{2-}

(C) CO_2 (D) CO

For Questions number 13 to 16, two statements are given — one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below.

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is ***not*** the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

13. ***Assertion (A) :*** Alcohols act as Bronsted bases as well as Bronsted acids.
Reason (R) : It is due to the presence of unshared electron pairs on oxygen atom and presence of polar O – H bond.

14. ***Assertion (A) :*** Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
Reason (R) : Diazonium salts of aliphatic amines undergo resonance.

15. ***Assertion (A) :*** For complex reaction, order of reaction is given by the slowest step.
Reason (R) : Order of a reaction is an experimental quantity.

16. ***Assertion (A) :*** $E^0_{Sc^{3+}/Sc^{2+}}$ has low value.
Reason (R) : Because of the stability of Sc^{3+} ion which has a noble gas configuration.

SECTION B

17. (a) Reactions of which order will show the rate to be independent of the concentration of the reactant ? Give one example of this order.

(b) State the condition under which a bimolecular reaction may be kinetically a first order reaction. *1+1=2*

18. (a) Explain the following with the help of Henry's law : *1+1=2*

(i) Bends (ii) Anoxia

OR

(b) How does sprinkling of salt help in clearing the snow covered roads in hilly areas ? Write the name of the colligative property involved in this process. *2*

19. Write IUPAC names of the following compounds : *1+1=2*

(a) $[Cr(NH_3)_4\ (ONO)Cl]\ NO_3$

(b) $Na[Ag(CN)_2]$

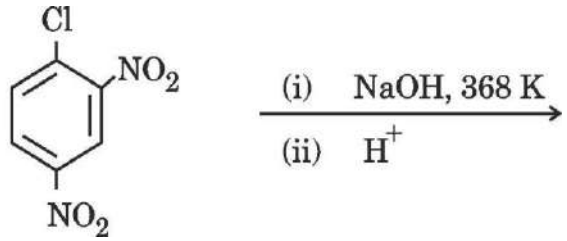
20. What are the hydrolysis products of the following ? *1+1=2*

(a) Lactose

(b) DNA containing Thymine

21. Draw the structures of major product(s) in each of the following reactions :

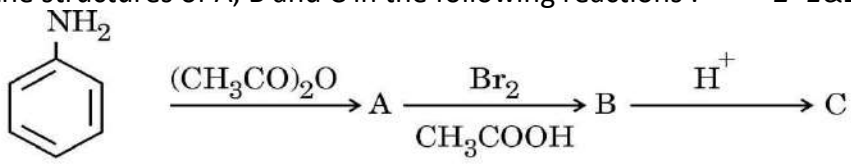
2×1=2

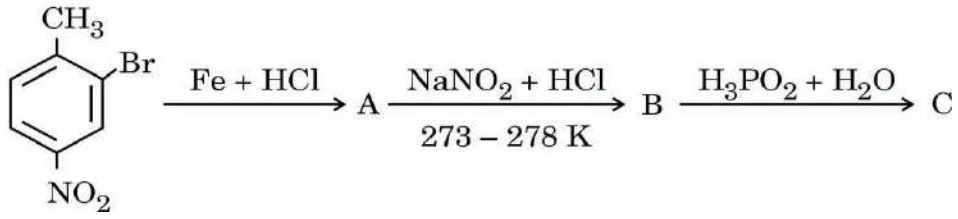
(a) 

(b) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

SECTION C

22. Write the structures of A, B and C in the following reactions : *2×1*&1/2*= 3*

(a) 

(b) 

23. What happens when :

(a) Propanenitrile is treated with phenyl magnesium bromide followed by hydrolysis ?

(b) p-fluorotoluene is treated with CrO_3 in the presence of acetic anhydride followed by hydrolysis with aqueous acid.

(c) Phthalic acid is treated with NH_3 followed by heating ?

Write chemical reactions in support of your answer. *3×1=3*

24. Answer the following questions : *3×1=3*

(a) Why is direct current (DC) not used to measure the resistance of an ionic solution ?

(b) Why are the products of electrolysis different for the electrolysis of aqueous solution of $AgNO_3$ with silver electrodes and electrolysis of aqueous solution of $AgNO_3$ with platinum electrodes ?

(c) Why are magnesium blocks fixed to the iron pipelines carrying water ?

25. (a) When a coordination 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 the structural formula of the complex, IUPAC name, its hybridisation and magnetic behaviour on the basis of valence bond theory. *3*

OR

(b) (i) How many geometrical isomers are possible in each of the following complexes ?

(I) $[Cr(C_2O_4)_3]^{3-}$ (II) $Co(NH_3)_3Cl_3]$

(ii) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. Why ? [Atomic number : Co = 27, Ni = 28]

(iii) Write the formula of Wilkinson catalyst and its use. *3×1=3*

26. Calculate the vapour pressure of a solution containing 61 g of benzoic acid (molar mass = 122 g mol^{-1}) dissolved in 500 g of benzene when the vapour pressure of pure benzene at this temperature of experiment is 66 torr. Assume complete dimerization of benzoic acid in benzene. *3*

27. Consider the decomposition of hydrogen peroxide (H_2O_2) as per the equation given below :

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2 \text{ (In Alkaline medium)}$$

The mechanism for this reaction was found to be :

Step I : $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

Step II : $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(a) Write the rate law expression.

(b) Determine the order of reaction with respect to H_2O_2, I^- and overall order of reaction.

(c) What is the molecularity of the reaction in Step II ? *3*

28. Answer the following : *3×1=3*

(a) Which isomer of C_4H_9Br is most reactive towards S_N1 reaction ?

(b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.

(c) Although chlorine shows strong – I effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why ?

SECTION D

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

29. Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron releasing groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents, while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation. The presence of – OH group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to ortho and para positions due to resonance effect.

Answer the following questions :

(a) Write the mechanism of acid dehydration of ethanol to yield ethene. *2*

(b) (i) Why are tertiary alcohols resistant to oxidation ? *1*

OR

(b) (ii) Write the structure of the major product expected from the dinitration of 3-methylphenol. *1*

(c) Why is ortho-nitrophenol more acidic than ortho-methoxyphenol ? *1*

30. Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. They have been broadly classified into three groups — monosaccharides, oligosaccharides and polysaccharides. The carbohydrates may also be classified as either reducing or non-reducing sugars. An important monosaccharide glucose is an aldohexose and is correctly named as D(+)–glucose. It was assigned the open structure on

the basis of its reactions with HI, NH_2OH, Br_2 water, $(CH_3CO)_2O$ and nitric acid. Despite having the – CHO group, glucose does not give Schiff's test and hydrogen sulphite addition product with $NaHSO_3$. It was found that glucose forms a six-membered ring in which one of the – OH groups add to the – CHO group and form a cyclic hemiacetal structure.

Answer the following questions :

(a) How do you explain the following ? *2×1=2*

(i) Presence of a carbonyl group in glucose

(ii) Presence of five – OH groups in glucose which are attached to different carbon atoms.

(b) What type of carbohydrates are called reducing sugars ? *1*

(c) (i) In D(+)–glucose, what do the letter 'D' and sign '(+)' represent ? *1*

OR

(c) (ii) Draw the six-membered ring structure of □–D(+)–glucose. *1*

SECTION E

31. (A) (a) Account for the following :

I. MnO is basic while Mn_2O_7 is acidic.

II. Iron has higher enthalpy of atomization than that of copper.

III. Mn^{3+} is a stronger oxidising agent than Cr^{3+}.

(b) How do you prepare potassium dichromate from sodium chromate ? Write balanced chemical equation for each step. *3+2=5*

OR

(B) (a) Answer the following questions : *5×1=5*

(i) Why is chemistry of actinoids more complicated as compared to lanthanoids ?

(ii) $E^{O}_{M/M2+}$values are not regular for first row transition elements (3d series). Why ?

(b) Identify the following :

(I) Oxoanion of chromium which is stable in acidic medium.

(II) The lanthanoid element that exhibits +4 oxidation ,state.

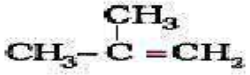
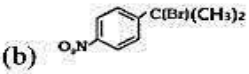
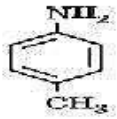
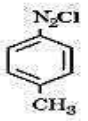
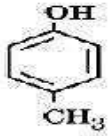
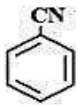
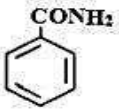
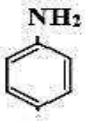
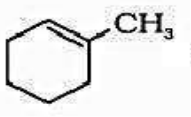
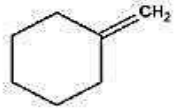
(iii) Write the products obtained on heating $KMnO_4$.

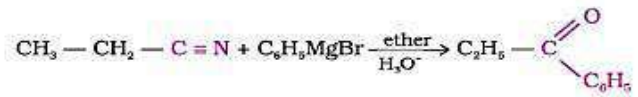
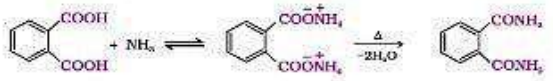
(V) Predict which of the following ions will be coloured in aqueous solution :

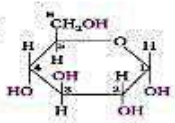
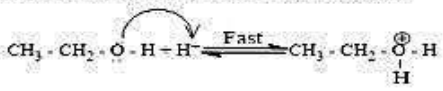
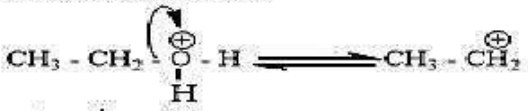
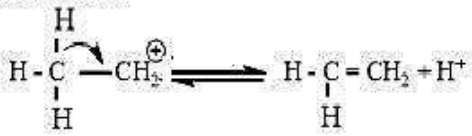
Cu^+, Sc^{3+}, Fe^{2+}, Ti^{3+}, Zn^{2+}

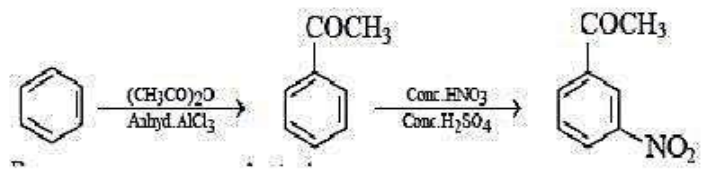
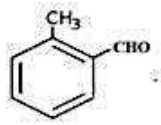
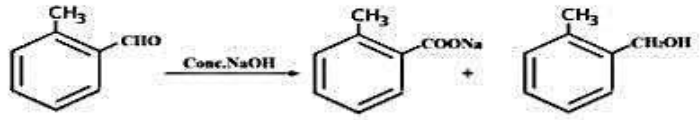
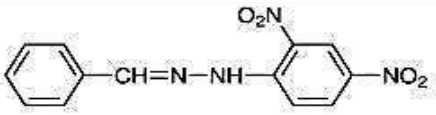
MARKING SCHEME
CHEMISTRY (Subject Code-043)
(PAPER CODE : 56/4/3) (26-04-43N)

Q.No.	EXPECTED OUTCOMES/VALUE POINTS	Marks
	SECTION - A	
1.	(D)	1
2.	(B)	1
3.	(C)	1
4.	(B)	1
5.	(B)	1
6.	(B)	1
7.	(A)	1
8.	(A)	1
9.	(C)	1
10.	(A)	1
11.	(D)	1
12.	(C)	1
13.	(A)	1
14.	(D)	1
15.	(C)	1
16.	(A)	1
	SECTION - B	
17	(a) Diamminesilver(I) dicyanidoargentate(I) (b) Tris(ethane-1,2–diamine)cobalt(III) sulphate	1 1
18	During denaturation secondary and tertiary structures are destroyed. α-helix and β-pleated sheet structure	1 ½+ ½
19	(a)Zero order, Example-Decomposition of gaseous ammonia on a hot platinum surface/ Decomposition of HI on gold surface (Or any other one suitable example) (b) When one of the reactants is in excess.	½ ½ 1
20	(a)(i) Bends is a painful medical condition experienced by Scuba divers when they come towards surface where the pressure gradually decreases leading to formation of bubbles of nitrogen in the blood blocking the capillaries. (ii) Anoxia is a condition experienced by people living at high altitudes due to low partial pressure of oxygen or due to low blood oxygen in their tissues making them feel weak and unable to think clearly.	1 1
	OR	

20	(b)Salt lowers the freezing point of snow which then melts and can be removed easily. Depression of Freezing point	1 1
21	(a)  (b) 	1 1
	SECTION - C	
22	(a) A B C    (b) A B C   	½×3 ½×3
23	(a)Tert-butyl bromide /$(CH_3)_3CBr$ /2-Bromo-2-methylpropane (b)  Or  (c) Because +R effect stabilises the intermediate carbocation.	1 1 1
24	(a)Rate $=k[H_2O_2][I^-]$ (b) Order w.r.t. $[H_2O_2]$ *is* 1 Order w.r.t $[I^-]$ is 1 Overall order of reaction is 2 (c) 2	1 ½ ½ ½ ½
25	$\frac{p_1^\circ - p_1}{p_1^\circ} = ix_2 = i\frac{w_2 \times M_1}{M_2 \times w_1}$ $\frac{66-p_1}{66} = 0.5 \times \frac{61\times78}{122\times500}$ $p_1 = 63.4torr$ Alternate method	1 1 1

	$\frac{p_1^\circ - p_1}{p_1^\circ} = ix_2 = i\frac{n_2}{n_1+n_2}$ $\frac{66-p_1}{66} = 0.5 \times \frac{\frac{61}{122}}{\frac{500}{78}+\frac{61}{122}}$ $p_1 = 63.61 torr$	1 1 1
26	(a) • $[Co(NH_3)_6]Cl_3$ • Hexaamminecobalt(III) chloride • d^2sp^3 • diamagnetic	1 1 ½ ½
	OR	
26	(b)(i) (I)NIL/Zero (II) 2 (ii) NH_3 being a strong field ligand pair up the unpaired electrons in Co^{3+} leaving two d-orbitals empty for d^2sp^3 hybridization forming inner orbital complex. Whereas it cannot pair up in Ni^{2+} as only one 'd' orbital is left empty after pairing which is not possible and hence outer d-orbital is used. (iii)$[(Ph_3P)_3\ RhCl]$ Used for hydrogenation of alkene	½ × 2 ½ ½ ½ ½
27.	(a) DC can change the composition of the solution. (b) Because silver electrode is reactive and participates in the electrode reactions whereas platinum is inert and does not take part in the chemical reaction and acts only as a source of electrons. (c) To prevent oxidation of Iron or rusting, as Mg gets readily oxidised in comparison to iron.	1 1 1
28	(a)  (b)  (c) 	1 1 1
	SECTION - D	

29	(a)(i)Glucose on reaction with H_2N-OH forms oxime / with HCN forms cyanohydrin (Or correct chemical equation)	1
	(ii) Glucose gives stable pentaacetate with $(CH_3CO)_2O$ (Or correct chemical equation)	1
	(b) Those which reduce Tollens' reagent/Fehling solution.	1
	(c)(i) D- stands for configuration	½
	(+) stands for dextrorotatory nature of the molecule.	½
	OR	
	(c) (ii) 	1
30	(a) Step 1: Formation of protonated alcohol 	1
	Step 2: Formation of carbocation 	½
	Step 3: Deprotonation 	½
	(b)(i) Due to the absence of α – hydrogen atom	1
	OR	
	(b) (ii) 	1
	(c) Because of electron with-drawing nature of $-NO_2$ group which increases the stability of phenoxide ion whereas methoxy is electron-donating group and decreases the stability of phenoxide ion.	1
	SECTION E	
31	(a) (i) (I) 	1

	(II) 	1
	(ii) 	1
		1
	(iii) $C_6H_5COOH < HCOOH < O_2N\text{-}CH_2\text{-}COOH < CF_3\text{-}COOH$	1
	OR	
31	(b) (i) (I) 	1
	(II) 	1
	(ii) (I) Because of the formation of salt where carboxyl group is deactivating and gets bonded with lewis acid (Anhydrous $AlCl_3$)	1
	(II) Because of more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. /Dimer formation takes place.	1
	(iii) On warming with freshly prepared ammoniacal $AgNO_3$ solution (Tollens' reagent) propanal forms bright silver mirror whereas propanone does not. (or any other suitable test)	1
32	(a)(i)	
	$E^\circ_{(cell)} = \frac{0.059}{2}\log K_c$	½
	$E^\circ_{(cell)} = \frac{0.059}{2}\log(10^{15})$	½
	$E^\circ_{(cell)} = \frac{0.059}{2}(15\log 10) \Rightarrow E^\circ_{(cell)} = \frac{0.059V}{2} \times 15$	
	$E^\circ_{(cell)} = 0.0295 \times 15 = 0.4425V$	1
	(ii) Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$	½
	Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	½
	Overall reaction $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$	1
	(iii) 96500 C	1

	OR	
32	(b)(i) $\Lambda_m = \frac{\kappa}{c}$ $\Lambda_m = \frac{7.2 \times 10^{-5} \times 1000}{0.0024}$ $\Lambda_m = 30\ Scm^2mol^{-1}$ $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$ $\alpha = \frac{30}{390.5}$ $\alpha = 0.0768$ or 0.077 (ii) $E_{(Ag^+/(Ag)} = E^\theta_{(Ag^+/(Ag)} - \frac{0.059}{1} \log \frac{[Ag]}{[Ag^+]}$ $E_{(Ag^+/(Ag)} = 0.80 - 0.059 \log \frac{1}{(0.01)}$ $E_{(Ag^+/(Ag)} = 0.80 - 0.059 \log 10^2$ $E_{(Ag^+/(Ag)} = 0.80 - 0.059 \times 2 \implies E_{(Ag^+/(Ag)} = 0.80 - 0.118$ $E_{(Ag^+/(Ag)} = 0.682V$ (iii) (I) NH_4Cl and $ZnCl_2$ (II) Aq NaOH solution / KOH solution	½ ½ ½ ½ ½ 1 ½ ½
33	(a) (i) (I) Because Mn is in lower Oxidation state (+2) in MnO while in Mn_2O_7, Mn is in higher Oxidation state (+7). (II) Because of more number of unpaired electrons in iron than copper. (III) Greater stability of Mn in +2 Oxidation state is due to $3d^5$ configuration whereas Cr is already stable in +3 oxidation state due to stable t_{2g}^3 configuration. (ii) $2Na_2CrO_4 + 2H^+ \longrightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$ $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	1 1 1 1 1
	OR	
33	(b) (i) Because of their radioactive nature and ability to show wide range of Oxidation states. (ii) Because the sum of ionisation enthalpies ($\Delta_iH_1 + \Delta_iH_2$) and sublimation enthalpies are irregular across 3d series. (iii) (I) $Cr_2O_7^{2-}$ (II) Cerium / Ce (Or any other correct example) (iv) $K_2MnO_4 + MnO_2 + O_2$ (v) Fe^{2+} , Ti^{3+}	1 1 ½ ½ 1 ½ +½
	- o 0 o -	

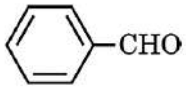
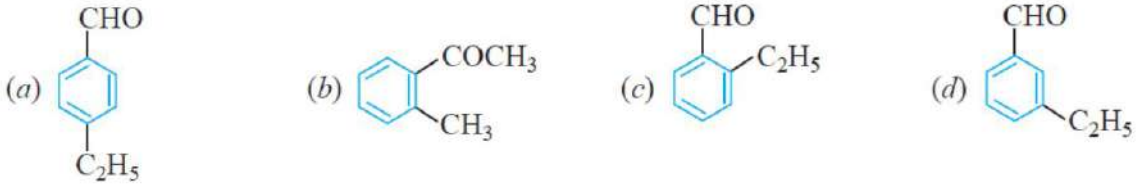
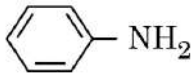
SAMPLE PAPER (2026-27)
SET-043/1
CLASS –XII
CHEMISTRY (043)

Max. Marks:70 **Time: 3 hours**

SECTION-A

The following questions arc multiple-choice questions with one correct answer. Each question carries l mark. There is no internal choice in this section.

Q.No	Questions	Marks
1	A galvanic cell can behave as an electrolytic cell when : (a) $E_{cell} = E_{ext}$ (b) $E_{cell} > E_{ext}$ (c) $E_{cell} = 0$ (d) $E_{ext} > E_{cell}$	1
2	For a chemical reaction, A ⊕B, it was observed that the rate of reaction doubles when the concentration of A is increased four times. The order of the reaction is : (a) 2 (b) 1 (c) ½ (d) zero	1
3	The rate of a reaction was found to be independent of concentration of the reactants ,the unit of rate constant of the reaction would be: (a) s^{-1} (b) $mol^{-1}\ L\ s^{-1}$ (c) $mol^{-2}\ L^2\ s^{-1}$ (d) $mol\ L^{-1}\ s^{-1}$	1
4	Which of the following ions has the highest magnetic moment ? [Atomic number : Fe = 26, V = 23, Ti = 22, Sc = 21] (a) Fe^{3+} (b) V^{3+} (c) Ti^{3+} (d) Sc^{3+}	1
5	The correct IUPAC name of $(CH_3)_3\ C - CH_2Br$ is : (a) 2,2-Dimethyl-2-bromopropane (b) 1-Bromo-2,2,2-trimethylethane (c) 2-Bromo-1,1,1-trimethylethane (d) 1-Bromo-2,2-dimethylpropane	1
6	Which of the following reactions are feasible ? (a) $CH_3CH_2Br + Na^+\ O^-C(CH_3)_3 \rightarrow CH_3CH_2{-}O - C\ (CH_3)_3$ (b) $(CH_3)_3\ C - Cl + Na^+\ O^-\ CH_2CH_3 \rightarrow CH_3CH_2 - O - C(CH_3)_3$ (c) Both (a) and (b) (d) Neither (a) nor (b)	1
7	Which of the following characteristics of transition metals is associated with their catalytic activity ? (i) Paramagnetic nature (ii) Colour of hydrated ions (iii) High enthalpy of atomisation (iv) Variable oxidation states (a) (i) & (iii) (b) (iii) & (iv) (c) (ii) & (iii) (d) (i) only	1

8	The correct order of reactivity of given compounds with Lucas reagent at room temperature is (a) butan-1-ol < butan-2-ol < 2-methylpropan-2-ol < 2-methylpropan-1-ol (b) butan-1-ol < butan-2-ol < 2-methylpropan-1-ol < 2-methylpropan-2-ol (c) butan-1-ol < 2-methylpropan-1-ol < butan-2-ol < 2-methylpropan-2-ol (d) 2-methylpropan-1-ol < 2-methylpropan-2-ol < butan-1-ol < butan-2-ol	1
9	Which of the following does not give Cannizaro reaction ? (a) $(CH_3)_3C-CHO$ (b) $(CH_3)_2CH-CHO$ (c)  (d) HCHO	1
10	An aromatic compound 'X' with molecular formula $C_9H_{10}O$ gives the following chemical tests. (i) Forms 2, 4-DNP derivative (ii) Reduces Tollens' reagent (iii) Undergoes Cannizzaro reaction (iv) On vigorous oxidation, 1-2-benzenedicarboxylic acid is obtained. X is: 	1
11	Which of the following is least basic ? (a) $(CH_3)_2NH$ (b) NH_3 (c)  (d) $(CH_3)_3N$	1
12	An -helix is a structural feature of : (a) Nucleoside (b) Polypeptides (c) Starch (d) Nucleotides	1

For Questions number 13 to 16, two statements are given one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below.

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

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

(c) Assertion (A) is true, but Reason (R) is false.

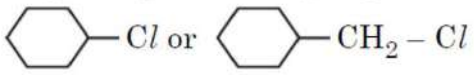
(d) Assertion (A) is false, but Reason (R) is true.

13	**Assertion (A) :** In a cell Current stops flowing when $E_{Cell} = 0$. **Reason (R) :** Equilibrium of the cell reaction is attained.	1
14	**Assertion (A)** : Phenol on oxidation with chromic acid gives benzoquinone. **Reason (R)** : Pure phenol is colourless but turn pink due to oxidation to phenoquinone.	1
15	**Assertion (A)** : The final product in Aldol condensation is always α,β-unsaturated Carbonyl compound.	1

	Reason (R) : α,β- unsaturated carbonyl compounds are stabilised due to conjugation.	
16	**Assertion (A)** : Maltose is a non-reducing sugar. **Reason (R)** : Maltose is composed of two glucose units in which C-1 of one glucose unit is linked to C-4 of another glucose unit.	1

SECTION-B

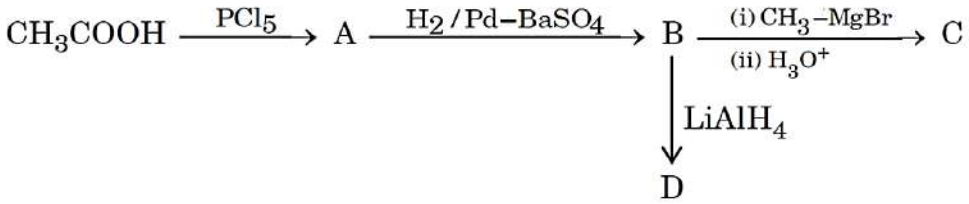
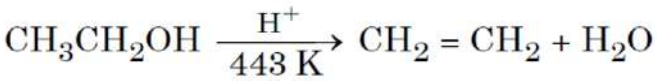
This section contains 5 questions with internal choice in one question. The following questions are very short answer type and carry 2 marks each.

17	(i) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y? (ii) Why are the aquatic species more comfortable in cold water in comparison to warm water?	2
18	The thermal decomposition of an acid is a first order reaction with a rate constant of 2.3×10^{-3} s^{-1} at a certain temperature. Calculate how long it will take for three-fourths of the initial quantity of acid to decompose. (log 4 = 0.6021, log 2 = 0.301)	2
19	Which one of the following in each pair is more reactive towards S_N2 reaction and why ? (i) $CH_3 - CH_2 - I$ or $CH_3CH_2 - Cl$ (ii)  or **Or** Arrange the following in the increasing order of their reactivity towards S_N1 reactions : (i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane (ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane	2
20	Give chemical tests to distinguish between the following pair of compounds : (i) Pentan-2-one and Pentan-3-one (ii) Benzaldehyde and Benzoic acid	2
21	(a) Which of the following biomolecules is insoluble in water? Justify. Insulin, Haemoglobin, Keratin. (b) Write the chemical reaction which give evidence of linear chain of six carbons in glucose.	2

SECTION-C

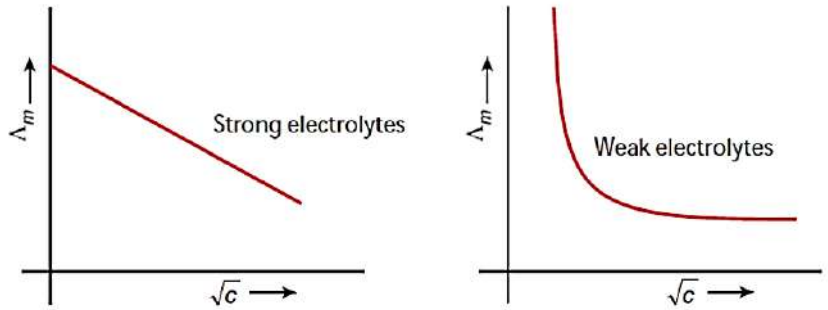
This section contains 7 questions with internal choice in one question. The following questions are short answer type and carry 3 Marks each.

22	Calculate the emf of the following cell at 298 K : Al (s) | Al^{3+} (0.001 M) || Ni^{2+}(0.1 M) | Ni (s) Given: [$E^o_{Al^{3+}/Al}$ = – 1.66 V, $E^o_{Ni^{2+}/Ni}$ = - 0.25 V]	3
23	A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy (E_a) for the reaction. [R = 8.314 J $K^{-1}mol^{-1}$] [Given : log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021]	3
24	(a) What are the hydrolysis products of (i) Lactose, (ii) Maltose ? (b) What is denatured protein?	2+1 =3
25	(a) An organic compound 'A', having the molecular formula C_3H_8O on treatment with Cu at 573 K, gives '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.	1+1+1 =3

	Or (b) (i) Identify A to D.  (ii) How will you convert Ethanal into But-2-en-1-al (Give chemical reaction)	2+1 =3
26	(a) Write the electronic configuration of Fe^{3+} on the basis of crystal field theory when it forms an octahedral complex in the presence of - (i) strong field ligand, and (ii) weak field ligand. [Atomic number : Fe = 26] (b) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic. Why ?	3x1=3
27	(a)Why Nucleophilic substitution is difficult in chlorobenzene? Explain. (b) How the following conversions can be carried out? (Write chemical reaction only) (i) 1-Bromopropane to 1-Fluoropropane (ii) Ethanol to propanenitrile	3x1=3
28	(a) Write the mechanism of the following reaction ::  (b) Write the equation involved in (i)Reimer-Tiemann reaction. (ii) Williamson's synthesis	1+1+1 =3

SECTION-D

The following questions are case-based questions. With internal choice in one question of both case based study question and carries 4 (2+1+1) marks each.

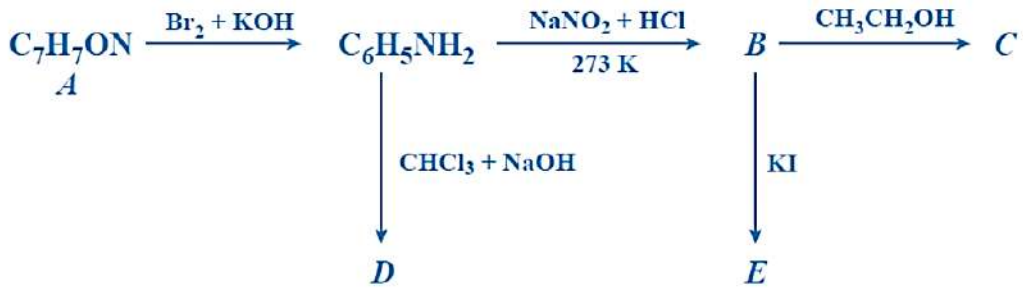
29	The conductivity or specific conductivity of an electrolytic solution varies with the concentration of the solutions of different electrolytes. For comparing the conductances of the solutions of different electrolytes, it is essential that the solutions should have equal volumes and they must contain 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 molar conductance of a solution does not vary linearly with concentration and it is related with specific conductance. The effect of molar 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.  *Answer the following questions-*	

a	What is meant by limiting molar conductivity?	1
b	Why on dilution the molar conductance of CH_3COOH increases drastically while that of CH_3COONa increases gradually?	1
c	The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. Or Calculate the degree of dissociation (α) of acetic acid if its molar conductivity (λ_m) is 39.05 S cm^2 mol^{-1}. Given $\lambda^o_{H^+}$ = 349.6 S cm^2mol^{-1} and $\lambda^o_{CH3COO^-}$ = 40.9 S cm^2mol^{-1}.	2
30	In coordination compounds, metals show two types of linkages, primary and secondary. Primary valencies are ionisable and are satisfied by negatively charged ions. Secondary valencies are non-ionisable and are satisfied by neutral or negative ions having lone pair of electrons. Primary valencies are non-directional while secondary valencies decide the shape of the complexes and is equal to the coordination number of the metal atom/ion. *Answer the following questions-*	
a	If $PtCl_2.2NH3$ does not react with $AgNO_3$, what will be its formula ?	1
b	What is the secondary valency of $[Co(en)_3]^{3+}$?	1
c	(i) Write the formula of Iron(III)hexacyanidoferrate(II). (ii) Write the IUPAC name of $[Cr(NH_3)_5Cl]$ Cl_2. Or	1+1=2
c	1 moles of AgCl is precipitated when 1 mole of $CoCl_3.4NH_3$ is treated with excess of $AgNO_3$ solution. Write the correct formula of complex and write its IUPAC name.	

SECTION-E

The following questions are long answer types and carry 5 marks each. All questions have an internal choice.

31	(a) (i) Blood cells are isotonic with 0.9 % sodium chloride solution. What happens if we place blood cells in a solution containing 0.4% sodium chloride solution?	1+1 +3
	(ii) Out of two 0.1 molal aqueous solutions of glucose and of potassium chloride, which one will have a higher boiling point and why?	
	(ii) When 2.56 g of sulphur was dissolved in 100 g of CS_2, the freezing point lowered by 0.383 K. Calculate the formula of sulphur (S_x). [K_f for CS_2 = 3.83 K kg mol^{-1}, Atomic mass of Sulphur = 32 g mol^{-1}]	Or
	Or	
	(b) (i)What type of deviation is shown by a mixture of ethanol and acetone? What type of azeotrope is formed by mixing ethanol and acetone?	1+1 +3
	(ii) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which one of the two gases will have the higher value of K_H (Henry's constant) and why?	
	(c) Calculate the boiling point of solution when 2 g of Na_2SO_4 (M = 142 g mol^{-1}) was dissolved in 50 g of water, assuming Na_2SO_4 undergoes complete ionisation. (Kb for water = 0.52 K kg mol^{-1})	

32	(A) An aromatic compound 'A' of molecular formula C_7H_7ON undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions:  Or (B)(a) Give reason (i) Aniline does not undergo Friedel-Crafts reaction. Explain why? (ii) Primary amines have higher boiling points than tertiary amines. Explain why? (b) Write the structures of A, B and C in the following: (*i*) $C_6H_5—CONH_2 \xrightarrow{Br_2/aq.\ KOH} A \xrightarrow[0-5°C]{NaNO_2 + HCl} B \xrightarrow{KI} C$ (*ii*) $CH_3—Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[\Delta]{CHCl_3 + alc.KOH} C$	5x1 =5 Or 2+1 $\frac{1}{2}$ +1$\frac{1}{2}$ =5
33	(a) Account for the following : (i) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4. (ii) Cr^{2+} is a strong reducing agent. (iii) Cu^{2+} salts are coloured while Zn^{2+} salts are white. (b) Complete and balance the following chemical equations : (1) $2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta}$ (2) $Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow$ **Or** (a) Account for the following : (i) E^o value for Mn^{3+}/ Mn^{2+} couple is much more positive than that for Cr^{3+}/ Cr^{2+}. (ii) Sc^{3+} is colourless whereas Ti^{3+} is coloured in an aqueous solution. (iii) Actinides show wide range of oxidation states. (b) Write the chemical equations for the preparation of $KMnO_4$ from MnO_2.	5*1 =5 Or 3+2 =5

Scan the QR code for marking scheme /solution of above Question Paper.

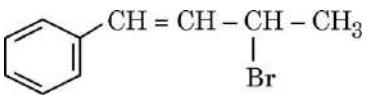
SET-043/2

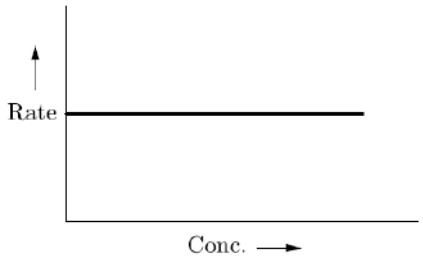
CLASS – XII

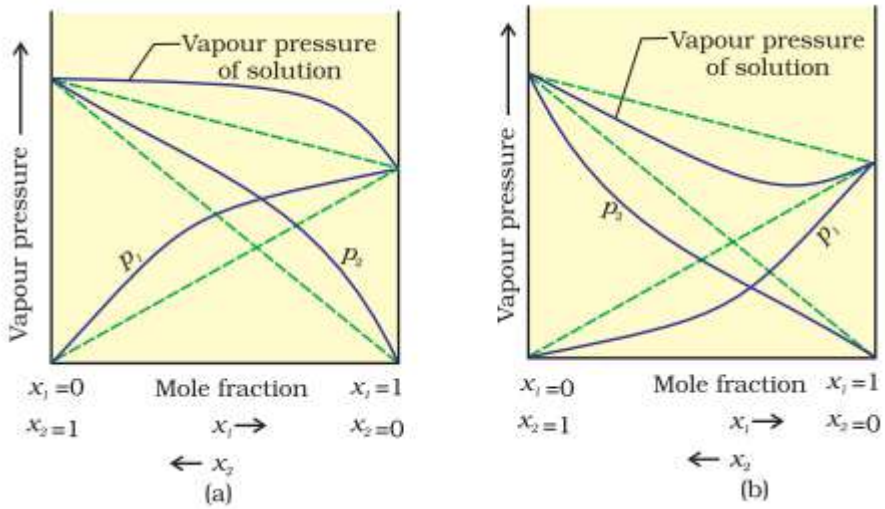
CHEMISTRY (043)

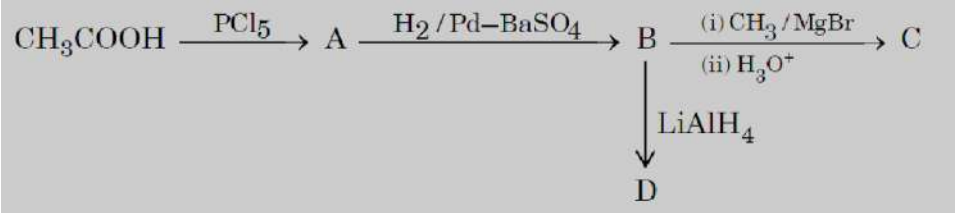
Max. Marks: 70 **Time: 3 Hours**

	SECTION-A Question 1to 16 are multiple choice questions. Only one of the choices is correct. Select and write the correct choice as well as the answer to these questions.	
1	The reaction $R\text{-}OH + Na \longrightarrow RO^-Na^+ + \frac{1}{2}H_2(g)$ suggests that alcohols are: (A) Acidic (B) Basic (C) Neutral (D) Amphoteric	**1**
2	Consider the following cell at 298 K : $Mg(s) \mid Mg^{2+}(1{\cdot}0\ M) \parallel Cu^{2+}(1{\cdot}0\ M) \mid Cu(s)$ How can we increase the emf of the cell using the same substances ? (A) By decreasing only the $[Mg^{2+}]$ to 0·1 M (B) By decreasing only the $[Cu^{2+}]$ to 0·1 M (C) By increasing both $[Mg^{2+}]$ and $[Cu^{2+}]$ to 2·0 M (D) By increasing only the $[Mg^{2+}]$ to 2·0 M	**1**
3	For the reaction A + 2B ----------㉀C + D , the rate law is given by $r = k[A][B]^2$, the concentration of A kept constant while that of B is doubled.The rate of the reaction will: (A)Double (B) become half (C) not change (D) quadruple	**1**
4	Manganate ion is paramagnetic due to the presence of : (A) one unpaired electron (B) two unpaired electrons (C) three unpaired electrons (D) fully paired electrons	**1**
5	The chelating ligand used for the treatment of lead poisoning is : (A) Ethane-1,2-diamine (B) Oxalate ion (C) Dimethylglyoxime (D) EDTA	**1**
6	Oxidation of chloroform by air in the presence of sunlight produces a poisonous gas known as (A) Mustard gas (B) Tear gas (C) Chlorine gas (D) Phosgene gas	**1**
7	Lucas reagent produces cloudiness immediately with : (A) 2-methyl-1-propanol (B) Butan-2-ol (C) 2-methyl-2-propanol (D) Butan-1-ol	**1**
8	In the reaction of NaOBr with amide, the carbonyl carbon is lost as : (A) HCO_3^- (B) CO_3^{2-} (C) CO_2 (D) CO	**1**
9	What is the correct order of pK_b values of the following amines? (A) Methanamine > Ethanamine > Benzenamine (B) Benzenamine > Ethanamine > Methanamine (C) Ethanamine > Methanamine > Benzenamine (D) Benzenamine > Methanamine > Ethanamine	**1**
10	Nucleic acids are polymers of : (A)amino acids (B) nucleosides (C) nucleotides (D) pentose sugar	**1**
11	The position of − Br in the compound	**1**

	 can be classified as : (A) Vinylic (B) Allylic (C) Benzylic (D) Aryl	
12	During electrolysis of dilute H_2SO_4 using platinum electrodes the gas evolved at the anode is (a) H_2gas (b) O_2 gas (c) SO_2 gas (d) SO_3 gas	**1**
13	**Assertion (A):** Chlorobenzene is less reactive towards nucleophilic substitution reactions than chloroethane. **Reason (R):** In chlorobenzene, the C–Cl bond has partial double bond character due to resonance. 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	**1**
14	**Assertion (A):** $KMnO_4$ acts as a strong oxidising agent in acidic medium. **Reason (R):** In acidic medium, Mn in $KMnO_4$ gets reduced from +7oxidation state to +2 oxidation state 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	**1**
15	**Assertion (A):** $[Fe(CN)_6]^{4-}$ is a low-spin complex, while $[FeF_6]^{3-}$ is a high-spin complex. **Reason (R):** F^- is a strong field ligand and causes pairing of electrons, whereas CN^- is a weak field ligand and does not cause pairing. 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	**1**
16	**Assertion (A):** Alcohols act as Lewis base. **Reason (R):** It is due to presence of shared electron pairs on oxygen which makes them proton donors. 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	**1**
	SECTION B Question No. 17 to 21 are very short answer questions carrying 2 marks each.	
17	(i) Aniline does not undergo Friedel-Crafts reaction. (ii) Diazonium salts of aromatic amines are more stable than those of aliphatic amines. **OR** Carry out following conversions : I. Nitrobenzene to 4- bromobenzenamine II. Chlorophenylmethane to 2-phenyl-ethanamine	2
18	For a chemical reaction variation in rate with cone is shown	**2**

	 (i) What is the order of the reaction? (ii) What are the units of rate constant *k* for the reaction?	
19	$[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?	**2**
20	Arrange the following compounds in increasing order of their property as indicated : (1) O_2N-CH_2-COOH, F-CH_2-COOH, CN-CH_2-COOH (Acidic character) (2) Ethanal, Propanal, Butanone, Propanone (Reactivity in nucleophilic addition reactions)	**2**
21	What are the hydrolysis product of (i) Sucrose (ii) Lactose	**2**
	SECTION C Question No. 22 to 28 are short answer questions, carrying 3 marks each.	
22	Write chemical tests to distinguish between: (Any 3) (i) ethanol and phenol (ii) propanol-1 and propanol-2. (Iii) propanol and propanal (iv) Pentanone - 2 and Pentanone – 3.	**3**
23	Calculate the mass of NaCl (molar mass = 58.5 g mol^{-1}) required to lower the freezing point of water by 2.0 K. (Given: K_f for water = 1.86 K kg mol^{-1}; assume complete dissociation of NaCl ; mass of water = 500 g).	**3**
24	The standard reduction potentials are: • $E^\circ Cu^{2+}/Cu$= +0.34 V • $E^\circ Ag^{+}/Ag$= +0.80 V A galvanic cell is constructed as: $Cu(s)\|Cu^{2+}(aq,1M)\|\|Ag+(aq,1M)\|Ag(s)$ 1. Identify which electrode acts as anode and which as cathode. 2. Write the cell reaction. 3. Calculate the standard emf of the cell.	**3**
25	A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K.Calculate activation energy (Ea) for the reaction. [R = 8.314 J K^{-1} mol^{-1}] [Given: log 2 = 0.3010, log 3 = 0.4771, log 4 = 0.6021]	**3**
26	Draw structures of geometrical isomers of $[Pt(NH_3)_2Cl_2]$. Which one shows optical isomerism?	**3**
27	An alkyl halide (A) of molecular formula $C_6H_{13}Cl$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12}. Both alkenes on hydrogenation give 2,3-dimethylbutane. Write the structures of (A), (B) and (C).	**3**
28	(a) Write the product when D-glucose reacts with conc. HNO_3. (b) A student adds a few drops of HCl to an aqueous solution of glycine and observes that it behaves like a cation. When NaOH is added instead, glycine behaves like an anion. Which property of amino acids does this experiment demonstrate? Explain the reason behind this property. (c) Write one difference between α -helix and β -pleated structure of protein.	**3**
	SECTION D Question No. 29 & 30 are case-based/data -based questions carrying 4 marks each.	

29	**Read the passage given below and answer the following questions:** A patient was admitted to the emergency ward after being rescued from a collapsed building where he had been trapped without food for nearly two days. He was extremely weak and unconscious. The doctors immediately provided him with an intravenous injection of 5% glucose solution instead of giving him solid food or starch solution. Within a short time, the patient regained consciousness and his energy levels improved. Doctors avoided giving starch solution. Medical staff also monitored his urine sample to check if there was an abnormal presence of glucose, which could indicate diabetes. **Questions:** a) Why was glucose preferred over starch as an immediate source of energy? b) Write the open chain structure of glucose. c) Give the reaction of glucose with bromine water. What does it indicate about the nature of glucose? **OR** d) Name the two cyclic structures of glucose and explain why they exist.	**4**
30	**Read the passage given below and answer the following questions:** Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. Dalton's law of partial pressure states that the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as: $P_{total} = P_1 + P_2$  a) What type of deviation from Raoult's law does the above graph represent? (i) First positive then negative (ii) Negative deviation (iii) Positive deviation (iv) First negative then positive b). In comparison to a 0.01 M solution of glucose, the depression in freezing point of a) 0.01 M $MgCl_2$ solution is _____. (i) the same (ii) about twice (iii) about three times (iv) about six times	**4**

	c). A solution of two liquids boils at a temperature more than the boiling point of either of them. What type of deviation will be shown by the solution formed in terms of Raoult's law ? **OR** During a laboratory experiment, a student mixes two miscible liquids. He notices that the vapour pressure of the solution is lower than predicted by Raoult's law. Consequently, the solution boils at a temperature higher than the boiling points of the pure components. What can be concluded about the solution? d)Which of the following aqueous solutions should have the highest boiling point ? (i) 1.0 M NaOH (ii) 1.0 M Na_2SO_4 (iii) 1.0 M NH_4NO_3 (iv) 1.0 M KNO_3	
	SECTION E Question No. 31 to 33 are long answer type questions carrying 5 marks each.	
31	a) From the given cells: Lead storage cell, Mercury cell, Fuel cell and Dry cell - (i) Which cell is used in hearing aids? (ii) Which cell was used in Apollo Space Programme? (iii) Which cell is used in automobiles and inverters? (iv) Which cell does not have long life? b) Write one difference between primary and secondary cells **OR** a) The electrical resistance of a column of 50 mol m^{-3} NaOH solution of diameter 1 cm and length 50 cm is $5.55X10^3$ ohm. Calculate its (i) resistivity (ii) conductivity (in S m^{-1}) (iii) molar conductivity (in S cm^2 mol^{-1}) b) State Kohlrausch's law of independent migration of ions. How is it useful in calculating molar conductivity of weak electrolytes?	**4+ 1**
32	**(**a) (i) Carry out the following conversions : (1) Ethanal to But-2-en-1-al (2) Propanoic acid to 2-chloropropanoic acid (ii) An alkene with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' positive Fehling test and also reacts with iodine and NaOH solution. Compound 'C' does not give Fehling solution test but forms Iodoform. Identify the compounds 'A', 'B' and 'C'. **OR** (b) (i) Distinguish with a suitable chemical test : (1) $CH_3COCH_2CH_3$ and $CH_3CH_2CH_2CHO$ (2) Ethanal and Ethanoic acid (ii) Write the structure of oxime of acetone. (iii) Identify A to D. 	**5**
33	Assign reason for each of the following : (Any 5) (i) Manganese exhibits the highest oxidation state of +7 among the 3d series of transition elements. (ii) Transition metals and their compounds are generally found to be good catalysts in chemical reactions.	**[5]**

	(iii) Cr^{2+} is reducing in nature while with the same d-orbital configuration (d^4) Mn^{3+} is an oxidising agent. (iv) Zn has lowest enthalpy of atomization. (v) Cu^+ is unstable in an aqueous solution. (vi) Most of the actinides radioactive. (vii) The enthalpies of atomisation of transition elements are high.	

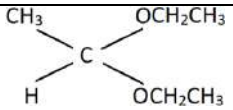
Scan the QR code for marking scheme /solution of above Question Paper

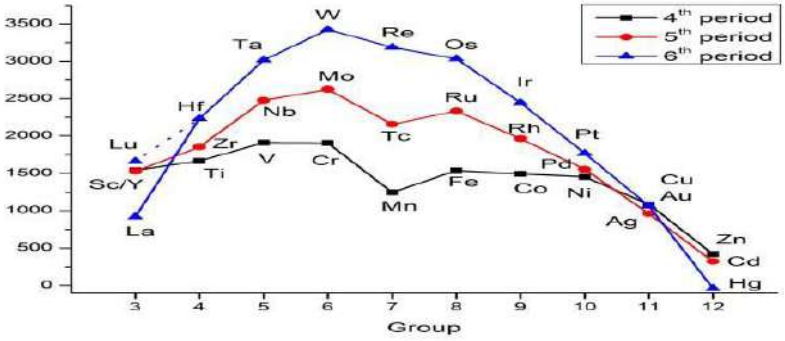
CHEMISTRY (043)

Max. Marks: 70 **Time: 3 Hours**

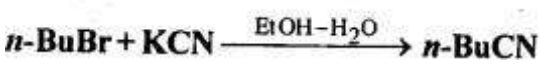
SECTION-A

Question 1 to 16 are multiple choice questions. Only one of the choices is correct. Select and write the correct choice as well as the answer to these questions.

1	Which of the following solutions of KCl will have the highest value of conductivity? a) 0.5 M b) 0.01M c) 0.1M d) 1.0 M	**[1]**
2	 Above shown Acetal is formed by the reaction between A &B in the presence of dry HCl. Identify A and B. a) A is Methanal, B is Methanol b) A is Methanal, B is Ethanol c) A is Ethanal, B is Methanol d) A is Ethanal, B is Ethanol	**[1]**
3	Vitamin deficiencies can manifest in a variety of symptoms and diseases depending on the specific vitamin lacking. Deficiency of Vitamin B1 in the body would cause- a) Convulsions b) Beri-Beri c) Cheilosis d) Sterility	**[1]**
4	What is the IUPAC name of the Ketone A, which undergoes Clemmensen reduction to form Ethyl benzene? a) Propan-2-one b) 1-Phenylethanone c) 3-Methylbut-2-en-one d) Butan-2-one	**[1]**
5	A molecule's dipole moment depends on two primary factors: the electronegativity difference between its bonded atoms and its overall molecular geometry. Which one of the following has the highest dipole moment ? a) CH_3F b) CH_3Cl c) CH_3Br d) CH_3I	**[1]**
6	Match the properties with the elements of 3d series: (i)Element with highest M.P. (p)Cr^{3+} (ii)Element showing +3 oxidation state (q)Cr (iii)Most stable ion in aqueous solution (r) Fe (s) Sc (a) (i) (q), (ii) (s),(iii) (p) (b) (i) (s),(ii) (q),(iii) (r) (c) (i) (q), (ii) (p), (iii) (r) (d) (i) (p),(ii) (q),(iii) (r)	**[1]**
7	Which of the following is not correct about the order of a reaction: (a) The order of a reaction can be a fractional number. (b) Order of reaction is experimentally determined quantity. (c) The order of a reaction is always equal to sum of the stoichiometric coefficients of reactant in the balanced chemical equation for a reaction. (d) The order of a reaction is the sum of the powers of molar concentrations of the reactants in the rate law expression.	**[1]**
8	Which of the following will be most stable diazonium salt RN^+X^-? (a) $CH_3CH_2N_2^+X^-$ (b) $C_6H_5N^+X^-$ (c) $CH_3N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$	**[1]**
9	The aromatic compounds having formula C_7H_8O which are easily identifiable by $FeCl_3$ solution test are: (a) o-cresol &benzyl alcohol (b) m-cresol & p-cresol (c) o-cresol & p- cresol (d) methyl phenyl ether and benzyl alcohol	**[1]**

10	The decomposition of NH_3 on platinum surface is zero order reaction. What is the rate of production of H2 If k = 2.5×10^{-4} mol/L/Sec? (a) 7.5×10^{-4} mol/L/Sec (b) 6.5×10^{-4} mol/L/Sec (c) 5.7×10^{-4} mol/L/Sec (d)7.1×10^{-4} mol/L/Sec	**[1]**
11	Why ortho- nitrophenol is less soluble in water than p—and m—nitrophenol? (a) Due to intramolecular H- bonding (b) Due to intermolecular H-bonding (c) M.P. of o-nitrophenol lower than p- and m- nitrophenol (d) o- nitrophenol is more steam volatile.	**[1]**
12	 The trend of which property is represented by the above graph? (a) Ionization enthalpy (b) Atomic radii (c) Melting point (d) Enthalpy of atomization	**[1]**
13	**Given below are two statements labelled as Assertion (A) and Reason (R):** **Assertion**: Ethers behave as bases in the presence of Mineral acids. **Reason**: Due to the presence of Lone pairs of electrons on Oxygen. **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.	**[1]**
14	**Given below are two statements labelled as Assertion (A) and Reason (R):** **Assertion**: Carboxylic acids are more acidic than phenol. **Reason**: Phenols are ortho and para directing. **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	**[1]**
15	**Given below are two statements labelled as Assertion (A) and Reason (R):** **Assertion**: Albumin is globular protein. **Reason**: Polypeptide chain coils around to give a straight chain. **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	**[1]**
16	**Given below are two statements labelled as Assertion (A) and Reason (R):** **Assertion**: Electrolysis of NaCl solution gives chlorine at anode instead of O_2. **Reason**: Formation of oxygen at anode requires overvoltage. **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.	**[1]**

	(c) A is true but R is false. (d) A is false but R is true	
	SECTION B **Question No. 17 to 21 are very short answer questions carrying 2 marks each.**	
17	(i) Gas (A) is more soluble in water than Gas (B) at the same temperature. Which one of the two gases will have the higher value of KH (Henry's constant) and why? (ii) What happens when we place the blood cell in water? Give reason for your answer.	**[2]**
18	A first order reaction takes 69.3 minutes for 50% completion. How much time will it take for 80% completion? (log 2 = 0.3010, log 5 = 0.6990, log 8 = 0.9030)	**[2]**
19	a) Arrange the following compounds in order of decreasing boiling point. Bromomethane, bromoform, chloromethane, dibromomethane (b) The treatment of alkyl chloride with aq. KOH leads to formation of alcohol but in presence of alcoholic KOH, alkenes are the major products. Explain why?	**[2]**
20	a) Propanone is less reactive than ethanal towards addition of HCN. Explain b) Give Chemical tests to distinguish between acetophenone and benzophenone **(OR)** a) Convert Ethylbenzene into benzoic acid (b) Convert Propanone to propene	**[2]**
21	Answer the following : (a) What type of linkage is responsible for the formation of proteins? (b) Show with the help of a reaction that glucose contains six carbon straight chain.	**[2]**
	SECTION C **Question No. 22 to 28 are short answer questions, carrying 3 marks each.**	
22	Answer any three? a) Write the formula for the following coordination compound: Amminebromidochloridonitrito-N- platinate(II) b) $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 ratio does not give test of Cu^{2+} ion. Explain why? c) A ligand has two donor sites but at a time it binds from only one donor site. Identify the ligand giving one suitable example? (d) $[NiCl_4]^{2-}$ is paramagnetic, while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?	**[3]**
23	a) Why it is a necessity to use a salt- bridge in a Galvanic cell? b) Calculate Λm^o for $CaCl_2$ from the following data: $\Lambda m^o (Ca^{2+}) = 119.0$ S cm^2 mol^{-1}, $\Lambda m^o (Cl^-) = 76.3$ S cm^2 mol^{-1} c) The electrical resistance of a column of 0.05 M NaOH solution of diameter 1 cm and length 50 cm, is 5.55×10^3 Ohm. Calculate its conductivity.	**[3]**
24	Write the structure and IUPAC name of product formed when- (a) Phenol is treated with NaOH followed by heating with CO_2 at 400 K at 4 to 7 atmospheres. (b) Sodium ethoxide reacts with bromomethane. (c) Phenol reacts with concentrated nitric acid and conc. H_2SO_4.	**[3]**
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.	**[3]**

26	(a) Differentiate between the following: (i) Essential and non-essential amino acids. (ii) Fibrous and globular proteins. (b) Which one of the following is a polysaccharide: Starch, Maltose, Fructose, Glucose	**[3]**
27	(a) Write the mechanism of the following reaction:  (b) Grignard reagents should be prepared under anhydrous condition. Explain	**[3]**
28	(a) Define order of reaction. (b) A reaction is first order with respect to A & second order with respect B. (i)How is the rate affected on increasing Concentration of B three times? (ii)How is the rate affected when concentration of A is reduced to half & that of B is doubled?	**[3]**
	SECTION D **Question No. 29 & 30 are case-based/data -based questions carrying 4 marks each. Read the passage given below and answer the following questions**	
29	A research team studies three complexes: • Complex A: $[Pt(NH_3)_2Cl_2][Pt(NH_3)_2Cl_2]$ — used in chemotherapy. • Complex B: $[Co(NH_3)_4Cl_2]Cl[Co(NH_3)_4Cl_2]Cl$ — violet solid, conducts electricity in water. • Complex C: $K_4[Fe(CN)_6]K_4[Fe(CN)_6]$ — pale yellow salt, diamagnetic. During tests, they note: • A shows geometrical isomerism. • B produces three ions in aqueous solution. • C shows no unpaired electrons. 1. Write the IUPAC name of Complex B. 2. Identify the type of isomerism shown by Complex A and name the medicinally active isomer. 3. Calculate the oxidation state of the central metal in Complex C.	**[4 (1+ 1+ 2)]**
30	The standard electrode potentials are very important and we can extract a lot of useful information from them. If the standard electrode potential of an electrode is greater than zero then its reduced form is more stable compared to hydrogen gas. Similarly, if the standard electrode potential is negative then hydrogen gas is more stable than the reduced form of the species. It can be seen that the standard electrode potential for fluorine is the highest in the electrochemical series indicating that fluorine gas (F_2) has the maximum tendency to get reduced to fluoride ions (F^-) and therefore fluorine gas is the strongest oxidising agent and fluoride ion is the weakest reducing agent. Lithium has the lowest electrode potential indicating that lithium ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution. It may be seen that as we go from top to bottom in in electrochemical series the standard electrode potential decreases and with this, decreases the oxidising power of the species on the left and increases the reducing power of the species on the right- hand side of the reaction. (a) Write cell reaction of Zn and Cu cell. (b) E^0 reduction of three metals A, B, C are respectively + 0.5 V, - 3.0 V, -1.2 V write the decreasing order of reducing power of these metals. (c) A student prepared 1 molar aqueous solution of silver nitrate and stirred the solution with copper spoon. Point out if he has committed any mistake. (OR)	**[4 (1+ 1+ 2)]**

	Silver articles get tarnished gradually due to the formation of Ag_2S layer. In order to remove the tarnish a student placed the silverware in aqueous solution of sodium chloride taken in aluminum vessel. Will he succeed or not? Justify. E^0 Al^{+3}/Al = - 1.66 V and E^0 $Ag_2S(s)/Ag(s)$ = - 0.71 V	
	SECTION E **Question No. 31 to 33 are long answer type questions carrying 5 marks each.**	
31	ANSWER THE FOLLOWING: (a) The d^4 species, Cr^{2+} is strongly reducing whereas manganese (III) is strongly oxidising. Why? (b) How would you account for the following: Zr (Z = 40) and Hf (Z = 72) have almost identical radii. (c) What are different oxidation states exhibited by lanthanoids? (d) Which of following cations are colored in aqueous solutions and why? Sc^{3+}, V^{3+}, Ti^{4+}, Mn^{2+} (At. No. Sc = 21, V = 23, Ti = 22, Mn = 25) (e) State reasons for the Cu (I) ion is not stable in an aqueous solution. OR (a) How do you prepare K_2MnO_4 from MnO_2? (b) Complete the given chemical equation- $Cr_2O_7^{2-} + Fe^{2+} + H \rightarrow$ (c) Account for the following : (i) Zn is considered as non transition element. (ii) Chemistry of all lanthanoids is quite similar. (iii) Transition element form alloys.	**[5]**
32	(i) Calculate the amount of KCl which must be added to 1kg of water so that the freezing point is depressed by 2 K (the Kf for water = 1.86 K kg mol^{-1}). (ii) Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. **Or** (i) A solution containing 15g urea (molarmass= 60gmol^{-1}) per litre of solution in water has the same osmotic pressure (isotonic)as a solution of glucose(molar mass = 180 g mol^{-1}) in water. Calculate the mass of glucose present in one litre of its solution. (ii) Define the term 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of Molar masses of solutes in solutions ?	**[5]**
33	(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 compound 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 basic strength: Aniline, p-nitroaniline and p-toluidine OR (a) Complete the following reactions: (i) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$	**[5]**

	(ii) $C_6H_5NH_2 + Br_2(aq) \rightarrow$ (b) Account for the following (i) p_{kb} of aniline is more than that of methyl amine (ii) Aniline does not undergo Friedel-Craft reaction (iii) Ethyl amine is soluble in water whereas aniline is not.	

Scan the QR code for marking scheme /solution of above Question Paper

SAMPLE PAPER (2026-27)

SET-043/4

CLASS – XII

CHEMISTRY (043)

Max. Marks: 70 **Time: 3 Hours**

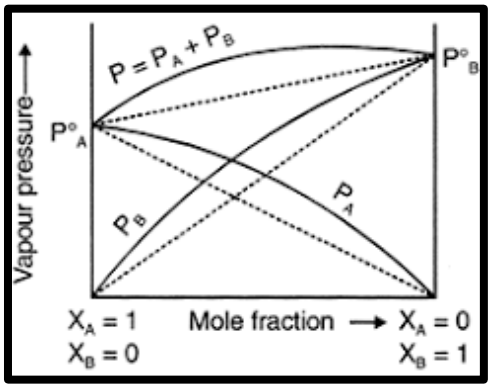
SECTION -A

Q.NO	Questions	Mark

1.	We have three aqueous solutions of NaCl labelled as 'A', 'B' and 'C' with concentrations 0.1M, 0.01M and 0.001M respectively. The value of van't Hoff factor for these solutions will be in the order_____. (a) $i_A < i_B < i_C$ (b) $i_A > i_B > i_C$ (c) $i_A = i_B = i_C$ (d) $i_A < i_B > i_C$	1
2.	Which of the following statement is **not** correct about an inert electrode in a cell? (a) It does not participate in the cell reaction. (b) It provides surface either for oxidation or for reduction reaction. (c) It provides surface for conduction of electrons. (d) It provides surface for redox reaction.	1
3.	K_H value for Ar(g), CO_2(g), HCHO(g) and CH_4(g) are 40.39,1.67, 1.83 x 10^{-5} and 0.413 respectively. Arrange these gases in the order of their **increasing** solubility. (a) HCHO < CH_4 < CO_2 < Ar (b) HCHO < CO_2 < CH_4 < Ar (c) Ar < CO_2 < CH_4 < HCHO (d) Ar < CH_4 < CO_2 < HCHO	1
4.	Which of the following statement is/are **correct**? Given that: $E^0_{Ag^+/Ag}$ = 0.80 V, $E^0_{Mg^{+2}/Mg}$ = -2.37 V, $E^0_{Cu^{+2}/Cu}$ = +0.34 V, (*i*) $AgNO_3$ can be stored in a copper vessel (*ii*) $Mg(NO_3)_2$ can be stored in a copper vessel (*iii*) $CuCl_2$ can be stored in silver vessel (a) (*ii*) and (*iii*) (b) (*i*) and (*ii*) (c) (*iii*) only (d) (*i*), (*ii*) and (*iii*)	1
5.	Acidified $K_2Cr_2O_7$ solution turns green when SO_2 gas is passed through it due to formation o (a) $Cr_2(SO_4)_3$ (b) CrO_4^{2-} (c) $Cr_2(SO_3)_3$ (d) $CrSO_4$.	1
6.	At high pressure the following reaction is zero order. $2NH_3(g) \quad 1130K\ platinum\ catalyst \quad \rightarrow N_2(g) + 3H_2(g)$ Which of the following option is **not** correct for this reaction? (a) Rate of reaction = Rate constant (b) Rate of the reaction depends on concentration of ammonia. (c) Rate of decomposition of ammonia will remain constant until ammonia disappears completely. (d) Further increase in pressure will change the rate of reaction.	1
7.	Which of the following has highest dipole moment? (a) CH_3F (b) CH_3Cl (c) CH_3Br (d) CH_3I	1
8.	Which of the following molecule is **not** tetrahedral? (a) $[Pt(en)_2]^{2+}$ (b) $[Ni(CO)_4]$ (c) $[Zn(NH_3)_4]^{2+}$ (d) $[NiCl_4]^{2-}$.	1
9.	Consider the following compounds : I- Cyclohexyl chloride ($C_6H_{11}Cl$) II- Cyclohexyl methyl chloride (C_6H_{11}-CH_2Cl) III- Phenyl chloride (C_6H_5Cl) The correct order of reactivity towards S_N2 reaction. (a) III > II > I (b) I > II > III (c) II > I > III (d) III > I > II	1
10.	The **correct** IUPAC name of the following compound: CH_3-CHCl-$CH(CH_3)$-CH(OH)-CH_2-CH_2-Br (a) 1-bromo-5-chloro-4-methylhexan-3-ol (b) 6-bromo-2-chloro-4-methylhexan-4-ol (c) 1-bromo-4-chloro-5-methylhexan-3-ol (d) 6-bromo-5-chloro-4-methylhexan-3-ol	1
11.	Which of the following is **not** soluble in $NaHCO_3$?	1

	(a) 2,4,6-Trinitrophenol (b) Benzoic acid (c) o - Nitrophenol (d) Benzene sulphonic acid	
12.	When hypophosphorus acid (H_3PO_2) is added to benzene diazonium chloride, the product formed is- (a) Benzene (b) Phenol (c) Aniline (d) Nitro benzene	1
	From Q. No. 1 to 16 are ASSERTION AND REASON QUESTIONS In the following questions a statement of assertion followed by statement of a reason is give Choose the correct answer out of the following choices. (a) Both A and R are true and R is the correct explanation of A. (b) Both A and R are true but R is not the correct explanation of A. (c) A is true but R is false. (d) A is false but R is true.	
13.	**Assertion (A)**: All collisions of reactant molecules lead to product formation. **Reason (R)**: Only those collisions in which molecules have correct orientation and sufficient kinetic energy lead to compound formation.	1
14.	**Assertion (A)**: Transition metals show variable valency. **Reason (R)**: Transition metals have less energy difference between the ns^2 and (n – 1)d electrons.	1
15.	**Assertion (A)**: Mohr's salt is a double salt. **Reason** (**R**): Mohr's salt gives Fe^{2+}, NH_4^+ and SO_4^{2-} in aqueous solution.	1
16.	**Assertion** (**A**): KCN reacts with methyl chloride to give methyl isocyanide. **Reason** (**R**): CN^- is an ambident nucleophile.	1
	SECTION - B	
17.	In Arrhenius plot of ln k Vs 1/T is a linear plot obtained with slope of -2×10^4 K. Calculate Ea of reaction in kJ mol^{-1}. **OR** A nuclear reaction completes 50% in 20 minutes and 87.55% in 1 hour. Calculate rate constant and time to reduce to its 25% .	2
18.	(a) Write the IUPAC name and hybridisation of the complex $[Fe(CN)_6]^{3-}$. (Given: Atomic number of Fe = 26) (b) What is the difference between an ambidentate ligand and a chelating ligand?	1+1
19.	Etherial solution of an organic compound 'A' when heated with magnesium gave 'B'. 'B' on treatment with ethanal followed by acid hydrolysis gave 2-propanol. Identify the Compound 'A' and justify that 'B' needs to be stored in anhydrous conditions.	2
20.	Give a chemical test that can be used to distinguish between (i) CH_3CHO and $C_6H_5CH_2CHO$ (ii) Phenol and Benzoic acid	1+1
21.	Draw structures of only primary amines with molecular formula C_4H_9N.	2
	SECTION – C	
22.	(i)State Kohlrausch Law. (ii) Represent the cell in which the following reaction takes place: $2Al\ (s) + 3Ni^{2+}\ (0.1M)\quad 2Al^{3+}\ (0.01M) + 3Ni(s)$ Calculate the emf if E_{cell} 1.41 V.	1+2

23.	The reaction between A and B is of first order with respect to A and zero order with respect to B. Fill in the blanks in the following table: Experiment | [A] / mol L^{-1} | [B] / mol L^{-1} | Initial rate in mol L^{-1} $Minute^{-1}$ I | 0.1 | 0.1 | $2.0X10^{-2}$ II | - | 0.2 | $4.0X10^{-2}$ III | 0.4 | 0.4 | - IV | - | 0.2 | $2.0X10^{-2}$	1+1+1
24.	(i) The CFSE for octahedral $[CoCl_6]^{4-}$ is 18,000 cm^{-1}.Calculate CFSE for tetrahedral $[CoCl_4]^{2-}$ (ii)What happens to the colour of complex $[Ti(H_2O)_6]^{3+}$ when heated gradually? (iii)Write the hybridization and magnetic behaviour of the complex $[Ni(CO)_4]$ (Atomic number Ni=28)	1+1+1
25.	Explain why- (i) What is the mechanism of the following reaction: $n-BuBr + KCN \quad EtOH - H_2O \quad \rightarrow n-BUCN$ (ii)Chloroform is stored in closed dark coloured bottles. (iii)Allyl chloride can be distinguished from vinyl chloride by NaOH and silver nitrate test. Comment.	1+1+1
26.	Complete the following equations- (a) C_6H_5OH + Conc. HNO_3 → (b) $CH_3CH_2ONa + (CH_3)_3C\text{-}Cl$ → (c) $CH_3\text{-}CH{=}CH_2 \xrightarrow[(ii)\ H_2O_2\ /OH^-]{(i)\ B_2H_6}$	1+1+1
27.	(i) Give one chemical test to distinguish between the following pair of compounds: Methylamine and dimethylamine. (ii) Account for the following: pK_b of aniline is more that of methylamine. (iii) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.	1+1+1
28.	(i) How do you explain the presence of five -OH groups in glucose molecule? (ii) What do you understand by the term glycosidic linkage? Give one example. (iii) List one difference between α- helical and β- pleated structure. **OR** (ii)Why cannot vitamin C be stored in our body?	1+1+1
29.	**SECTION – D** **Read the passages given below in Question no.29 and 30, then answer the questions given at the end** Metallic conductance involves movement of electrons whereas electrolytic conductance involves movement of ions. Conductivity increases with increase in concentration whereas $\wedge_m$ (molar conductivity) decreases with increase in concentration. Resistance of ionic solution was measured by wheat stone bridge but it had some challenge in modern time conductivity cells are used. It is basically, consists of two platinum electrode coated with platinum black. $\wedge_m{}^o$ of strong electrolytes can be obtained by extrapolation but for weak electrolyte it is not applicable. Kohlrausch law helps to determine limiting molar conductivity ,degree of ionisation and dissociation constant of weak electrolyte.	1+1+2

	(a) Out of 0.1 M and 0.01 M KCl which has higher Conductivity and why? (b) Ag metal at 30°C or 60°C will have higher conductance and why? (c) Calculate $\wedge_m$ of 0.1 M KCl if resistance is 100 ohms and cell constant is 1.29 cm^{-1}. **OR** (c) What will be the ionization constant of CH_3COOH if 0.01 M has $\wedge_m$ 40 $Scm^2\ mol^{-1}$ and $\wedge_m^o$ is 400 S $cm^2\ mol^{-1}$.	
30.	**Read the given passage and answer the questions given at the end :** Dr. Watson received his Ph.D. (1950) from Indiana University in Zoology and best known for his discovery of the structure of DNA for which he shared with Francis Crick and Maurice Wilkins the 1962 Nobel prize in Physiology and Medicine. They proposed that DNA molecule takes the shape of a double helix, an elegantly simple structure that resembles a gently twisted ladder DNA finger printing and gene therapy are most advance streams of biotechnology . DNA finger printing is used in forensic laboratories for identification of criminals and to determine paternity of an individual. Gene therapy rapidly improves Night Vision. The patients had Leber Congenital Amaurosis (LCA), a congenital blindness caused by mutation in the gene GUCY2D. Scientist delivered AAV gene therapy, which carries the DNA of healthy version of the gene, into the retina of one eye for each of the patients in accordance with the clinical test protocol. Within days of being treated, each patient showed large increase in the treated eye, of visual functions mediated by rod type photoreceptor cells. GUCY2D is Retinal guanylyl cyclase 1 is an enzyme. These exciting results demonstrates that the basic molecular machinery of photo transduction remains largely in some cases of LCA, and thus can be amenable to gene therapy even after decades of blindness. There are more than two dozen genes whose dysfunction can cause LCA. GUCY2D: a gene encodes a key protein needed in retinal photoreceptor cells for photo transduction cascade. Re-supply of missing protein to start alive and intact cells working, more or less immediately, was successful. (a) What is meant by DNA finger printing? Write its one application. **OR** (a) What are the hydrolysis products of DNA with Adenine as Nitrogenous base? (b) Give two structural differences between DNA and RNA (c) (i)What is GUCY2D? what is its function? (iii) What are enzymes? What is their function?	1+1 +2
31.	**SECTION – E**  	2+2 +1

	(i) What kind of azeotrope will be formed by the solution, shown in the figure? Give one example of the same. (ii) A decimolar solution of K_4 [$Fe(CN)_6$] is 50% ionised. Calculate its osmotic pressure at 300 K. [R=0.0821 L atm K^{-1} mol^{-1}] (iii) Elevation of boiling point of 1 M KCl solution is nearly double than that of 1 M sugar solution. Give reason. (iv) Write possible values of 'i' when CH_3COOH dissolved in- (a) Water (b) Benzene, justify each case also. **OR** (i) Blood cells are isotonic with 0.9% sodium chloride solution. What happens if we place blood cells in a solution containing 1.2% sodium chloride solution? (ii) In non-ideal solution, what type of deviation shows the formation of maximum boiling azeotropes? Give one example also. (iii) What is better- 1M NaCl or 0.5M $MgCl_2$ for decreasing the freezing point of water more effectively and why? (iv) If X & Y form ideal solution P^o_X = 450mm, P^o_Y = 200mm if P_X=P_Y, then calculate mole Fraction of X_x	1+1+1+2
32.	A black brown coloured mineral X on treatment with KOH & O_2 produces a green Coloured paramagnetic mass 'Y', Y on treatment with Cl_2 water or O_3. Produces 'Z' which forms a purple pink solution with water. Identify, X,Y and Z. and also complete the following reaction $Anion\ of\ Z + I^-\quad H^+ \rightarrow I_2 + H_2O + ?$ $Anion\ of\ Z + C_2O_4^{--}\quad H^+ \rightarrow CO_2 + H_2O + ?$ **OR** (i) The third ionization enthalpy of manganese (Z=25) is exceptionally high. (ii) Cr^{2+} is a stronger reducing agent than Fe^{2+}. (iii) Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. (iv) Out of Mn^{3+} and Cr^{3+} , which more paramagnetic and why? (Atomic no.: Mn=25, Cr=24) (iv) What is the effect of pH on dichromate ion solution?	5 1X5
33.	(a) An organic compound (A), having the formula, C_3H_8O, on treatment with copper at 573 K, gives (B). (B) does not reduce Fehling's solution but on reaction with with I_2 and NaOH gives a yellow precipitate with a colourless compound (C). Deduce the structure of (A), (B) and (C) and also write their IUPAC names. (b) Write the chemical equation to illustrate Cannizzaro reaction (c) Give a chemical test to distinguish between formic acid and acetic acid **OR** An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollens' reagent but forms an addition compound with sodium hydrogensulphite and gives a positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the structure of the compound. Also write all the equations of the reactions involved.	1 x 5 5

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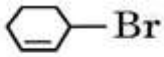
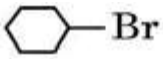
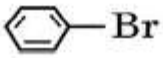
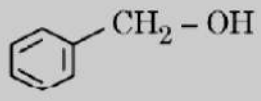
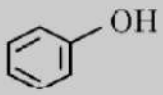
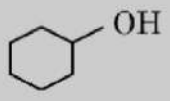
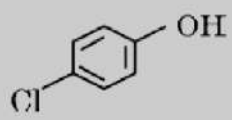
Scan the QR code for marking scheme /solution of above Question Paper

SAMPLE PAPER (2026-27)
SET-043/5
CLASS – XII
CHEMISTRY (043)

Max. Marks: 70 **Time: 3 Hours**

	SECTION-A Question 1 to 16 are multiple choice questions. Only one of the choices is correct. Select and write the correct choice as well as the answer to these questions.	
1	Which one of the following first row transition elements is expected to have the highest second ionization enthalpy ? (A) Iron (Z = 26) (B)Manganese (Z = 25) (C)Chromium (Z = 24) (C) Vanadium (Z = 23)	**[1]**
2	For an electrolyte undergoing dissociation in a solvent, the vant hoff factor : (A) is always greater than one (B) has negative value	**[1]**

	(C) has zero value (D) is always less than one	
3	Which of the following compounds will give a ketone on oxidation with chromic anhydride (CrO_3) ? (A) $(CH_3)_2CH-CH_2OH$ (B) $CH_3CH_2CH_2OH$ (C) $(CH_3)_3C-OH$ (D) $CH_3-CH_2-\underset{\displaystyle OH}{\underset{\vert}{CH}}-CH_3$	**[1]**
4	Two among the three components of RNA are β-D--ribose and a heterocyclic base. The third component is : (A) Adenine (B) Phosphoric acid (C) Sulphuric acid (D) Uracil	**[1]**
5	The reaction of an alkyl halide with sodium alkoxide forming ether is known as : (A) Wurtz reaction (B) Reimer-Tiemann reaction (C) Williamson synthesis (D) Kolbe reaction	**[1]**
6	Rate law for the reaction A + 2B → C is found to be Rate = k [A][B] Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be_____. (A) The same (B) Doubled (C) Quadrupled (D) Halved	**[1]**
7	The compound which undergoes S_N2 reaction most rapidly is : (A)  (B)  (C)  (D) 	**[1]**
8	The formation of hemiacetal from an aldehyde is an example of : (A) nucleophilic addition (B) electrophilic addition (C) nucleophilic substitution (D) electrophilic substitution	**[1]**
9	When Acetic acid is heated with red P_4/Cl_2 gives : (A) Cl _ CH_2 _ COCl (B) Cl _ CH_2 _ COOH (C) CH_3 _ COCl (D) CCl_3 _ COOH	**[1]**
10	The value of rate constant of a pseudo first order reaction _____. (A) Depends only on temperature (B) Depends on the concentration of reactants present in excess. (C) Is independent of the concentration of reactants. (D) Depends on the concentration of reactants present in small amount.	**[1]**
11	Which of the following is most acidic ?:	**[1]**

	(A)  (B)  (C)  (D) 	
12	The vitamin which plays an important role in coagulating blood is : (A) Vitamin D (B) Vitamin E (C) Vitamin K (D) Vitamin A	**[1]**

For Questions number 13 to 16, two statements are given one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C) and (D) as given below.

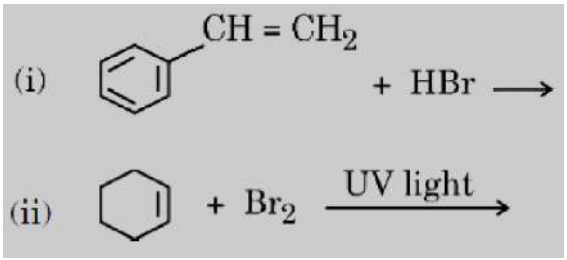
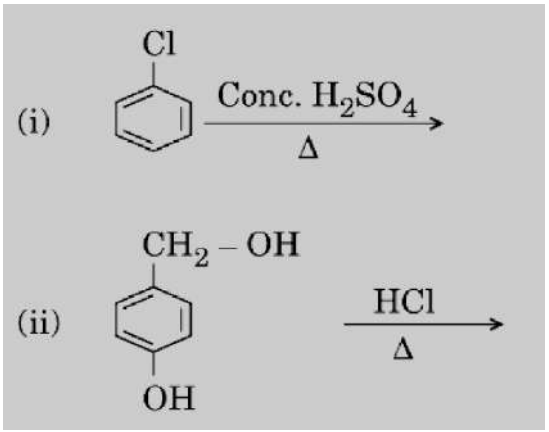
(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

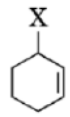
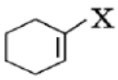
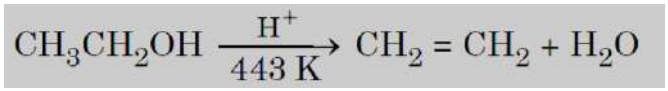
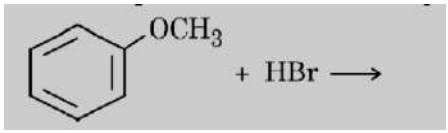
(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

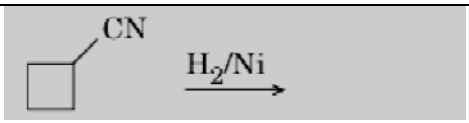
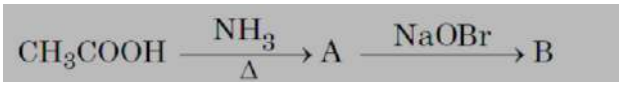
13	Assertion (A) : Separation of Zr and Hf is difficult. Reason (R) : Zr and Hf have similar radii due to lanthanoid contraction.	**[1]**
14	Assertion (A) : Addition of ethylene glycol to water lowers its freezing point. Reason (R) : Ethylene glycol is insoluble in water due to lack of its ability to form hydrogen bonds with water molecules.	**[1]**
15	Assertion (A) : Benzoic acid do not undergo Friedel Crafts Reaction Reason (R) :Carboxyl group is deactivating and the catalyst aluminum Chloride gets bonded to the carboxyl group.	**[1]**
16	Assertion (A) : Methanamine is a weak base than ammonia. Reason (R) : The electron density increases on nitrogen atom in methanamine due to +I effect of methyl group.	**[1]**
	SECTION B Question No. 17 to 21 are very short answer questions carrying 2 marks each.	
17	Calculate the half-cell potential at 298 K for the reaction $Zn^{2+} + 2e^- \longrightarrow Zn$ if $[Zn^{2+}] = 0{\cdot}1\ M$ and $E^\circ_{Zn^{2+}/Zn} = -0{\cdot}76\ V$.	**[2]**
18	Define order of reaction. How does order of a reaction differ from molecularity for a complex reaction?	**[2]**
19	What happens when D-glucose is treated with the following reagents ? (a) Br_2 water (b) HCN	**[2]**

20	(a) Draw the structures of major monohalo products in each of the following reactions :  OR (b) Write the major product(s) of the following reactions :  	**[2]**
21	Give chemical equation for the following reactions : (i) Propanone is treated with dil. $Ba(OH)_2$. (ii) Acetophenone is treated with Zn(Hg)/Conc. HCl.	**[2]**
	SECTION C Question No. 22 to 28 are short answer questions, carrying 3 marks each.	
22	The following data were obtained for the reaction : 2A + B → C (a) Find the order of reaction with respect to A and B. (b) Write the rate law and overall order of reaction. (c) Calculate the rate constant (k).	**[3]**
23	(a) Write the formula for the following coordination compound : Tetraamminechloridonitrito-N-cobalt(III) chloride (b) Arrange the following complexes in the increasing order of conductivity of their solution : $[Cr(NH_3)_5Cl]Cl_2$, $[Cr(NH_3)_3Cl_3]$, $[Cr(NH_3)_6]Cl_3$ (c) Identify the type of isomerism exhibited by the following complexes : (i) $[Co(NH_3)_5(SO_4)]Cl$ (ii) $[Co(en)_3]Cl_3$	**[3]**

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

24	(a) Out of  and  , which is an example of allylic halide? (b) Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why ? (c) Which isomer of C_4H_9Cl has the lowest boiling point?	**[3]**
25	(a) Write the mechanism of the following reaction :  (b) Write the main product in each of the following reaction : 	**[3]**
26	Give reasons for any 3 of the following observations : (a) Penta-acetate of glucose does not react with hydroxylamine. (b) Amino acids behave like salts. (c) Water soluble vitamins must be taken regularly in diet. (d) The two strands in DNA are complimentary to each other.	**[3]**
27	Compound (A) ($C_6H_{12}O_2$) on reduction with $LiAlH_4$ gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F).	**[3]**
28	The electrical resistance of a column of 0.05 M KOH solution of length 50 cm and area of cross-section 0.625 cm^2 is 5 x 10^3 ohm. Calculate its resistivity, conductivity and molar conductivity.	**[3]**
	SECTION D Question No. 29 & 30 are case-based/data -based questions carrying 4 marks each.	
29	Fuel cells and batteries are both electrochemical energy storage and conversion devices, but they differ fundamentally in their operation. Batteries store a fixed amount of chemical energy and convert it to electrical energy, while fuel cells generate electricity continuously as long as they are supplied with fuel like hydrogen, methane etc and an oxidant like oxygen. Batteries are also classified as primary batteries if they can be used only once or secondary batteries if they can be recharged by passing current through it in the opposite direction. *Answer the following questions :* (a) What are the fundamental differences between batteries and fuel cells? (b) The cell potential of Mercury cell is 1·35 V, and remains constant during its life. Give reason. (c) Write the reactions involved in the discharging of the lead storage battery. OR (c) Write the reactions involved in H_2-O_2 fuel cell.	**[4]**
30	The nature of bonding, structure of the coordination compound can be explained to some extent by valence bond theory. The central metal atom/ion makes	**[4]**

	available a number of vacant orbitals equal to its coordination number. The appropriate atomic orbitals (s, p and d) of the metal hybridize to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral, octahedral and so on. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. The d-orbitals involved in the hybridisation may be either inner d-orbitals i.e. (n-1) d or outer d-orbitals i.e. nd. The complexes formed are called inner orbital complex (low spin complex) and outer orbital complex (high spin complex) respectively. Further, the complexes can be paramagnetic or diamagnetic in nature. The drawbacks of this theory are that this involves number of assumptions and also does not explain the colour of the complex. *Answer the following questions:* (a) Predict whether $[Co(NH_3)_6]^{3+}$ is diamagnetic or paramagnetic and why? [Atomic number: Co=27] (b) What is the coordination number of Co in $[Co(ox)_2$ Br Cl$]^{3-}$? (c) (i) Write the IUPAC name of the given complex: $[Fe(CN)_6]^{3-}$ (ii) Explain $[CoF_6]^{3-}$ is an inner orbital or outer orbital complex. OR (c) Using valence bond theory, deduce the shape and hybridisation of $[Ni(NH_3)_6]^{2+}$ [Atomic number of Ni = 28]	
	SECTION E Question No. 31 to 33 are long answer type questions carrying 5 marks each.	
31	**A**. (a) Measurement of osmotic pressure method is preferred for the determination of molar masses of macromolecules such as proteins and polymers. (b) Red Blood Cells (RBC) shrink when placed in saline water but swell in distilled water. (c) 3.9 g of benzoic acid dissolved in 49 g of benzene shows a depression in freezing point of 1.62 K. Calculate the van't Hoff factor and predict the nature of solute (associated or dissociated). (Given: Molar mass of benzoic acid = 122 $gmol^{-1}$ for benzene = 4.9 K Kg $K\ mol^{-1}$) OR **B**. (a) Identify which liquid will have a higher vapour pressure at 90°C if the boiling points of two liquids A and B are 140°C and 180°C, respectively. (b) Differentiate between Ideal solution and Non-ideal solution. (c) The freezing point of a solution containing 5g of benzoic acid (M = 122 g mol^{-1}) in 35g of benzene is depressed by 2.94 K. What is the percentage association of benzoic acid if it forms a dimer in solution? (K_f for benzene = 4.9 K kg mol^{-1})	**[5]**
32	A) (i) Aniline does not undergo Friedal-Crafts reactions. (ii) $(CH_3)_2NH$ is more basic than $(CH_3)_3N$ in an aqueous solution. (iii) Primary amines have higher boiling point than tertiary amines (iv) Write a chemical test to distinguish between N,N-dimethylaniline and aniline. (v) How will you convert Aniline to benzene OR B) (i) Complete the following reaction :	**[5]**

	 (ii) Write the structures of A and B in the following reaction :  (iii) Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines. (iv) Give reason why Ammonolysis of alkyl halides is not a good method to prepare pure primary amines. (v)) How will you convert Benzoic acid to benzenamine	
33	(a) (i) Account for the following : (1) A new element is discovered whose electronic configuration is found to be $6d^{10}\ 7s^2$. Comment on the expected melting and boiling points of the element. (2) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing. (3) A lanthanoid element forms M^{4+} ion. Whether this ion will be oxidizing or reducing agent and why? . (ii) Complete and balance the following chemical equations : (A) $HgCl_2 + SnCl_2$ ⟶ (B) $MnO_4^- + Mn^{2+} + H_2O$ ⟶ OR (b) (i) Out of Cu_2Cl_2 and $CuCl_2$, which is more stable in aqueous solution and why ? (ii) Consider the reaction: $Cr_2O_7^{2-} + 14\ H^+ + 6e^-$ ⟶ $2Cr^{3+} + 8H_2O$ What is the quantity of electricity in coulombs needed to reduce 1 mol of $Cr_2O_7^{2-}$. (iii) The oxidizing power of oxyanions are in the order $VO2+ < Cr_2O_7^{2-} < MnO_4^-$ (iv) What is colour change of chromate ion by the action of an acid and why? (v) Many of the transition elements and their compounds can act as good catalysts.	**[5]**

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