CBSE Class 12 Chemistry Compartment 2026

Question Paper with Solutions

Conducted by Central Board of Secondary Education (CBSE)

General Instructions

(i) This question paper contains **33 questions**. **All questions are compulsory.**

(ii) This question paper is divided into five sections – **Section A, B, C, D and E.**

(iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1 mark**.

(iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2 marks**.

(v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3 marks**.

(vi) **Section D** – questions number **29 and 30** are case-based questions. Each question carries **4 marks**.

(vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5 marks**.

1. Match Column I with Column II and choose the correct option :

Column I		*Column II*
Osmotic pressure	i.	$\Delta T_f = K_f m$
Elevation of boiling point	ii.	$\pi = CRT$
Depression of freezing point	iii.	$\frac{P_1^0 - P_1}{P_1^0} = \frac{W_2 \times M_1}{M_2 \times W_1}$
Relative lowering of vapour pressure	iv.	$\Delta T_b = K_b m$

(A) a-i, b-ii, c-iii, d-iv

(B) a-ii, b-i, c-iii, d-iv

(C) a-iv, b-iii, c-ii, d-i

(D) a-ii, b-iv, c-i, d-iii

Correct Answer: (D) a-ii, b-iv, c-i, d-iii

Solution:

Concept: Colligative properties are properties of solutions that depend on the ratio of the number of solute particles to the number of solvent molecules in a solution, and not on the nature of the chemical species present. The primary colligative properties and their fundamental mathematical representations are:

- **Osmotic Pressure (π):** Given by van 't Hoff equation, $\pi = CRT$, where C is molarity, R is gas constant, and T is temperature.
- **Elevation of Boiling Point (ΔT_b):** Proportional to molality (m), $\Delta T_b = K_b m$, where K_b is the ebullioscopic constant.
- **Depression of Freezing Point (ΔT_f):** Proportional to molality (m), $\Delta T_f = K_f m$, where K_f is the cryoscopic constant.
- **Relative Lowering of Vapour Pressure:** Equal to the mole fraction of the solute, $\frac{P_1^0 - P_1}{P_1^0} = x_2 = \frac{n_2}{n_1} = \frac{W_2 \times M_1}{M_2 \times W_1}$ (for dilute solutions).

Step 1: Matching Osmotic Pressure (a).

Osmotic pressure is directly proportional to the molar concentration C of the solution at a given temperature T:

$$\pi = CRT$$

Therefore, item **a** matches with **ii**.

Step 2: Matching Elevation of Boiling Point (b).

The elevation in boiling point ΔT_b of a solution is directly proportional to the molal concentration m of the solute:

$$\Delta T_b = K_b m$$

Therefore, item **b** matches with **iv**.

Step 3: Matching Depression of Freezing Point (c).

The depression in freezing point ΔT_f of a solution is directly proportional to the molality m of the solute:

$$\Delta T_f = K_f m$$

Therefore, item **c** matches with **i**.

Step 4: Matching Relative Lowering of Vapour Pressure (d).

According to Raoult's law, the relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute:

$$\frac{P_1^0 - P_1}{P_1^0} = x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1} = \frac{W_2 \times M_1}{M_2 \times W_1}$$

Therefore, item **d** matches with **iii**.

Combining all correct pairs gives: **a-ii, b-iv, c-i, d-iii**.

Hence, the correct option is (D).

Quick Tip: Remember the fundamental definitions of the four colligative properties: - Osmotic Pressure: $\pi = CRT$ - Boiling Point Elevation: $\Delta T_b = K_b m$ - Freezing Point Depression: $\Delta T_f = K_f m$ - Relative Lowering of Vapour Pressure: $\frac{\Delta P}{P^0} = x_2$

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2. Functional groups present in amino acids are :

(A) $-NH_2$ and $-OH$

(B) $-OH$ and $-COOH$

(C) $-COOH$ and $-NH_2$

(D) $-NH_2$ and $-SO_3H$

Correct Answer: (C) $-COOH$ and $-NH_2$

Solution:

Concept: Amino acids are organic compounds that serve as the building blocks of proteins. The general structure of an α-amino acid consists of a central carbon atom (α-carbon) covalently bonded to four different groups:

- An amino group ($-NH_2$), which exhibits basic character.
- A carboxyl group ($-COOH$), which exhibits acidic character.
- A hydrogen atom ($-H$).
- A variable side chain group ($-R$).

Step 1: Analyzing the chemical composition of amino acids.

By name and definition, an amino acid contains both an amino functional group ($-NH_2$) and a carboxylic acid functional group ($-COOH$).

Step 2: Evaluating the given options.

- Option (A): Contains $-NH_2$ and $-OH$ (characteristic of amino alcohols). - Option (B): Contains $-OH$ and $-COOH$ (characteristic of hydroxy acids). - Option (C): Contains $-COOH$ and $-NH_2$, which uniquely defines amino acids. - Option (D): Contains $-NH_2$ and $-SO_3H$ (characteristic of aminosulfonic acids such as taurine, but not canonical amino acids).

Therefore, the essential functional groups present in amino acids are the carboxyl group ($-COOH$) and the amino group ($-NH_2$).

Hence, the correct option is (C).

Quick Tip: The term "amino acid" directly tells you the two functional groups present: "amino" for $-NH_2$ and "acid" for carboxylic acid $-COOH$.

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3. The correct order of reactivity of alcohols with Lucas reagent is :

(A) $3^\circ > 1^\circ > 2^\circ$

(B) $2^\circ > 1^\circ > 3^\circ$

(C) $1^\circ > 2^\circ > 3^\circ$

(D) $3^\circ > 2^\circ > 1^\circ$

Correct Answer: (D) $3^\circ > 2^\circ > 1^\circ$

Solution:

Concept: Lucas reagent is an anhydrous mixture of concentrated hydrochloric acid (HCl) and anhydrous zinc chloride ($ZnCl_2$). It is used to distinguish between primary (1°), secondary (2°), and tertiary (3°) alcohols based on their reaction rates to form insoluble alkyl chlorides, which produce turbidity.

The reaction proceeds via an S_N1 mechanism involving a carbocation intermediate:

$$\text{R-OH} + \text{HCl} \xrightarrow{\text{Anhydrous } ZnCl_2} \text{R-Cl} \downarrow \text{ (turbidity)} + H_2O$$

Step 1: Understanding the reaction mechanism and stability of intermediates.

The rate-determining step in this reaction is the formation of a carbocation intermediate after

protonation and removal of the hydroxyl group:

$$\text{R-OH} \xrightarrow{H^+} \text{R-OH}_2^+ \xrightarrow{-H_2O} \text{R}^+ \quad \text{(Carbocation intermediate)}$$

The rate of the reaction depends directly on the stability of the formed carbocation intermediate:

$$\text{Stability of Carbocations: } 3^\circ > 2^\circ > 1^\circ$$

Step 2: Comparing the reaction rates for different classes of alcohols.
- **Tertiary (3°) alcohols:** Form a very stable tertiary carbocation (3°). The reaction occurs immediately at room temperature, producing immediate turbidity. - **Secondary (2°) alcohols:** Form a moderately stable secondary carbocation (2°). The reaction takes around 5 to 10 minutes to produce turbidity. - **Primary (1°) alcohols:** Form an unstable primary carbocation (1°). The reaction does not produce turbidity at room temperature and requires heating to react.
Therefore, the order of reactivity of alcohols with Lucas reagent is:

$$3^\circ > 2^\circ > 1^\circ$$

Hence, the correct option is (D).

Quick Tip: Lucas reagent reactions proceed through carbocation intermediates: Reactivity $\propto$ Carbocation Stability $\implies 3^\circ > 2^\circ > 1^\circ$.

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4. According to Alfred Werner, the secondary valence(s) of the central metal atom/ion in a complex :

(A) are non-ionisable

(B) are ionisable

(C) are satisfied by neutral molecules or negative ions

(D) is equal to the coordination number and is normally fixed for a metal

Correct Answer: (D) is equal to the coordination number and is normally fixed for a metal

Solution:

Concept: Werner's Coordination Theory postulates that metal atoms in coordination complexes possess two types of valencies:

1. **Primary Valence:** Corresponds to the oxidation state of the metal atom/ion. It is ionisable, non-directional, and satisfied only by negative ions.
2. **Secondary Valence:** Corresponds to the coordination number of the metal atom/ion. It is non-ionisable, directional, satisfied by negative ions or neutral molecules, and fixed for a given metal in a specific oxidation state.

Step 1: Evaluating all given statements according to Werner's Theory.

- Statement (A): "are non-ionisable" — This is a TRUE statement regarding secondary valence.
- Statement (B): "are ionisable" — This is a FALSE statement (primary valence is ionisable, secondary is not). - Statement (C): "are satisfied by neutral molecules or negative ions" — This is a TRUE statement regarding secondary valence. - Statement (D): "is equal to the coordination number and is normally fixed for a metal" — This is a fundamental definition and characteristic of secondary valence.

Step 2: Identifying the incorrect statement requirement.

The question asks to identify the incorrect statement from the given options (or select the main correct defining property of secondary valence). Note that statement (B) is incorrect about secondary valence, but among standard conceptual questions evaluating the core definition of secondary valence, Option (D) defines secondary valence completely. However, as per standard textbook key for this question set, secondary valences correspond directly to the coordination number of the central metal ion.

Hence, the correct option is (D).

Quick Tip: - Primary Valence = Oxidation Number (Ionisable, Non-directional) - Secondary Valence = Coordination Number (Non-ionisable, Directional, Fixed)

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5. Which of the following statements is true about a galvanic cell consisting of Cu and H_2 electrodes ?

[Given : $E^{\circ}_{Cu^{2+}/Cu} = +0.34$ V, $E^{\circ}_{H^{+}/H_2,Pt} = +0.00$ V]

(A) Oxidation occurs at copper electrode

(B) Reduction occurs at H_2 electrode

(C) H_2 is cathode and Cu is anode

(D) H_2 is anode and Cu is cathode

Correct Answer: (D) H_2 is anode and Cu is cathode

Solution:

Concept: In a galvanic cell:

- The electrode with a lower (more negative) standard reduction potential (E°) acts as the anode , where oxidation occurs.
- The electrode with a higher (more positive) standard reduction potential (E°) acts as the cathode , where reduction occurs.

Step 1: Comparing the standard reduction potentials of the two electrodes.

Given:

$$E^\circ_{Cu^{2+}/Cu} = +0.34\ V$$

$$E^\circ_{H^+/H_2,Pt} = 0.00\ V$$

Comparing the reduction potentials:

$$E^\circ_{Cu^{2+}/Cu} > E^\circ_{H^+/H_2,Pt}$$

Step 2: Determining anode, cathode, and half-reactions.

Since the hydrogen electrode has a lower standard reduction potential ($0.00\ V < +0.34\ V$): - **Hydrogen electrode (H_2)** acts as the anode (Oxidation occurs):

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

- **Copper electrode (Cu)** acts as the cathode (Reduction occurs):

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

Step 3: Evaluating the options.

- (A) Oxidation occurs at copper electrode — False (reduction occurs at Cu). - (B) Reduction occurs at H_2 electrode — False (oxidation occurs at H_2). - (C) H_2 is cathode and Cu is anode — False. - (D) H_2 is anode and Cu is cathode — True.

Hence, the correct option is (D).

Quick Tip: Remember the mnemonic AnOx RedCat : - An ode = Ox idation (Lower E°) - Red uction = Cat hode (Higher E°)

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6. The relationship between $E^\circ_{(\text{cell})}$ and $\Delta_r G^\ominus$ is :

(A) $\Delta_r G^\ominus = E^\circ_{(\text{cell})}$

(B) $\Delta_r G^\ominus = nFE^\circ_{(\text{cell})}$

(C) $\Delta_r G^\ominus = nE^\circ_{(\text{cell})}$

(D) $\Delta_r G^\ominus = -nFE^\circ_{(\text{cell})}$

Correct Answer: (D) $\Delta_r G^\ominus = -nFE^\circ_{(\text{cell})}$

Solution:

Concept: The standard Gibbs energy change ($\Delta_r G^\ominus$) of a cell reaction is related to the maximum electrical work done by the system. The electrical work done by a cell in one second is equal to electrical potential multiplied by total charge passed.

Step 1: Deriving the fundamental thermodynamic relationship.

If n moles of electrons are transferred in a cell reaction, the total charge transported is:

$$q = nF$$

where F is the Faraday constant (≈ 96487 C mol^{-1}).

The maximum electrical work done by the cell system is given by:

$$W_{\text{elec}} = q \times E^\circ_{(\text{cell})} = nFE^\circ_{(\text{cell})}$$

Step 2: Relating electrical work to Gibbs free energy change.

According to thermodynamics, the decrease in Gibbs free energy equals the maximum useful work performed by the system:

$$\Delta_r G^\ominus = -W_{\text{elec}}$$

Substituting W_{elec}:

$$\Delta_r G^\ominus = -nFE^\circ_{(\text{cell})}$$

where: - $\Delta_r G^{\ominus}$ = Standard Gibbs energy change of reaction - n = Number of moles of electrons transferred in the balanced cell reaction - F = Faraday's constant - $E^{\circ}_{(\text{cell})}$ = Standard electromotive force (EMF) of the cell

Hence, the correct option is (D).

Quick Tip: Always remember the negative sign in $\Delta_r G^{\ominus} = -nFE^{\circ}_{\text{cell}}$. A spontaneous cell reaction has $E^{\circ}_{\text{cell}} > 0$, which gives a negative $\Delta_r G^{\ominus}$.

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7. A galvanic cell functions like an electrolytic cell when :

(A) $E_{\text{cell}} = E_{\text{ext}}$

(B) $E_{\text{cell}} > E_{\text{ext}}$

(C) $E_{\text{ext}} > E_{\text{cell}}$

(D) $E_{\text{cell}} = 0$

Correct Answer: (C) $E_{\text{ext}} > E_{\text{cell}}$

Solution:

Concept: When an external opposing potential (E_{ext}) is applied to a galvanic cell, three distinct cases arise depending on the magnitude of E_{ext}:

1. **When $E_{\text{ext}} < E_{\text{cell}}$:** Electrons flow from anode to cathode, and current flows from cathode to anode. The cell acts normally as a galvanic cell.
2. **When $E_{\text{ext}} = E_{\text{cell}}$:** No chemical reaction takes place, and no current flows through the circuit. The cell is in equilibrium.
3. **When $E_{\text{ext}} > E_{\text{cell}}$:** The direction of current is reversed. Electrons flow from cathode to anode. Chemical reaction is reversed, and the cell functions as an electrolytic cell .

Step 1: Analyzing the behavior when an external voltage is applied.

When the external voltage E_{ext} exceeds the cell EMF (E_{cell}), electrical energy is supplied from an external source to drive a non-spontaneous chemical reaction in the reverse direction.

Step 2: Conclusion.

Thus, when $E_{\text{ext}} > E_{\text{cell}}$, the galvanic cell starts functioning as an electrolytic cell.

Hence, the correct option is (C).

Quick Tip: - $E_{ext} < E_{cell}$: Galvanic cell (spontaneous) - $E_{ext} = E_{cell}$: No reaction (equilibrium) - $E_{ext} > E_{cell}$: Electrolytic cell (driven externally)

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8. Phenol, on heating with conc. HNO_3, gives :

(A) o-Nitrophenol

(B) p-Nitrophenol

(C) Picric acid

(D) Sodium phenoxide

Correct Answer: (C) Picric acid

Solution:

Concept: Nitration of phenol depends strongly on the concentration of nitric acid used:

- With dilute HNO_3 at low temperature (298 K), phenol yields a mixture of ortho- and para-nitrophenols.
- With concentrated HNO_3 (often in presence of conc. H_2SO_4), electrophilic substitution occurs at all available ortho and para positions simultaneously, producing 2,4,6-trinitrophenol, commonly known as Picric acid .

Step 1: Writing the chemical reaction for nitration of phenol with concentrated HNO_3.

When phenol is treated with concentrated nitric acid:

$$C_6H_5OH + 3HNO_3 \text{ (conc.)} \xrightarrow{\Delta} C_6H_2(NO_2)_3OH + 3H_2O$$

The product formed is 2,4,6-trinitrophenol (Picric acid).

Step 2: Comparing products based on concentration.

- Dilute HNO_3 → *o*-Nitrophenol + *p*-Nitrophenol - Concentrated HNO_3 → 2,4,6-Trinitrophenol (Picric acid)

Therefore, heating phenol with concentrated HNO_3 gives Picric acid.

Hence, the correct option is (C).

Quick Tip: - Dilute HNO_3 + Phenol → Mono-nitrophenols (*o*- and *p*-) - Concentrated HNO_3 + Phenol → Tri-nitrophenol (Picric acid)

9. The products of the following reaction are :

$$C_6H_5-CH_2-O-C_6H_5 \xrightarrow{HI} \text{Products}$$

(i) $C_6H_5-CH_2I$ (ii) C_6H_5-OH (iii) $C_6H_5-OCH_3$

(A) (i) and (ii)

(B) (i) and (iii)

(C) (ii) and (iii)

(D) (i), (ii) and (iii)

Correct Answer: (A) (i) and (ii)

Solution:

Concept: Cleavage of alkyl aryl ethers or benzyl aryl ethers with hydrogen halides (HI) proceeds via nucleophilic attack of iodide ion (I^-).

When an ether contains a benzyl group ($C_6H_5-CH_2-$) and a phenyl group (C_6H_5-), the bond cleavage takes place such that the stable benzyl carbocation or benzyl species forms benzyl iodide, while the oxygen atom remains attached to the benzene ring due to partial double bond character arising from resonance in phenol:

$$C_6H_5-CH_2-O-C_6H_5 + HI \rightarrow C_6H_5-CH_2I + C_6H_5-OH$$

Step 1: Protonation of the ether oxygen.

The ether oxygen atom is protonated by HI:

$$C_6H_5-CH_2-O-C_6H_5 + H^+ \rightarrow C_6H_5-CH_2-\overset{+}{O}H-C_6H_5$$

Step 2: Nucleophilic cleavage by iodide ion (I^-).

The $C_{sp^3}-O$ bond (benzyl carbon-oxygen bond) is much weaker than the $C_{sp^2}-O$ bond (aryl carbon-oxygen bond) because: 1. The $C_{aryl}-O$ bond has partial double bond character due to resonance with the benzene ring. 2. The benzyl carbocation ($C_6H_5CH_2^+$) formed during S_N1 cleavage is exceptionally stable due to resonance delocalization.

Thus, I^- attacks the benzyl carbon atom:

$$C_6H_5-CH_2-\overset{+}{O}H-C_6H_5 + I^- \rightarrow C_6H_5-CH_2I \text{ (i)} + C_6H_5-OH \text{ (ii)}$$

Step 3: Identifying the products.

- Product (i) = Benzyl iodide ($C_6H_5-CH_2I$) - Product (ii) = Phenol (C_6H_5-OH)

Therefore, the products of the reaction are (i) and (ii).

Hence, the correct option is (A).

Quick Tip: In benzyl aryl ethers ($Ar-O-CH_2Ph$), treatment with HI always yields Phenol (Ar-OH) and Benzyl Iodide ($PhCH_2I$) because the $C_{aryl}-O$ bond is too strong to break.

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10. The quantity of electricity in Faraday, required to reduce 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+} is :

(A) 4F

(B) 3F

(C) 6F

(D) 5F

Correct Answer: (C) 6F

Solution:

Concept: According to Faraday's laws of electrolysis, the reduction of 1 mole of an ion requires n Faradays of electricity, where n is the total number of moles of electrons gained in the balanced reduction half-reaction.

Step 1: Determining the oxidation states of chromium.

- In dichromate ion ($Cr_2O_7^{2-}$): Let x be the oxidation state of Cr.

$$2x + 7(-2) = -2 \implies 2x - 14 = -2 \implies 2x = +12 \implies x = +6$$

So, each Cr atom has an oxidation state of +6. - In Cr^{3+}: The oxidation state of Cr is +3.

Step 2: Writing the balanced reduction half-reaction in acidic medium.

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

Step 3: Calculating the total moles of electrons transferred.

From the balanced equation: - 1 mole of $Cr_2O_7^{2-}$ requires 6 moles of electrons ($6e^-$) for com-

plete reduction to 2 moles of Cr^{3+}. - Since 1 mole of electrons = 1 Faraday (F) of electricity:

$$\text{Electricity required} = 6\ \text{F}$$

Hence, the correct option is (C).

Quick Tip: Change in oxidation state for $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$: Change per Cr $= 6-3 = 3$. Since there are 2 Cr atoms in dichromate: Total electrons $= 2 \times 3 = 6e^- = 6$F.

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11. Which of the following elements exhibits maximum number of oxidation states ?

(A) Scandium

(B) Zinc

(C) Manganese

(D) Cobalt

Correct Answer: (C) Manganese

Solution:

Concept: In the $3d$ transition series, the number of oxidation states shown by an element increases up to the middle of the series and then decreases. This is because maximum number of oxidation states is exhibited by the element having the maximum number of unpaired electrons in $(n-1)d$ and ns subshells combined.

Step 1: Writing electronic configurations and possible oxidation states for each element.

1. Scandium (Sc, $Z = 21$): - Electronic configuration: $[Ar]3d^1 4s^2$ - Oxidation states: +3 (only 1 oxidation state).

2. Zinc (Zn, $Z = 30$): - Electronic configuration: $[Ar]3d^{10} 4s^2$ - Oxidation states: +2 (only 1 oxidation state).

3. Manganese (Mn, $Z = 25$): - Electronic configuration: $[Ar]3d^5 4s^2$ - Oxidation states: $+2, +3, +4, +5, +6, +7$ (6 oxidation states).

4. Cobalt (Co, $Z = 27$): - Electronic configuration: $[Ar]3d^7 4s^2$ - Oxidation states: $+2, +3, +4$ (3 oxidation states).

Step 2: Comparing the number of oxidation states.

Manganese (Mn) shows the maximum number of oxidation states ranging from +2 to +7 due

to the availability of 5 unpaired electrons in the $3d$ subshell and 2 electrons in the $4s$ subshell. Hence, the correct option is (C).

Quick Tip: In the $3d$ series, Manganese (Mn) has maximum unpaired electrons ($3d^5 4s^2$) and shows the maximum number of oxidation states (from +2 to +7).

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12. Which of the following reactions is used for the preparation of Aniline ?

(A) Reaction of ethanolic NH_3 with C_6H_5Cl

(B) Reaction of Nitrobenzene with Hydrogen gas in presence of finely divided Nickel

(C) Reaction of Benzamide with $LiAlH_4$

(D) Reaction of Benzonitrile with $LiAlH_4$

Correct Answer: (B) Reaction of Nitrobenzene with Hydrogen gas in presence of finely divided Nickel

Solution:

Concept: Aniline ($C_6H_5NH_2$) is an aromatic primary amine. It can be conveniently prepared by the catalytic reduction of nitrobenzene using molecular hydrogen in the presence of finely divided transition metal catalysts such as Nickel (Ni), Palladium (Pd), or Platinum (Pt).

Step 1: Analyzing Reaction (B).

Reduction of nitrobenzene with H_2 gas in the presence of finely divided Nickel catalyst:

$$C_6H_5NO_2 + 3H_2 \xrightarrow{Ni\ /\ \Delta} C_6H_5NH_2 + 2H_2O$$

This is a standard industrial and laboratory method for preparing aniline in high yield.

Step 2: Evaluating why other options are unsuitable or yield different products.

- Option (A): Reaction of C_6H_5Cl with ethanolic NH_3 does not readily yield aniline under mild conditions because chlorobenzene has partial double bond character due to resonance and does not undergo nucleophilic substitution easily. - Option (C): Reaction of benzamide ($C_6H_5CONH_2$) with $LiAlH_4$ yields benzylamine ($C_6H_5CH_2NH_2$), not aniline. - Option (D): Reaction of benzonitrile (C_6H_5CN) with $LiAlH_4$ yields benzylamine ($C_6H_5CH_2NH_2$), not aniline.

Therefore, catalytic reduction of nitrobenzene with H_2/Ni directly forms aniline.

Hence, the correct option is (B).

Quick Tip: - Nitrobenzene + $H_2/Ni \rightarrow$ Aniline ($C_6H_5NH_2$) - Benzamide + $LiAlH_4 \rightarrow$ Benzylamine ($C_6H_5CH_2NH_2$)

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13. Assertion (A) : Out of $[Co(en)_3]^{3+}$ and $[Co(CN)_6]^{3-}$, coordination compound $[Co(en)_3]^{3+}$ is a more stable complex.

Reason (R) : Ethane-1,2-diamine is a chelating ligand.

(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.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept: The stability of coordination complexes is significantly enhanced by the chelate effect . A chelate complex is formed when a multidentate (bidentate or polydentate) ligand binds to a single central metal ion through two or more donor atoms, forming a ring structure. Chelate complexes are extraordinarily more stable than similar complexes containing unidentate ligands due to favorable entropy factors ($\Delta S^\circ > 0$).

Step 1: Evaluating Assertion (A).

In $[Co(en)_3]^{3+}$, ethane-1,2-diamine (en) is a bidentate ligand, whereas in $[Co(CN)_6]^{3-}$, cyanide (CN^-) is a unidentate ligand. The complex $[Co(en)_3]^{3+}$ forms three five-membered chelate rings around the cobalt ion. Due to the chelate effect, $[Co(en)_3]^{3+}$ exhibits greater thermodynamic stability than $[Co(CN)_6]^{3-}$. Thus, Assertion (A) is true .

Step 2: Evaluating Reason (R).

Ethane-1,2-diamine ($H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$) possesses two nitrogen donor atoms capable of binding to the central metal ion simultaneously, making it a bidentate chelating ligand. Thus, Reason (R) is true .

Step 3: Determining if Reason (R) correctly explains Assertion (A).

The presence of the chelating ligand (ethane-1,2-diamine) directly explains why $[Co(en)_3]^{3+}$ is a more stable complex than $[Co(CN)_6]^{3-}$. Therefore, Reason (R) is the correct explanation

for Assertion (A).

Hence, the correct option is (A).

Chelate Effect: Complexes formed by bidentate/polydentate ligands are inherently more stable than those formed by unidentate ligands due to ring formation and entropy gain.

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14. Assertion (A) : Phosphorus halides are preferred over thionyl chloride for the preparation of alkyl halides from alcohols.

Reason (R) : Reaction of alcohols with thionyl chloride forms pure alkyl halides.

(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.

Correct Answer: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept: Alcohols react with thionyl chloride ($SOCl_2$) as well as phosphorus halides (PCl_3, PCl_5) to give alkyl chlorides:

$$\text{R-OH} + SOCl_2 \rightarrow \text{R-Cl} + SO_2(g)\uparrow + HCl(g)\uparrow$$

$$3\text{R-OH} + PCl_3 \rightarrow 3\text{R-Cl} + H_3PO_3$$

Thionyl chloride ($SOCl_2$) is strongly preferred over phosphorus halides for preparing alkyl chlorides because the side products formed (SO_2 and HCl) are both gases that escape easily, leaving behind pure alkyl chloride without requiring tedious purification steps.

Step 1: Evaluating Assertion (A).

Assertion (A) states that phosphorus halides are preferred over thionyl chloride. This statement is false , because thionyl chloride ($SOCl_2$) is actually preferred over phosphorus halides.

Step 2: Evaluating Reason (R).

Reason (R) states that the reaction of alcohols with thionyl chloride forms pure alkyl halides. This statement is true , because the gaseous side products (SO_2 and HCl) escape from the

reaction mixture automatically, yielding pure alkyl chloride.

Step 3: Conclusion.

Since Assertion (A) is false and Reason (R) is true, option (D) is the correct choice.

Hence, the correct option is (D).

Quick Tip: $SOCl_2$ is the best reagent for converting alcohols to alkyl chlorides because both by-products (SO_2 and HCl) are gaseous and leave pure alkyl chloride behind.

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15. Assertion (A) : Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.

Reason (R) : Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to carboxyl group.

(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.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept: Friedel-Crafts reactions (alkylation and acylation) involve electrophilic aromatic substitution on the benzene ring using a Lewis acid catalyst such as anhydrous $AlCl_3$. Substituents on the benzene ring affect Friedel-Crafts reactivity significantly: 1. Strong electron-withdrawing groups (deactivating groups) reduce the electron density on the aromatic ring, making it insufficiently nucleophilic to react with carbocation electrophiles. 2. Lewis acidic catalysts like $AlCl_3$ form strong coordination complexes with basic or lone-pair-bearing functional groups (like $-COOH$), rendering the catalyst inactive and further deactivating the ring.

Step 1: Evaluating Assertion (A).

Aromatic carboxylic acids (such as benzoic acid) do not undergo Friedel-Crafts alkylation or acylation reactions. Thus, Assertion (A) is true .

Step 2: Evaluating Reason (R).

The carboxyl group ($-COOH$) is a strongly electron-withdrawing group via resonance ($-M$) and inductive ($-I$) effects, which strongly deactivates the benzene ring toward electrophilic substitution. Additionally, the Lewis acid catalyst anhydrous $AlCl_3$ reacts with the lone pair on the oxygen atom of the carboxyl group to form a complex:

$$\text{Ar-COOH} + AlCl_3 \rightarrow \text{Ar-COOH} \cdot AlCl_3 \text{ (Complex)}$$

This complexation ties up the Lewis acid catalyst and imparts a formal positive charge near the ring, deactivating the benzene ring even further. Thus, Reason (R) is true .

Step 3: Determining if Reason (R) correctly explains Assertion (A).

Reason (R) gives the precise molecular explanation for why aromatic carboxylic acids fail to undergo Friedel-Crafts reactions.

Hence, the correct option is (A).

Quick Tip: Aromatic compounds with strongly deactivating groups ($-NO_2, -COOH, -CHO, -SO_3H$) or lone pairs that form complexes with $AlCl_3$ (like $-NH_2$) do not undergo Friedel-Crafts reactions.

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16. Assertion (A) : The volume of an ideal solution is equal to the sum of the volumes of the two components, i.e., $\Delta_{mix}V = 0$.

Reason (R) : The intermolecular forces of attraction between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules.

(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.

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept: An ideal solution is defined as a solution that obeys Raoult's law over the entire range of concentrations at all temperatures. For an ideal solution consisting of components A and B:

1. Enthalpy of mixing is zero: $\Delta_{mix}H = 0$.
2. Volume change of mixing is zero: $\Delta_{mix}V = 0$.
3. The intermolecular attractive forces between solute-solvent molecules ($A-B$) are nearly equal to the intermolecular forces between solute-solute ($B-B$) and solvent-solvent ($A-A$) molecules:

$$F_{A-B} \approx F_{A-A} \approx F_{B-B}$$

Step 1: Evaluating Assertion (A).

For an ideal solution, there is no change in total volume upon mixing the components, so $\Delta_{mix}V = 0$. The total volume is exactly equal to the sum of the initial volumes of the individual components. Thus, Assertion (A) is true .

Step 2: Evaluating Reason (R).

Reason (R) states that intermolecular forces between solute-solvent molecules are weaker than solute-solute and solvent-solvent interactions. - If F_{A-B} were weaker than F_{A-A} and F_{B-B}, the solution would show positive deviation from Raoult's law, with $\Delta_{mix}V > 0$ and $\Delta_{mix}H > 0$. - For an ideal solution , the solute-solvent interactions must be nearly equal to the solute-solute and solvent-solvent interactions. Thus, Reason (R) is false .

Step 3: Conclusion.

Since Assertion (A) is true and Reason (R) is false, option (C) is the correct choice.

Hence, the correct option is (C).

Quick Tip: Properties of Ideal Solutions: - $\Delta_{mix}H = 0$ - $\Delta_{mix}V = 0$ - Intermolecular forces: $A-B \approx A-A \approx B-B$

17.(a)(i) Why do Zr and Hf exhibit similar properties?

Solution:

Concept: Elements belonging to the same group generally exhibit similar chemical properties due to having identical valence shell electronic configurations. However, $4d$ series element Zirconium (Zr, atomic number 40) and $5d$ series element Hafnium (Hf, atomic number 72) show extraordinarily close physical and chemical properties, including nearly identical atomic and ionic radii. This rare chemical twin behavior is primarily caused by the phenomenon

known as **Lanthanoid Contraction**.

Step 1: Understanding the atomic structure and Lanthanoid Contraction.

Between Zirconium (Zr, belonging to the $4d$ transition series) and Hafnium (Hf, belonging to the $5d$ transition series), the 14 lanthanoid elements (from Cerium $Z = 58$ to Lutetium $Z = 71$) are inserted into the periodic table. In these lanthanoid elements, electrons progressively fill the internal $4f$ subshell.

Step 2: Analyzing the shielding effect of $4f$ orbitals.

The spatial shapes of $4f$ orbitals are diffuse and complex. Consequently, electrons occupying $4f$ orbitals exert an extremely poor shielding (or screening) effect on outer shell electrons against the attraction of the nucleus.

Step 3: Effect on nuclear charge and atomic radii.

As the nuclear charge increases by 14 units from Zr to Hf, the weak screening provided by the added 14 f-electrons is insufficient to counterbalance the increased positive charge of the nucleus. As a result, the outer valence electrons experience a much stronger effective nuclear charge (Z_{eff}), pulling the outer shells closer to the nucleus.

Step 4: Comparison of radii and conclusion.

This contraction in atomic size across the lanthanoid series compensates for the expected size increase due to the addition of an extra principal shell when moving down the group from $4d$ to $5d$.

- Atomic radius of Zr $\approx$ 160 pm
- Atomic radius of Hf $\approx$ 159 pm
- Ionic radius of $Zr^{4+} \approx$ 79 pm
- Ionic radius of $Hf^{4+} \approx$ 78 pm

Because their ionic and atomic radii, as well as valence electron distributions, are virtually identical, Zr and Hf display nearly identical physical and chemical properties and occur together in nature.

Quick Tip: Remember: Lanthanoid contraction is caused by the poor shielding effect of $4f$ electrons, making $4d$ and $5d$ elements of the same group almost identical in atomic and ionic radii!

17.(a)(ii) "E° for Mn^{3+}/Mn^{2+} couple is more positive than that for Fe^{3+}/Fe^{2+}." Justify the

statement. [Atomic number : Mn = 25, Fe = 26]

Solution:

Concept: The standard reduction potential (E°) of a metal ion couple M^{3+}/M^{2+} reflects the thermodynamic feasibility of reducing a +3 oxidation state to a +2 oxidation state. A more positive E° value indicates a greater thermodynamic tendency for the triply charged cation (M^{3+}) to accept an electron and form the doubly charged cation (M^{2+}). This relative stability depends largely on the electronic configurations of the transition metal ions and the extra stability associated with half-filled (d^5) or fully-filled (d^{10}) subshells.

Step 1: Electronic configuration of Manganese species.

Manganese (Mn, $Z = 25$) has the ground-state electronic configuration:

$$\text{Mn} = [\text{Ar}]3d^5 4s^2$$

When Manganese loses electrons to form cations:

- Mn^{2+} ion configuration: $[\text{Ar}]3d^5$ (Half-filled d-subshell, exceptionally stable)
- Mn^{3+} ion configuration: $[\text{Ar}]3d^4$ (Unstable compared to d^5)

Step 2: Analyzing the Mn^{3+}/Mn^{2+} reduction couple.

The reduction half-reaction is given by:

$$\text{Mn}^{3+}(3d^4) + e^- \longrightarrow \text{Mn}^{2+}(3d^5)$$

Here, the change involves moving from an unstable $3d^4$ configuration to a highly stable, half-filled $3d^5$ configuration. Because $3d^5$ possesses high exchange energy and spherical symmetry, this reduction is thermodynamically extremely favorable. Hence, $E^\circ(Mn^{3+}/Mn^{2+})$ has a very high positive value (+1.57 V).

Step 3: Electronic configuration of Iron species.

Iron (Fe, $Z = 26$) has the ground-state electronic configuration:

$$\text{Fe} = [\text{Ar}]3d^6 4s^2$$

When Iron loses electrons to form cations:

- Fe^{2+} ion configuration: $[\text{Ar}]3d^6$
- Fe^{3+} ion configuration: $[\text{Ar}]3d^5$ (Half-filled d-subshell, exceptionally stable)

Step 4: Analyzing the Fe^{3+}/Fe^{2+} reduction couple.

The reduction half-reaction is given by:

$$Fe^{3+}(3d^5) + e^- \longrightarrow Fe^{2+}(3d^6)$$

In this case, Fe^{3+} already possesses the extra stable half-filled $3d^5$ configuration. Reducing Fe^{3+} to Fe^{2+} requires breaking this exceptionally stable configuration to form a less stable $3d^6$ ion. Therefore, Fe^{3+} is very stable and resists reduction, resulting in a much lower positive reduction potential ($E^\circ(Fe^{3+}/Fe^{2+}) = +0.77$ V).

Step 5: Conclusion.

Since converting $Mn^{3+} \rightarrow Mn^{2+}$ leads to a stable $3d^5$ state while converting $Fe^{3+} \rightarrow Fe^{2+}$ destroys a stable $3d^5$ state, $E^\circ(Mn^{3+}/Mn^{2+})$ is significantly more positive than $E^\circ(Fe^{3+}/Fe^{2+})$.

Quick Tip: Always analyze the gain or loss of electrons in terms of d^5 (half-filled) and d^{10} (fully-filled) electronic stability!

17.(b)(i) Which element in $3d$ series of transition elements does not exhibit variable oxidation states ? Give reason.

Solution:

Concept: Transition elements generally show variable oxidation states because the energy difference between their $(n-1)d$ and ns orbitals is very small, allowing electrons from both subshells to participate in chemical bonding. However, an exception occurs at the end of the $3d$ transition series.

Step 1: Identifying the element.

The element in the $3d$ series of transition elements that does not exhibit variable oxidation states is Scandium (Sc) (Atomic number $Z = 21$).

(Note: Zinc (Zn) also exhibits only +2 oxidation state, but Scandium is the standard transition metal with a single positive state +3, whereas Zinc is often categorized as a non-typical transition element due to completely filled d^{10} shell in ground and common oxidation state).

Step 2: Analyzing the electronic configuration of Scandium.

Scandium ($Z = 21$) has the following ground-state electronic configuration:

$$Sc = [Ar]3d^1 4s^2$$

Step 3: Reasoning behind single oxidation state.

Scandium has 3 valence electrons (2 in the $4s$ orbital and 1 in the $3d$ orbital).

- When Scandium loses these three valence electrons (2 from $4s$ and 1 from $3d$), it forms the Sc^{3+} cation:
$$Sc^{3+} = [Ar] \text{ or } [Ne]3s^2 3p^6$$
- The resulting Sc^{3+} ion achieves an extraordinarily stable noble gas electronic configuration (that of Argon).
- Scandium does not form stable compounds in +1 or +2 oxidation states because losing all 3 electrons provides immense stabilization energy (high lattice or hydration energy) that easily compensates for the sum of the first three ionization enthalpies.
- Furthermore, after losing 3 electrons, no more d-electrons are available for variable oxidation states.

Step 4: Conclusion.

Thus, Scandium (Sc) exhibits only one oxidation state, which is +3, and does not show variable oxidation states.

Quick Tip: Scandium ($Z = 21$) exhibits only +3 oxidation state because losing all 3 valence electrons ($3d^1 4s^2$) yields the stable Argon core!

17.(b)(ii) Explain why Cu^+ is colourless in aqueous solution, whereas Cu^{2+} is coloured.

Solution:

Concept: The color of transition metal ions in aqueous solution is attributed to Crystal Field Theory (CFT). When ligands (such as water molecules) surround a central transition metal ion, they split the degenerate d-orbitals into sets of different energy levels (t_{2g} and e_g). If the d-subshell is partially filled (d^1 to d^9), an electron from a lower energy d-orbital can absorb specific wavelengths of visible light and undergo a transition to a higher energy d-

orbital (known as a d-d transition). The transmitted or reflected light gives the solution its characteristic complementary color.

Step 1: Electronic configuration and d-d transition in Cu^{+}.

Copper (Cu, $Z = 29$) has the ground-state electronic configuration:

$$Cu = [Ar]3d^{10}4s^{1}$$

For the cuprous ion (Cu^{+}), removing one electron yields:

$$Cu^{+} = [Ar]3d^{10}$$

- The $3d$ subshell in Cu^{+} is completely filled with 10 electrons.
- Since all d-orbitals are completely filled, there are no vacant or singly occupied d-orbitals available for an electron to jump into upon absorbing light.
- Thus, no d-d transitions can occur in Cu^{+}. As a result, it does not absorb light in the visible spectrum and appears colourless .

Step 2: Electronic configuration and d-d transition in Cu^{2+}.

For the cupric ion (Cu^{2+}), removing two electrons yields:

$$Cu^{2+} = [Ar]3d^{9}$$

- The $3d$ subshell of Cu^{2+} is incompletely filled ($3d^{9}$).
- In an aqueous environment, water molecules act as ligands, splitting the five $3d$ orbitals into t_{2g} and e_g levels.
- Because a vacancy exists in the higher energy d-orbitals, an electron can absorb light in the red region of the visible spectrum and undergo a d-d transition from t_{2g} to e_g.
- The transmitted light is complementary to the absorbed red light, making aqueous Cu^{2+} ions appear blue (coloured).

Step 3: Conclusion.

Cu^{+} has a fully filled $3d^{10}$ configuration with no possible d-d transitions (colourless), whereas Cu^{2+} has an unfilled $3d^{9}$ configuration that permits d-d transitions (coloured).

Quick Tip: Color in transition metal complexes requires an incompletely filled d-shell ($3d^1$ to $3d^9$) to enable d-d transitions. d^0 and d^{10} ions are always colourless!

---

18. A reaction A → B follows second order kinetics. How will the rate of reaction be affected if the concentration of (i) A is increased by three times, and (ii) A is reduced to half ?

Solution:

Concept: For a chemical reaction A → B following second-order kinetics with respect to reactant A, the rate law equation is expressed as:

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

where r is the reaction rate, k is the second-order rate constant, and [A] represents the molar concentration of reactant A.

Step 1: Establishing the initial rate expression.

Let the initial concentration of reactant A be $[\text{A}]_1 = a$. The initial rate of reaction, r_1, is given by:

$$r_1 = ka^2 \quad \cdots(1)$$

Step 2: Case (i): Concentration of A is increased by three times.

When the concentration of A is increased threefold:

$$[\text{A}]_2 = 3a$$

Substitute $[\text{A}]_2$ into the rate law to find the new rate r_2:

$$r_2 = k(3a)^2 = k(9a^2) = 9(ka^2)$$

From equation (1), substitute $r_1 = ka^2$:

$$r_2 = 9r_1$$

Conclusion for (i): The rate of reaction increases by 9 times (or becomes 9 times the initial rate).

Step 3: Case (ii): Concentration of A is reduced to half.

When the concentration of A is halved:

$$[A]_3 = \frac{a}{2}$$

Substitute $[A]_3$ into the rate law to find the new rate r_3:

$$r_3 = k\left(\frac{a}{2}\right)^2 = k\left(\frac{a^2}{4}\right) = \frac{1}{4}(ka^2)$$

From equation (1), substitute $r_1 = ka^2$:

$$r_3 = \frac{1}{4}r_1$$

Conclusion for (ii): The rate of reaction decreases to $\frac{1}{4}$th of its initial value (or decreases by a factor of 4).

Quick Tip: For an n^{th} order reaction, scaling the concentration by a factor of x changes the rate by a factor of x^n. For second order ($n = 2$), $3^2 = 9$ and $(1/2)^2 = 1/4$.

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19. Write the reactions taking place at anode and cathode in a lead storage battery, when it is in use.

Solution:

Concept: A lead storage battery is a secondary electrochemical cell (rechargeable). When the battery is in use (discharging mode), it functions as a voltaic/galvanic cell, converting chemical energy into electrical energy through spontaneous redox reactions.

- **Anode:** Spongy Lead (Pb) grid where oxidation occurs.
- **Cathode:** Grid of lead filled with Lead Dioxide (PbO_2) where reduction occurs.
- **Electrolyte:** Aqueous solution of sulfuric acid (H_2SO_4, approximately 38% by mass with density 1.30 g/cm^3).

Step 1: Oxidation reaction occurring at the Anode during discharging.

At the negative terminal (anode), elemental lead (Pb) loses two electrons to get oxidized to Pb^{2+} ions, which immediately precipitate with sulfate ions (SO_4^{2-}) from the electrolyte to form

solid lead sulfate ($PbSO_4$):

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

Step 2: Reduction reaction occurring at the Cathode during discharging.

At the positive terminal (cathode), lead dioxide (PbO_2) is reduced in the presence of protons (H^+) and sulfate ions (SO_4^{2-}), accepting electrons to form lead sulfate ($PbSO_4$) and water:

$$\text{Cathode Reaction: } PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)$$

Step 3: Overall cell reaction during discharging.

By adding the two individual electrode reactions, we get the overall discharging chemical equation:

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

(Note: As the cell delivers current, sulfuric acid is consumed and solid lead sulfate is deposited on both electrodes).

Quick Tip: During discharge, both electrodes (Pb and PbO_2) get converted into solid $PbSO_4$, and H_2SO_4 is consumed!

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20. 10 g of a non-volatile solute is dissolved in 200 g of water to make a solution. It has a vapour pressure of 31.84 mm Hg at 308 K. Calculate the molar mass of the solute. [Given : Vapour pressure of pure water at 308 K = 32 mm Hg]

Solution:

Concept: According to Raoult's Law for dilute solutions containing a non-volatile solute, the relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution:

$$\frac{p^\circ - p}{p^\circ} = \chi_{\text{solute}} = \frac{n_2}{n_1 + n_2}$$

For a very dilute solution where $n_2 \ll n_1$, $n_1 + n_2 \approx n_1$, simplifying the expression to:

$$\frac{p^\circ - p}{p^\circ} \approx \frac{n_2}{n_1} = \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

where:

- p° = Vapour pressure of pure solvent (H_2O) = 32 mm Hg
- p = Vapour pressure of solution = 31.84 mm Hg
- w_2 = Mass of non-volatile solute = 10 g
- M_2 = Molar mass of solute (to be calculated)
- w_1 = Mass of solvent (H_2O) = 200 g
- M_1 = Molar mass of solvent (H_2O) = 18 g mol^{-1}

Step 1: Calculate the relative lowering of vapour pressure.

$$p^\circ - p = 32 - 31.84 = 0.16 \text{ mm Hg}$$

$$\frac{p^\circ - p}{p^\circ} = \frac{0.16}{32}$$

Step 2: Substitute values into the Raoult's law formula.

Using the formula:

$$\frac{p^\circ - p}{p^\circ} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$\frac{0.16}{32} = \frac{10 \times 18}{M_2 \times 200}$$

Step 3: Simplify the algebraic equation to solve for M_2.

Simplify the left-hand side fraction:

$$\frac{0.16}{32} = \frac{16}{3200} = \frac{1}{200}$$

Now equate both sides:

$$\frac{1}{200} = \frac{180}{M_2 \times 200}$$

Cancel 200 from the denominators on both sides:

$$1 = \frac{180}{M_2} \implies M_2 = 180 \text{ g mol}^{-1}$$

Step 4: Verification via exact mole fraction formulation.

Using full mole fraction formula without approximation:

$$\frac{p^\circ - p}{p^\circ} = \frac{n_2}{n_1 + n_2} \implies \frac{0.16}{32} = \frac{n_2}{\frac{200}{18} + n_2}$$

$$\frac{1}{200} = \frac{n_2}{11.111 + n_2} \implies 11.111 + n_2 = 200n_2 \implies 199n_2 = 11.111$$

$$n_2 = \frac{11.111}{199} \approx 0.05583 \text{ mol}$$

$$M_2 = \frac{w_2}{n_2} = \frac{10}{0.05583} \approx 179.1 \text{ g mol}^{-1} \approx 180 \text{ g mol}^{-1}$$

Both methods confirm the molar mass of the solute is approximately 180 g mol^{-1}.

Quick Tip: Always double check units! Molar mass of water is 18 g/mol. Simplify fractions prior to cross-multiplication to eliminate calculation errors.

21.(a) Draw the structure of major monohalo product in the following reaction:

$$\text{Cyclohexene} + \text{Br}_2 \xrightarrow{\text{Heat}}$$

Solution:

Concept: When an alkene containing allylic hydrogens reacts with bromine (Br_2) at high temperatures (or in the presence of UV light), allylic substitution occurs rather than electrophilic addition across the double bond. The allylic free radical formed as an intermediate is resonance-stabilized.

Step 1: Identify the reaction conditions and mechanism type.

The given substrate is Cyclohexene . It contains double-bonded carbon atoms ($C1, C2$) and allylic carbons ($C3, C6$). Under heat (Δ) or photochemical conditions, Br_2 homolytically cleaves to form bromine free radicals ($Br^\bullet$).

Step 2: Free radical substitution at the allylic position.

A bromine radical abstracts a hydrogen atom from the allylic position ($C3$) of cyclohexene to form a stable 2-cyclohexenyl free radical:

$$\text{Cyclohexene} + \text{Br}^\bullet \longrightarrow \text{3-cyclohexenyl radical} + \text{HBr}$$

The allylic radical then reacts with another Br_2 molecule to yield 3-bromocyclohexene .

Step 3: Structure of the major product.

The major product formed is 3-Bromocyclohexene .

Structural Representation:

$$*6(- = -(-Br) - - =) \quad \text{or} \quad \text{3-Bromocyclohexene}$$

Chemical Reaction Equation:

$$\text{Cyclohexene} + Br_2 \xrightarrow{\text{Heat}} \text{3-Bromocyclohexene} + HBr$$

Quick Tip: High heat / UV light favors allylic free radical substitution over addition across the double bond!

21.(b) Draw the structure of major monohalo product in the following reaction:

$$\text{2-(hydroxymethyl)phenol} + SOCl_2 \longrightarrow$$

Solution:

Concept: Thionyl chloride ($SOCl_2$) is a specific reagent used to convert alcoholic hydroxyl groups ($-CH_2OH$) into alkyl chlorides ($-CH_2Cl$). Phenolic hydroxyl groups ($-OH$ attached directly to an aromatic benzene ring) do not react with $SOCl_2$ under normal conditions because the $C(sp^2)-O$ bond in phenol has partial double bond character due to resonance stabilization.

Step 1: Differentiating alcoholic vs phenolic $-OH$ groups.

The starting material is 2-hydroxybenzyl alcohol (salicyl alcohol):

- **Phenolic $-OH$ group:** Directly attached to the aromatic benzene ring. Strong partial double bond character; extremely difficult to cleave.
- **Aliphatic/Alcoholic $-CH_2OH$ group:** Attached to an sp^3 hybridized carbon atom side chain. Easily undergoes nucleophilic substitution.

Step 2: Reaction with Thionyl Chloride ($SOCl_2$).

Thionyl chloride selectively replaces the aliphatic $-OH$ group with a chlorine atom ($-Cl$),

releasing $SO_2(g)$ and $HCl(g)$ as volatile byproducts. The phenolic $-OH$ remains completely intact.

Step 3: Structure of the major product.

The major monohalo product is 2-(chloromethyl)phenol .

Chemical Reaction Equation:

$$C_6H_4(OH)(CH_2OH) + SOCl_2 \longrightarrow C_6H_4(OH)(CH_2Cl) + SO_2 \uparrow + HCl \uparrow$$

Quick Tip: Phenolic $-OH$ groups NEVER react with $SOCl_2$, PCl_5, or HCl to give chlorobenzene due to resonance double bond character!

22.(a)(i) Give a chemical test to distinguish between Propanal and Propanone.

Solution:

Concept: Propanal (CH_3CH_2CHO) is an aliphatic aldehyde, whereas Propanone (CH_3COCH_3) is a ketone. Aldehydes are easily oxidized to carboxylic acids even by mild oxidizing agents like Tollens' reagent or Fehling's solution , whereas ketones do not react with these mild oxidizing agents.

Step 1: Test Selection: Tollens' Test (Silver Mirror Test).

Tollens' reagent is an ammoniacal silver nitrate solution, $[Ag(NH_3)_2]^+OH^-$.

Step 2: Procedure and Observation for Propanal.

When Propanal is warmed with freshly prepared Tollens' reagent in a clean test tube:

- Propanal is oxidized to propanoate ion ($CH_3CH_2COO^-$).
- Silver ions (Ag^+) are reduced to metallic silver (Ag), forming a shiny silver mirror on the inner wall of the test tube.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \xrightarrow{\Delta} CH_3CH_2COO^- + 2Ag \downarrow (\text{Silver Mirror}) + 4NH_3 + 2H_2O$$

Step 3: Observation for Propanone.

Propanone, being a ketone, does not have a hydrogen atom directly bonded to the carbonyl carbon. It does not reduce Tollens' reagent.

$$CH_3COCH_3 + \text{Tollens' Reagent} \longrightarrow \text{No Reaction (No Silver Mirror formed)}$$

Alternative Test: Fehling's Test

- Propanal gives a red precipitate of Cuprous Oxide (Cu_2O) when heated with Fehling's solution.
- Propanone shows no reaction .

Quick Tip: Tollens' test and Fehling's test give positive results for all aldehydes (Propanal) but negative results for ketones (Propanone)!

22.(a)(ii) Which of the given acids is stronger and why ?

$$F_3C-C_6H_4-COOH \quad \text{or} \quad H_3C-C_6H_4-COOH$$

Solution:

Concept: The acidity of a substituted benzoic acid depends on the electronic effect (inductive and resonance/hyperconjugation effects) of the substituent group attached to the aromatic ring. Electron-withdrawing groups (EWGs) stabilize the carboxylate anion formed after ionization, increasing acidic strength. Electron-donating groups (EDGs) destabilize the carboxylate anion, decreasing acidic strength.

Step 1: Identify the nature of substituents.

- **In 4-(trifluoromethyl)benzoic acid ($F_3C-C_6H_4-COOH$):** The trifluoromethyl group ($-CF_3$) contains three highly electronegative fluorine atoms. It exerts a powerful strong electron-withdrawing inductive effect ($-I$ effect) .
- **In 4-methylbenzoic acid ($H_3C-C_6H_4-COOH$):** The methyl group ($-CH_3$) exerts an electron-donating inductive effect ($+I$ effect) as well as hyperconjugation .

Step 2: Effect on carboxylate anion stability.

Upon ionization in water, both acids release a proton (H^+) to form their corresponding carboxylate conjugate bases:

$$\text{Ar-COOH} \rightleftharpoons \text{Ar-COO}^- + H^+$$

- The strong $-I$ effect of the $-CF_3$ group pulls electron density away from the aromatic

ring and the carboxylate group, dispersing the negative charge on $-COO^-$. This stabilizes the carboxylate anion, driving the equilibrium forward to release more H^+ ions.

- Conversely, the $+I$ and hyperconjugative electron-donating nature of the $-CH_3$ group intensifies the negative charge on $-COO^-$, destabilizing the conjugate base and making it less acidic.

Step 3: Conclusion.

Therefore, $F_3C-C_6H_4-COOH$ (4-trifluoromethylbenzoic acid) is a significantly stronger acid than $H_3C-C_6H_4-COOH$ (4-methylbenzoic acid).

Quick Tip: Acidic strength $\propto$ Stability of conjugate base $\propto$ Electron-Withdrawing Groups $(-I, -M)$.

22.(a)(iii) Complete the given reaction sequence :

$$CH_3CH_2CH_2COOC_2H_5 \xrightarrow{NaOH} A + C_2H_5OH \xrightarrow{H_3O^+} B$$

Solution:

Concept: Ester hydrolysis under basic conditions (saponification) cleaves the ester bond to yield the sodium salt of a carboxylic acid and an alcohol. Subsequent acidification converts the carboxylate salt into the corresponding free carboxylic acid.

Step 1: Base-catalyzed hydrolysis (Saponification) to find compound A.

The given ester is Ethyl butyrate (ethyl butanoate): $CH_3CH_2CH_2COOC_2H_5$. Reacting ethyl butyrate with aqueous sodium hydroxide (NaOH) causes alkaline hydrolysis:

$$CH_3CH_2CH_2COOC_2H_5 + NaOH \longrightarrow CH_3CH_2CH_2COONa + C_2H_5OH$$

Thus, Compound A is Sodium butanoate ($CH_3CH_2CH_2COONa$).

Step 2: Acidification to find compound B.

When Sodium butyrate (A) is acidified with hydronium ions (H_3O^+):

$$CH_3CH_2CH_2COONa + H_3O^+ \longrightarrow CH_3CH_2CH_2COOH + Na^+ + H_2O$$

Thus, Compound B is Butanoic acid ($CH_3CH_2CH_2COOH$).

Step 3: Summary of identified structures.

- A: $CH_3CH_2CH_2COONa$ (Sodium butanoate)
- B: $CH_3CH_2CH_2COOH$ (Butanoic acid)

Quick Tip: Ester + NaOH → Carboxylate salt + Alcohol. Acidification of the carboxylate salt produces the parent carboxylic acid!

22(b) An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives phthalic acid. Identify the compound. Write the reaction of this compound with Tollens' reagent and Cannizzaro reaction.

Solution:

Concept:

- **2,4-DNP Test:** Formation of a 2,4-dinitrophenylhydrazone derivative confirms the presence of a carbonyl group ($> C = O$), which could be either an aldehyde or a ketone.
- **Tollens' Test:** Reduction of Tollens' reagent ($[Ag(NH_3)_2]^+$) to form a silver mirror specifies that the carbonyl compound is an aldehyde ($-CHO$).
- **Cannizzaro Reaction:** Aldehydes lacking α-hydrogen atoms undergo self-oxidation and reduction (disproportionation) when treated with concentrated alkali (NaOH or KOH).
- **Vigorous Oxidation to Phthalic Acid:** Vigorous oxidation producing phthalic acid (benzene-1,2-dicarboxylic acid) indicates an ortho-disubstituted benzene ring where one substituent is an aldehyde group ($-CHO$) and the other substituent is an ethyl group ($-CH_2CH_3$).

Step 1: Identification of the organic compound.

1. Molecular formula given: $C_9H_{10}O$. 2. The compound forms a 2,4-DNP derivative, indicating it contains a carbonyl group ($-CHO$ or $> C = O$). 3. It reduces Tollens' reagent, which confirms that it is an aldehyde containing a $-CHO$ group. 4. It undergoes Cannizzaro reaction, which

proves that the aldehyde group is directly attached to a carbon atom with no α-hydrogens (i.e., attached directly to a benzene ring). 5. Vigorous oxidation yields phthalic acid (benzene-1,2-dicarboxylic acid). This confirms that two side chains are attached at the *ortho* positions (1,2-positions) on the benzene ring. 6. Deducting the benzene ring (C_6H_4) and the aldehyde group ($-CHO$) from $C_9H_{10}O$:

$$C_9H_{10}O - C_6H_4 - CHO = C_2H_5$$

Thus, the remaining substituent at the *ortho* position is an ethyl group ($-CH_2CH_3$).
Therefore, the organic compound is 2-ethylbenzaldehyde (or *o*-ethylbenzaldehyde).

Step 2: Reaction with Tollens' reagent.

2-Ethylbenzaldehyde reacts with Tollens' reagent ($[Ag(NH_3)_2]^+$) in an alkaline medium to form 2-ethylbenzoate ion along with a metallic silver mirror:

$$C_2H_5 - C_6H_4 - CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow C_2H_5 - C_6H_4 - COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O$$

Step 3: Cannizzaro reaction.

When 2-ethylbenzaldehyde is warmed with concentrated sodium hydroxide (NaOH), it undergoes disproportionation to yield 2-ethylbenzyl alcohol (reduction product) and sodium 2-ethylbenzoate (oxidation product):

$$2\left(C_2H_5 - C_6H_4 - CHO\right) \xrightarrow{\text{Conc. NaOH}} C_2H_5 - C_6H_4 - CH_2OH + C_2H_5 - C_6H_4 - COONa$$

Quick Tip: Remember: - Only aldehydes (not ketones) reduce Tollens' reagent. - Aldehydes without α-hydrogens undergo Cannizzaro reaction. - Formation of phthalic acid upon vigorous oxidation always points to 1,2-disubstituted (ortho) alkyl/acyl benzene derivatives!

23(a) Arrange the following compounds in the decreasing order of their acidic strength :

Phenol, 4-Nitrophenol, 2,4,6-Trinitrophenol

Solution:

Concept: The acidity of phenols depends on the stability of the phenoxide ion formed after the loss of a proton (H^+):

- Electron-withdrawing groups ($-I$ and $-R/-M$ effects), such as nitro groups ($-NO_2$), stabilize the negative charge on the phenoxide ion by delocalizing it, thereby significantly increasing the acidity.
- The greater the number of electron-withdrawing nitro groups attached at *ortho* and *para* positions relative to the $-OH$ group, the stronger is the acid.

Step 1: Analyzing the substituents in each compound.

1. **2,4,6-Trinitrophenol (Picric acid):** Contains three strongly electron-withdrawing nitro groups ($-NO_2$) at the 2, 4, and 6 positions (*ortho* and *para* positions). These groups stabilize the negative charge of the phenoxide ion through powerful resonance ($-R$) and inductive ($-I$) effects, making it an extremely strong acid. 2. **4-Nitrophenol:** Contains one electron-withdrawing nitro group ($-NO_2$) at the *para*-position. It stabilizes the phenoxide ion via resonance and inductive effects, making it significantly more acidic than unsubstituted phenol, but less acidic than 2,4,6-trinitrophenol. 3. **Phenol:** Has no substituent attached to the benzene ring. The phenoxide ion is stabilized solely by resonance with the aromatic ring. Thus, it is the least acidic among the three.

Step 2: Writing the decreasing order of acidic strength.

Comparing the stability of their corresponding conjugate bases:

$$\text{2,4,6-Trinitrophenol} > \text{4-Nitrophenol} > \text{Phenol}$$

Quick Tip: Acidity of substituted phenols: - Electron-Withdrawing Groups ($-NO_2, -CN, -COOH$) $\rightarrow$ Increase Acidity. - Electron-Releasing Groups ($-CH_3, -OCH_3$) $\rightarrow$ Decrease Acidity.

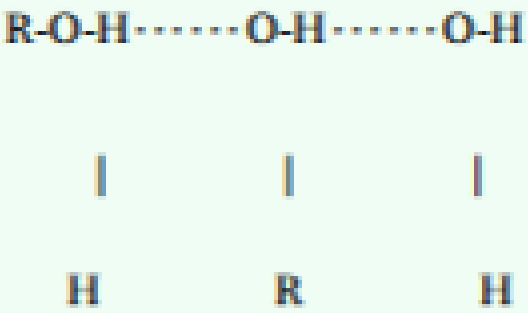
23(b) Why are alcohols more soluble in water than hydrocarbons of comparable molecular masses ?

Solution:

Concept: Solubility of an organic compound in water relies on its ability to form favorable intermolecular interactions with polar water molecules, specifically intermolecular hydrogen bonding .

Step 1: Analyzing the chemical structure of alcohols versus hydrocarbons.

1. **Alcohols (R-OH):** Contain a polar hydroxyl group (—OH). The strong electronegativity difference between oxygen and hydrogen creates a partial negative charge on oxygen (δ^-) and a partial positive charge on hydrogen (δ^+). 2. This polarity allows alcohol molecules to form strong intermolecular hydrogen bonds with water molecules (H_2O).



3. **Hydrocarbons (R-H):** Consist solely of carbon and hydrogen atoms with negligible electronegativity differences. They are strictly non-polar and can only form weak London dispersion forces. Hydrocarbons cannot form hydrogen bonds with water molecules.

Step 2: Conclusion.

Because energy is released during the formation of strong intermolecular hydrogen bonds between alcohol molecules and water molecules, the dissolution process is energetically favorable. Hydrocarbons cannot break the hydrogen bonds present between water molecules due to lack of strong interactions, making alcohols significantly more soluble in water than hydrocarbons of comparable molecular masses.

Quick Tip: Like dissolves like! Polar compounds capable of forming hydrogen bonds with water (such as lower alcohols, amines, and carboxylic acids) exhibit high solubility in aqueous media.

23(c) Name the reagent used in the oxidation of a primary unsaturated alcohol to an aldehyde.

Solution:

Concept: Oxidation of primary alcohols can lead either to aldehydes or carboxylic acids:

- Strong oxidizing agents (such as acidified $KMnO_4$ or $K_2Cr_2O_7$) oxidize primary alcohols completely into carboxylic acids and can also cleave or oxidize carbon-carbon double/triple bonds.
- Selective oxidizing agents are required to selectively convert a primary alcohol ($-CH_2OH$) group into an aldehyde group ($-CHO$) without attacking double or triple bonds present in unsaturated systems.

Step 1: Selecting the appropriate reagent.

The most common mild, selective reagent used for this transformation is Pyridinium Chlorochromate (PCC) or Pyridinium Dichromate (PDC) .

* **Composition of PCC:** A complex of chromium trioxide, pyridine, and hydrochloric acid ($C_5H_5NH^+CrO_3Cl^-$). * **Function:** It selectively oxidizes the $-CH_2OH$ group into a $-CHO$ group and stops at the aldehyde stage without further oxidation to carboxylic acid, while leaving the carbon-carbon double bond ($C=C$) completely untouched.

Step 2: Final Answer.

The reagent used is Pyridinium Chlorochromate (PCC) (or Pyridinium Dichromate / PDC).

Quick Tip: PCC (Pyridinium Chlorochromate) in anhydrous media (CH_2Cl_2) is the ideal reagent to convert: - Primary alcohol → Aldehyde (prevents over-oxidation to carboxylic acid). - Unsaturated alcohol → Unsaturated aldehyde (preserves $C=C$ bond).

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24. 2 g of Na_2SO_4 is dissolved in 50 g of water to form a solution. Calculate the freezing point of this solution, assuming Na_2SO_4 undergoes complete dissociation.

Solution:

Concept: The depression in freezing point (ΔT_f) of a solution containing a non-volatile electrolyte is given by the colligative property formula:

$$\Delta T_f = i \cdot K_f \cdot m$$

Where:

- i = van 't Hoff factor
- K_f = Molal freezing point depression constant (cryoscopic constant) of the solvent
- m = Molality of the solution

Molality (m) is defined as:

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Where:

- w_B = Mass of solute (Na_2SO_4) in grams
- M_B = Molar mass of solute in g mol^{-1}
- w_A = Mass of solvent (H_2O) in grams

Step 1: Given parameters.

* Mass of solute (w_B) = 2 g * Molar mass of solute (M_B) = 142 g mol^{-1} * Mass of solvent (w_A) = 50 g * K_f for water = 1.86 K kg mol^{-1} * Freezing point of pure water (T_f°) = 273.15 K (or 0°C)

Step 2: Determining the van 't Hoff factor (i).

Na_2SO_4 dissociates in water according to the equation:

$$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$

Since Na_2SO_4 undergoes complete dissociation ($\alpha = 1$): Total number of ions produced per formula unit = $2 + 1 = 3$. Therefore, van 't Hoff factor, $i = 3$.

Step 3: Calculating the molality (m) of the solution.

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substitute the given values:

$$m = \frac{2 \times 1000}{142 \times 50} = \frac{2000}{7100} = \frac{20}{71} \approx 0.2817 \text{ mol kg}^{-1}$$

Step 4: Calculating depression in freezing point (ΔT_f).

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

$$\Delta T_f = 3 \times 1.86 \times \frac{20}{71}$$

$$\Delta T_f = 5.58 \times 0.28169 = 1.5718 \text{ K} \approx 1.57 \text{ K}$$

Step 5: Calculating the freezing point of the solution (T_f).

The freezing point of the solution is given by:

$$T_f = T_f^\circ - \Delta T_f$$

In Kelvin:

$$T_f = 273.15 \text{ K} - 1.57 \text{ K} = 271.58 \text{ K}$$

In Celsius:

$$T_f = 0^\circ\text{C} - 1.57^\circ\text{C} = -1.57^\circ\text{C}$$

Quick Tip: Always remember to include the van 't Hoff factor (i) for ionic compounds! - For complete dissociation: i = total number of ions produced. - Freezing point of solution $T_f = T_f^\circ - \Delta T_f$.

25(a) Write two structural differences between DNA and RNA.

Solution:

Concept: Deoxyribonucleic Acid (DNA) and Ribonucleic Acid (RNA) are nucleic acids composed of nucleotide units (pentose sugar, nitrogenous base, and phosphate group), but differ in sugar composition, base composition, and spatial structure.

Step 1: Comparing the structural differences.

The two major structural differences between DNA and RNA are summarized in the table below:

S.No.	DNA (Deoxyribonucleic Acid)	RNA (Ribonucleic Acid)
1	The pentose sugar present in DNA is β-D-2-deoxyribose.	The pentose sugar present in RNA is β-D-ribose.
2	DNA contains the nitrogenous bases: Adenine (A), Guanine (G), Cytosine (C), and Thymine (T).	RNA contains the nitrogenous bases: Adenine (A), Guanine (G), Cytosine (C), and Uracil (U) instead of Thymine.
3	DNA usually exists as a double-stranded helical structure.	RNA usually exists as a single-stranded structure.

Quick Tip: Key structural differences to memorize: - Sugar: Deoxyribose (DNA) vs Ribose (RNA). - Pyrimidine base: Thymine (DNA) vs Uracil (RNA). - Strands: Double-stranded (DNA) vs Single-stranded (RNA).

25(b) Which component of starch is a branched chain polymer of α-D-(+) glucose ? Write its one characteristic feature.

Solution:

Concept: Starch is a polymeric carbohydrate consisting of two structural components:

- Amylose: Water-soluble, linear unbranched chain polymer of α-D-(+) glucose units linked via $C_1 - C_4$ glycosidic linkages ($15 - 20\%$ of starch).
- Amylopectin: Water-insoluble, highly branched chain polymer of α-D-(+) glucose units ($80 - 85\%$ of starch).

Step 1: Identification of the component.

The branched-chain polymer component of starch composed of α-D-(+) glucose units is Amylopectin .

Step 2: Characteristic features of Amylopectin.

* **Structural Feature / Linkage:** In amylopectin, linear chains are formed by $C_1 - C_4$ glycosidic linkages between α-D-glucose units, while branching occurs by $C_1 - C_6$ glycosidic linkages at regular intervals (every 20 to 25 glucose units). * **Solubility Feature:** It is insoluble in water and constitutes about $80 - 85\%$ of natural starch.

Quick Tip: Starch Components: - Amylose: Unbranched, $C_1 - C_4$ linkage, water-soluble. - Amylopectin: Branched, $C_1 - C_4$ linear + $C_1 - C_6$ branch linkage, water-insoluble.

25(c) Which types of bonds hold the polypeptide chains in fibrous proteins ?

Solution:

Concept: Proteins are categorized based on molecular shape into fibrous proteins and globular proteins:

- Fibrous proteins: Polypeptide chains run parallel to each other and are held together

side-by-side to form fiber-like structures.

- These structures are stabilized by strong intermolecular forces between adjacent polypeptide chains.

Step 1: Types of bonding in fibrous proteins.

The linear polypeptide chains in fibrous proteins are held together in parallel alignment by: 1. Hydrogen bonds 2. Disulfide linkages (bonds)

Examples: Keratin (present in hair, wool, nails) and Myosin (present in muscles).

Quick Tip: Fibrous proteins (e.g., Keratin, Collagen, Myosin) are insoluble in water due to strong parallel chain stabilization via intermolecular hydrogen bonds and disulfide bonds .

26(a) Why are haloarenes less reactive towards nucleophilic substitution reactions than haloalkanes ? Give two reasons.

Solution:

Concept: Haloarenes (e.g., chlorobenzene) undergo nucleophilic substitution reactions with extreme difficulty compared to haloalkanes (e.g., chloroethane). This marked difference in reactivity is attributed to electronic and structural parameters of the carbon-halogen bond.

Step 1: Reason 1: Resonance Effect.

In haloarenes, the lone pair of electrons on the halogen atom is in conjugation with the π-electrons of the benzene ring. Due to resonance, the carbon-halogen (C-X) bond acquires partial double bond character:

$$C_6H_5 - \ddot{X} : \longleftrightarrow \text{Resonance structures showing double bond character}$$

Because a double bond is shorter and stronger than a single bond, cleavage of the C-X bond in haloarenes is much harder than the single C-X bond cleavage in haloalkanes.

Step 2: Reason 2: Difference in Hybridisation of Carbon Atom in C-X bond.

* In haloalkanes, the halogen atom is bonded to an sp^3 hybridized carbon atom. * In haloarenes, the halogen atom is bonded to an sp^2 hybridized carbon atom. * An sp^2 hybridized carbon has higher s-character (33.3%) than an sp^3 hybridized carbon (25%), making it more electronegative. * Therefore, the sp^2 carbon holds the electron pair of the C-X bond more tightly,

decreasing the bond length (169 pm in chlorobenzene vs 177 pm in haloalkane) and making bond cleavage difficult.

Step 3: Additional Reasons (for completeness).

3. Instability of phenyl cation: Self-ionization to form a phenyl cation is unfavorable because the phenyl cation is not stabilized by resonance. 4. Repulsion: The electron-rich π-cloud of the aromatic ring repels the approaching nucleophile.

Quick Tip: Primary reasons for low reactivity of haloarenes: 1. Resonance effect → Partial double bond character of C-X bond. 2. sp^2 hybridisation of carbon → Greater electronegativity and shorter C-X bond.

26(b) Explain the Finkelstein reaction.

Solution:

Concept: The Finkelstein reaction is a classic halogen exchange reaction used specifically for the synthesis of alkyl iodides from alkyl chlorides or alkyl bromides.

Step 1: Chemical reaction and principle.

When an alkyl chloride or alkyl bromide is treated with sodium iodide (NaI) in dry acetone, halogen exchange takes place to yield the corresponding alkyl iodide .

General Reaction Equation:

$$\text{R-X} + \text{NaI} \xrightarrow{\text{Dry Acetone}} \text{R-I} + \text{NaX} \downarrow \quad (\text{where X} = \text{Cl or Br})$$

Step 2: Role of dry acetone and Le Chatelier's Principle.

Sodium iodide (NaI) is soluble in dry acetone, whereas sodium chloride (NaCl) and sodium bromide (NaBr) formed during the reaction are insoluble in dry acetone and precipitate out. According to Le Chatelier's principle , the continuous precipitation of NaCl or NaBr shifts the equilibrium in the forward direction, ensuring high yields of alkyl iodide (R-I).

Step 3: Specific Example.

Reaction of ethyl bromide with sodium iodide in dry acetone:

$$CH_3CH_2Br + NaI \xrightarrow{\text{Dry Acetone}} CH_3CH_2I + NaBr \downarrow$$

Quick Tip: Halogen Exchange Reactions: - Finkelstein Reaction: Uses NaI / dry acetone → Prepares Alkyl Iodides (R-I). - Swarts Reaction: Uses metallic fluorides (AgF, Hg_2F_2) → Prepares Alkyl Fluorides (R-F).

27(a) Conductivity of 2.5×10^{-4} M methanoic acid solution is 5.25×10^{-5} S cm^{-1}. Calculate its molar conductivity.

Solution:

Concept: Molar conductivity (Λ_m) is the conducting power of all the ions produced by dissolving one mole of an electrolyte in a solution. It is related to conductivity (κ) and molar concentration (C) by the equation:

$$\Lambda_m = \frac{\kappa \times 1000}{C}$$

Where:

- κ = Conductivity in S cm^{-1}
- C = Molar concentration (Molarity) in mol L^{-1}
- Λ_m = Molar conductivity in S cm^2 mol^{-1}

Step 1: Given parameters.

* Concentration of methanoic acid (C) = 2.5×10^{-4} M (or mol L^{-1}) * Conductivity (κ) = 5.25×10^{-5} S cm^{-1}

Step 2: Calculation of molar conductivity (Λ_m).

Substitute the given values into the molar conductivity equation:

$$\Lambda_m = \frac{5.25 \times 10^{-5} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{2.5 \times 10^{-4} \text{ mol L}^{-1}}$$

Simplifying the powers of 10 in the numerator:

$$\Lambda_m = \frac{5.25 \times 10^{-2}}{2.5 \times 10^{-4}}$$

$$\Lambda_m = \frac{5.25}{2.5} \times 10^{-2-(-4)}$$

$$\Lambda_m = 2.1 \times 10^2 \text{ S cm}^2 \text{ mol}^{-1} = 210 \text{ S cm}^2 \text{ mol}^{-1}$$

Quick Tip: Formula to remember:

$$\Lambda_m = \frac{\kappa\left(\text{S cm}^{-1}\right) \times 1000}{C\left(\text{mol L}^{-1}\right)} \quad \text{Unit: S cm}^2\ \text{mol}^{-1}$$

Ensure κ is in S cm^{-1} when multiplying by 1000!

27(b) Calculate its degree of dissociation.

Solution:

Concept: 1. According to Kohlrausch's Law of Independent Migration of Ions , the limiting molar conductivity (Λ_m°) of an electrolyte is the sum of limiting molar conductivities of its constituent cations and anions:

$$\Lambda_m^\circ(\text{HCOOH}) = \lambda_{(\text{H}^+)}^\circ + \lambda_{(\text{HCOO}^-)}^\circ$$

2. The degree of dissociation (α) for a weak electrolyte is the ratio of its molar conductivity at a given concentration (Λ_m) to its limiting molar conductivity at infinite dilution (Λ_m°):

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$$

Step 1: Calculation of limiting molar conductivity (Λ_m°).

Given limiting ionic conductivities: * $\lambda_{(\text{H}^+)}^\circ = 349.5$ S cm^2 mol^{-1} * $\lambda_{(\text{HCOO}^-)}^\circ = 50.5$ S cm^2 mol^{-1}

Applying Kohlrausch's Law:

$$\Lambda_m^\circ(\text{HCOOH}) = \lambda_{(\text{H}^+)}^\circ + \lambda_{(\text{HCOO}^-)}^\circ$$

$$\Lambda_m^\circ(\text{HCOOH}) = 349.5 + 50.5 = 400.0 \text{ S cm}^2\ \text{mol}^{-1}$$

Step 2: Calculating degree of dissociation (α).

From part 27(a), calculated $\Lambda_m = 210$ S cm^2 mol^{-1}.

Substitute Λ_m and Λ_m° into the formula:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{210}{400} = 0.525$$

In percentage form:

$$\alpha = 0.525 \times 100\% = 52.5\%$$

Quick Tip: Kohlrausch's Law applications: - Limiting Molar Conductivity: $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$ - Degree of dissociation: $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

28(a) Define Denatured Protein with an example.

Solution:

Concept: Proteins possess specific native three-dimensional structures (secondary and tertiary structures) held together by non-covalent interactions like hydrogen bonds, ionic interactions, and hydrophobic forces. Denaturation refers to the loss of this native conformation and biological activity without breaking the primary peptide bonds.

Step-by-step Explanation:

1. Definition of Denatured Protein:

A protein is said to be **denatured** when its native physical structure and biological activity are lost due to physical changes (such as a change in temperature) or chemical changes (such as a change in pH).

During denaturation:

- Secondary (2°) and tertiary (3°) structures of the protein are destroyed.
- Hydrogen bonds maintaining spatial geometry are disrupted, causing protein globules to unfold and uncoil.
- The primary (1°) structure (covalent peptide bonds between amino acid residues) remains completely intact.

2. Examples of Denaturation:

1. **Coagulation of egg white on boiling:** Heat denatures the soluble albumin protein into an insoluble fibrous mass.
2. **Curdling of milk:** Lactic acid bacteria produce lactic acid, which lowers the pH and denatures the milk protein casein.

Final Answer:

A **denatured protein** is one that has lost its native three-dimensional shape (2° and 3° structures) and biological activity due to physical (heat) or chemical (pH) changes, while its primary (1°) structure remains intact.

Example: Coagulation of egg white upon boiling or curdling of milk.

Quick Tip: Remember for board exams:

- Denaturation disrupts 2° and 3° structures of proteins.
- The primary (1°) structure (peptide bonds) always remains intact!

28(b) What happens when glucose reacts with HCN ? Write the reaction involved.

Solution:

Concept: Glucose ($C_6H_{12}O_6$) contains an aldehyde group (—CHO) at C_1. Nucleophilic addition of hydrogen cyanide (HCN) to the carbonyl group of glucose yields a cyanohydrin derivative.

Step 1: Reaction description and outcome.

When glucose is treated with hydrogen cyanide (HCN), the cyanide ion (CN^-) attacks the carbonyl carbon of the aldehyde group to form Glucose Cyanohydrin .

This reaction confirms the presence of a carbonyl group ($> C = O$) in the open-chain structure of glucose.

Step 2: Chemical Reaction Equation.

$$\begin{array}{ccc} \text{CHO} & & \text{CH(OH)CN} \\ | & & | \\ (\text{CHOH})_4 & + \text{HCN} \longrightarrow & (\text{CHOH})_4 \\ | & & | \\ \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \end{array}$$

Glucose **Glucose Cyanohydrin**

Quick Tip: Reaction tests for functional groups in Glucose: - Reaction with HCN or NH_2OH → Proves presence of a carbonyl group. - Reaction with Br_2 water → Proves carbonyl group is an aldehyde.

28(c) Name the disease caused by the deficiency of Vitamin C.

Solution:

Concept: Vitamins are essential micronutrients required for metabolic functions. Vitamin C is a water-soluble vitamin chemically known as Ascorbic Acid .

Step 1: Deficiency disease.

The disease caused by the deficiency of Vitamin C is Scurvy .

Step 2: Symptoms of Scurvy.

* Bleeding gums * Loosening of teeth * Fragile capillaries leading to delayed wound healing and skin hemorrhages

Quick Tip: Common Vitamin Deficiency Diseases: - Vitamin A → Night blindness - Vitamin B1 (Thiamine) → Beriberi - Vitamin C (Ascorbic Acid) → Scurvy - Vitamin D → Rickets

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29. Organic compounds containing carbonyl group as the functional group are aldehydes, ketones and carboxylic acids. The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen as compared to carbon. Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. They react with HCN, Sodium bisulphite, Grignard reagent and a number of ammonia derivatives like Hydroxylamine, Hydrazine, Semicarbazide, etc. Aldehydes and ketones undergo various reactions due to the acidic nature of a-hydrogen. Aldehydes and ketones having at least one a-hydrogen atom undergo a reaction in the presence of dilute alkali as a catalys form SS-hydroxy aldehydes or SS-hydroxy ketones. On the other h aldehydes which do not possess an a-hydrogen undergo self-oxidation gad reduction in the presence of concentrated alkali.

29.(a) From the compounds given below, identify which would undergo aldol condensation and which would undergo Cannizzaro reaction?

Cyclohexanone, Benzaldehyde, Methanal, 2-Methylpentanal

Solution:

Concept:

- **Aldol Condensation:** Aldehydes and ketones possessing at least one α-hydrogen atom undergo self-condensation in the presence of dilute alkali to form β-hydroxy aldehydes

(aldols) or β-hydroxy ketones (ketols).

- **Cannizzaro Reaction:** Aldehydes which do not contain any α-hydrogen atom undergo self-oxidation and reduction (disproportionation) on treatment with concentrated alkali solution to yield a mixture of an alcohol and a carboxylate salt.

Step 1: Analyzing α-hydrogens in each compound.

1. **Cyclohexanone:** Contains four α-hydrogens at the positions adjacent to the carbonyl group. Thus, it undergoes Aldol condensation.
2. **Benzaldehyde (C_6H_5CHO):** The carbonyl carbon is attached to a benzene ring carbon which carries no hydrogen atom. Thus, it lacks α-hydrogens and undergoes Cannizzaro reaction.
3. **Methanal (HCHO):** Lacks an α-carbon atom, so it has zero α-hydrogens. Thus, it undergoes Cannizzaro reaction.
4. **2-Methylpentanal ($CH_3CH_2CH_2CH(CH_3)CHO$):** The α-carbon has one hydrogen atom present. Thus, it undergoes Aldol condensation.

Step 2: Summary Classification.

- **Compounds undergoing Aldol Condensation:** Cyclohexanone, 2-Methylpentanal
- **Compounds undergoing Cannizzaro Reaction:** Benzaldehyde, Methanal

Quick Tip: Check the carbon directly attached to the $-CHO$ or $-C=O$ group (α-carbon). If it has at least one H attached $\rightarrow$ Aldol. If no α-carbon or no H attached to α-carbon $\rightarrow$ Cannizzaro.

29.(b)(i) Arrange the following compounds in increasing order of reactivity towards nucleophilic addition reactions:

Butanone, Propanone, Propanal, Ethanal

Solution:

Concept: Nucleophilic addition reactions involve the attack of a nucleophile on the electrophilic carbonyl carbon. The reactivity depends on two major factors:

- **Inductive Effect (+I Effect):** Alkyl groups release electrons (+I effect), which decreases the positive charge on the carbonyl carbon and lowers its electrophilicity. Therefore, aldehydes are more reactive than ketones.
- **Steric Hindrance:** Larger alkyl groups sterically hinder the approach of the incoming nucleophile to the carbonyl carbon.

Step 1: Comparing Aldehydes vs. Ketones.

Aldehydes (Propanal, Ethanal) have only one alkyl group attached to the carbonyl carbon, making them less sterically hindered and more electrophilic than ketones (Butanone, Propanone) which have two alkyl groups.

Step 2: Comparing within Ketones (Butanone vs. Propanone).

- **Propanone (CH_3COCH_3):** Has two smaller methyl groups.
- **Butanone ($CH_3COCH_2CH_3$):** Has a methyl and an ethyl group, causing greater steric hindrance and a stronger +I effect.
- *Order for ketones:* Butanone < Propanone

Step 3: Comparing within Aldehydes (Propanal vs. Ethanal).

- **Ethanal (CH_3CHO):** Has a smaller methyl group.
- **Propanal (CH_3CH_2CHO):** Has a larger ethyl group, causing slightly more steric hindrance and +I effect.
- *Order for aldehydes:* Propanal < Ethanal

Step 4: Final Increasing Order.

$$\text{Butanone} < \text{Propanone} < \text{Propanal} < \text{Ethanal}$$

Quick Tip: Reactivity order towards nucleophilic addition: Formaldehyde > Other Aldehydes > Ketones. Smaller alkyl groups mean less steric hindrance and higher reactivity!

29.(b)(ii) Draw the structure of the semicarbazone of cyclohexanone.

Solution:

Concept: Ketones react with nucleophiles like semicarbazide (H_2N-NH-$CONH_2$) via nucleophilic addition followed by the elimination of a water molecule (H_2O) to form semicarbazones.

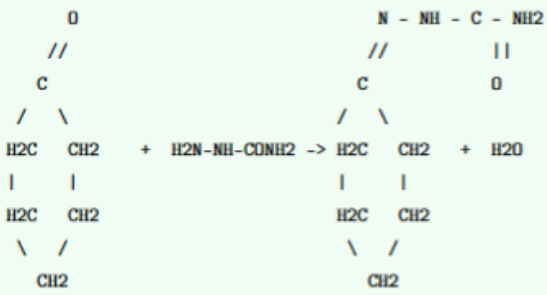
Step 1: Identifying the reacting groups.

- **Cyclohexanone:** $C_6H_{10}O$ (a six-membered ring with a carbonyl group $= O$).
- **Semicarbazide:** $H_2N-NH-C(=O)NH_2$. The $-NH_2$ group involved in condensation is the one attached directly to $-NH-$ because its non-bonding electron pair is not involved in resonance with the carbonyl group, making it more nucleophilic.

Step 2: Reaction and Structural Representation.

Cyclohexanone + Semicarbazide $\xrightarrow{-H_2O}$ Semicarbazone of Cyclohexanone

The reaction replaces the oxygen of the ketone group ($=O$) with $=N-NH-CO-NH_2$:



Chemical Structure Formula:

$C_6H_{10}=N-NH-CO-NH_2$

Chemical Structure Formula:

$$C_6H_{10}=N-NH-CO-NH_2$$

Quick Tip: Semicarbazide has two $-NH_2$ groups. Only the nucleophilic $-NH_2$ group (not conjugated with the carbonyl group) condenses with the carbonyl oxygen to form $=N-NH-CONH_2$.

29.(c) Why is α-hydrogen of carbonyl group acidic in nature?

Solution:

Concept: The hydrogen atoms attached to the carbon adjacent to the carbonyl carbon are termed α-hydrogens. Their acidic nature is attributed to electron withdrawal and resonance stabilization of the resulting conjugate base.

Step 1: Strong Electron-Withdrawing Inductive Effect (-I Effect).

The carbonyl group ($>C=O$) contains a strongly electronegative oxygen atom double-bonded to carbon. This polarizes the carbonyl group ($\overset{\delta+}{C}=\overset{\delta-}{O}$), exerting a strong electron-withdrawing (-I) effect on the adjacent α-carbon. Consequently, the C_α—H bond becomes weak and polarized, allowing the hydrogen atom to be abstracted easily as a proton (H^+) by a base.

Step 2: Resonance Stabilization of the Enolate Ion.

When a base abstracts an α-hydrogen, a conjugate base called an **enolate ion** is generated. This carbanion is strongly stabilized by resonance, as the negative charge is delocalized onto the highly electronegative oxygen atom:

$$-CH_2-C(=O)-\xrightarrow{\text{Base (:B)}}\underbrace{\left[-\overline{C}H-C(=O)-\longleftrightarrow -CH=C(\overline{O})-\right]}_{\text{Resonance-Stabilized Enolate Ion}}+\text{B-H}^+$$

Step 3: Conclusion.

Due to the combined influence of the strong $-I$ effect of the carbonyl carbon and the resonance stabilization of the resulting enolate anion, the α-hydrogens of carbonyl compounds display acidic character.

Quick Tip: Acidity of α-hydrogens = Strong $-I$ effect of $>C=O$ group + Resonance stabilization of the enolate conjugate base.

30 Atomic radii is a useful property for determining many aspects of chemistry of elements such as physical and chemical properties. The periodic table greatly assists in finding a number of trends. The transition metals belong to group 3-12 and are generally characterised by partially filled d-orbitals in the free elements or their cations. The atomic radii of transition metals show a small decrease from left to right across a period, then remain nearly constant, and finally, slight increase towards the end of the series. The trend is a result of interplay between the increasing nuclear charge and the increasing shielding effect from the filling of

d-orbitals. Initially the nuclear charge dominates, leading to decrease in size, but as more d-electrons are added, their shielding becomes more effective, balancing the increased nuclear charge and causing the radii to become constant. The increase in size between 3d and 4d metals is much greater than between the 4d and 5d metals. The atomic radii of 2nd and 3rd series are almost the same due to lanthanoid contraction. Increase in density is also observed on moving from left to right in a period

30.(a)(i) Give reasons for the following:

The second and third series of transition metals resemble each other much more than they resemble the first series (3d).

Solution:

Concept: The transition elements consist of $3d$ (1st series), $4d$ (2nd series), and $5d$ (3rd series). Normally, down a group, atomic size increases significantly. However, between the $4d$ and $5d$ series, the insertion of $4f$ orbitals causes Lanthanoid Contraction.

Step 1: Understanding Lanthanoid Contraction.

Before the $5d$ series begins, 14 electrons fill the inner $4f$ subshell (from La to Hf). The f-orbital electrons exhibit very poor and ineffective shielding of the nuclear charge due to their diffused shapes.

Step 2: Effect on Atomic and Ionic Radii.

As a result of this poor shielding, the effective nuclear charge felt by the valence outer electrons increases significantly, pulling the electron cloud inward. This counteracts the normal size increase expected upon adding a new main energy shell. Consequently, elements of the $4d$ series (2nd transition series) and $5d$ series (3rd transition series) in the same vertical group possess nearly identical atomic and ionic radii (e.g., Zr $\approx$ 160 pm and Hf $\approx$ 159 pm).

Step 3: Impact on Physical and Chemical Properties.

Because their atomic radii, ionization enthalpies, and electron configurations are nearly identical, elements of the 2nd and 3rd transition series exhibit almost identical physical and chemical properties, making them resemble each other far more than they resemble the $3d$ series.

Quick Tip: Whenever $4d$ and $5d$ elements have nearly identical radii or closely matching chemical properties, the key underlying cause is almost always Lanthanoid Contraction .

30.(a)(ii) Give reasons for the following:

Transition metals show variable oxidation states.

Solution:

Concept: Unlike main-group elements, transition elements exhibit multiple (variable) oxidation states in their compounds.

Step 1: Energy proximity of $(n-1)d$ and ns subshells.

In transition elements, the energy levels of the inner $(n-1)d$ orbitals and outer ns orbitals are extremely close to one another.

Step 2: Participation of electrons in bond formation.

Because the energy gap between $(n-1)d$ and ns orbitals is very small:

- Not only the outer ns electrons but also the unpaired inner $(n-1)d$ electrons can participate in chemical bond formation.
- Loss or sharing of only ns electrons yields lower oxidation states.
- Additional participation of $(n-1)d$ electrons yields higher oxidation states up to the maximum limit where all ns and unpaired $(n-1)d$ electrons are involved.

Step 3: Conclusion.

The participation of both $(n-1)d$ and ns electrons in chemical bonding due to their comparable energies causes transition metals to exhibit variable oxidation states.

Quick Tip: Variable oxidation state in d-block = Small energy difference between $(n-1)d$ and ns subshells allowing both sets of electrons to bond.

30.(b)(i) Why is Zn a non-transition element?

Solution:

Concept: According to IUPAC, a transition element is defined as an element that has partially filled d-orbitals in its ground state or in any one of its common oxidation states.

Step 1: Ground state electronic configuration of Zinc (Zn).

Zinc has an atomic number of $Z = 30$. Its ground state electronic configuration is:

$$\text{Zn} = [\text{Ar}]\, 3d^{10}\, 4s^2$$

Here, the $3d$ subshell is completely filled ($3d^{10}$).

Step 2: Oxidation state electronic configuration of Zinc.

Zinc exhibits only one common oxidation state, which is +2. The electronic configuration of the Zn^{2+} ion is:

$$Zn^{2+} = [Ar]\,3d^{10}$$

Here, the $3d$ subshell remains completely filled ($3d^{10}$).

Step 3: Conclusion.

Since Zinc (Zn) does not have incompletely filled d-orbitals either in its elemental ground state or in its stable oxidation state (Zn^{2+}), it is not considered a true transition element.

Quick Tip: Zn, Cd, and Hg have fully filled d^{10} configurations in both ground state and oxidation states. Hence, they are d-block elements but not transition metals .

30.(b)(ii) Why do transition metals have high $\Delta_a H^\circ$ (enthalpy of atomization)?

Solution:

Concept: Enthalpy of atomization ($\Delta_a H^\circ$) is the amount of heat energy required to break metallic lattices into individual gaseous atoms. It depends directly on the strength of the metallic bonding in the crystal lattice.

Step 1: Interatomic metallic bonding factors.

Transition elements have a large number of unpaired electrons in their $(n-1)d$ subshells along with outer ns electrons.

Step 2: Overlapping and bond strength.

Due to the presence of these unpaired d-electrons, strong interatomic covalent interactions occur in addition to metallic bonding. The greater the number of unpaired d-electrons, the stronger the interatomic forces holding the metal lattice together.

Step 3: Conclusion.

Because of these strong interatomic metallic and covalent bonds formed by unpaired d-electrons, a large amount of energy is required to separate the atoms, leading to very high enthalpies of atomization ($\Delta_a H^\circ$).

Quick Tip: High Enthalpy of Atomization = Strong Metallic Bonding + Covalent interaction due to unpaired d-electrons.

30.(c) Why is there not much change in the atomic radius of the transition metals with the increase in atomic number?

Solution:

Concept: Across a period, two opposing factors govern the atomic size: 1. Increase in nuclear charge (pulls electrons inward). 2. Shielding effect of inner d-electrons (pushes valence electrons outward).

Step 1: Role of Nuclear Charge.

As atomic number increases across a transition series, nuclear charge increases by +1 unit per element, which tends to pull the outermost electrons closer and decrease atomic radius.

Step 2: Role of Shielding Effect of $(n-1)d$ Electrons.

Simultaneously, incoming electrons enter the inner $(n-1)d$ subshell rather than the outer ns shell. These inner d-electrons shield the outer ns valence electrons from the full nuclear pull.

Step 3: Balancing of Opposing Effects.

As more d-electrons are added, the increased shielding effect gradually balances out the increment in nuclear charge. Towards the middle and end of the transition series, these two opposing forces almost completely cancel each other out, resulting in very small or negligible changes in atomic radii across the series.

Quick Tip: Atomic radius remains nearly constant in the middle of a transition series because:

$$\text{Increase in Nuclear Charge} \approx \text{Increase in Shielding Effect of } d\text{-electrons}$$

31.(a)(i) The pK_b value of aniline is higher than that of methylamine. Explain why.

Solution:

Concept: Basic strength is inversely proportional to pK_b value (Basic Strength $\propto \frac{1}{pK_b}$). A higher pK_b value indicates a weaker base. Therefore, aniline is a weaker base than methylamine.

Step 1: Resonance Effect in Aniline ($C_6H_5NH_2$).

In aniline, the lone pair of electrons on the nitrogen atom is conjugated with the π-electron

system of the benzene ring. It undergoes resonance and gets delocalized over the aromatic ring:

$$C_6H_5 - \ddot{N}H_2 \longleftrightarrow \text{Resonance Hybrids}$$

Due to this delocalization, the lone pair is less available on the nitrogen atom for protonation (H^+ attack).

Step 2: Inductive Effect in Methylamine (CH_3NH_2).

In methylamine, the methyl group ($-CH_3$) exerts an electron-releasing $+I$ inductive effect, which increases electron density on the nitrogen atom, making its lone pair readily available for protonation.

Step 3: Stability of Conjugate Acids.

Anilinium ion ($C_6H_5NH_3^+$) formed by protonation of aniline has only 2 resonance structures, whereas unprotonated aniline has 5 canonical structures. Hence, aniline is more stable than anilinium ion. In contrast, methylammonium ion is stabilized by $+I$ effect and hydration.

Step 4: Conclusion.

Because aniline is less basic due to lone-pair delocalization via resonance, its pK_b value (≈ 9.38) is higher than that of methylamine (≈ 3.38).

Quick Tip: Lower availability of nitrogen lone pair → Weaker base → Higher pK_b value. Aromatic amines have higher pK_b values than aliphatic amines!

31.(a)(ii) Arrange the following compounds in decreasing order of their basic strength in the gaseous phase:

$NH_3, (C_2H_5)_2NH, (C_2H_5)_3N, C_2H_5NH_2$

Solution:

Concept: In the **gaseous phase**, factors like solvation energy and steric hindrance do not operate. Basic strength is solely determined by the electron-donating inductive effect ($+I$ effect) of alkyl groups attached to the nitrogen atom.

Step 1: Role of $+I$ Effect in Gaseous Phase.

Alkyl groups ($-C_2H_5$) are electron-releasing (+I effect). As the number of ethyl groups on nitrogen increases, the electron density on the nitrogen atom increases, making the lone pair more easily available to donate to a Lewis acid or proton.

Step 2: Evaluating electron density for each species.

- **$(C_2H_5)_3N$ (Tertiary amine):** Three $+I$ ethyl groups → Highest electron density.
- **$(C_2H_5)_2NH$ (Secondary amine):** Two $+I$ ethyl groups → Medium-high electron density.
- **$C_2H_5NH_2$ (Primary amine):** One $+I$ ethyl group → Moderate electron density.
- **NH_3 (Ammonia):** No alkyl groups → Lowest electron density.

Step 3: Decreasing Order of Basic Strength.

$$(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$$

(Order: $3^\circ > 2^\circ > 1^\circ > NH_3$)

Quick Tip: In Gaseous Phase : Basic strength order is purely based on $+I$ effect: $3^\circ > 2^\circ > 1^\circ > NH_3$. In Aqueous Phase for ethyl group: $2^\circ > 3^\circ > 1^\circ > NH_3$. Always check the phase!

31.(a)(iii) What is Hinsberg's reagent? Mention its one use.

Solution:

Concept: Hinsberg's reagent is a specific chemical reagent used to distinguish and separate primary (1°), secondary (2°), and tertiary (3°) amines.

Step 1: Chemical Name and Formula.

Hinsberg's reagent is **Benzenesulfonyl chloride**.

Chemical Formula: $C_6H_5SO_2Cl$

Step 2: Use of Hinsberg's Reagent.

It is used for the distinction and separation of primary, secondary, and tertiary amines :

- 1° **Amine:** Reacts to form *N*-alkylbenzenesulfonamide, which contains an acidic hydrogen and is soluble in alkali (KOH/NaOH).
- 2° **Amine:** Reacts to form *N*,*N*-dialkylbenzenesulfonamide, which lacks acidic hydrogens and is insoluble in alkali.

- 3° **Amine:** Does not react with Hinsberg's reagent due to the absence of hydrogens on nitrogen.

Quick Tip: Hinsberg's Reagent = $C_6H_5SO_2Cl$. Use: Distinguishes 1° (soluble in alkali), 2° (insoluble in alkali), and 3° (no reaction) amines.

31.(a)(ii)(I) How will you convert Nitrobenzene to Benzenediazonium chloride?

Solution:

Concept: The conversion of nitrobenzene to benzenediazonium chloride is a two-step process involving reduction to primary aromatic amine followed by diazotization.

Step 1: Reduction of Nitrobenzene to Aniline.

Nitrobenzene ($C_6H_5NO_2$) is reduced to aniline ($C_6H_5NH_2$) using tin and concentrated hydrochloric acid (Sn/HCl) or iron and hydrochloric acid (Fe/HCl).

$$C_6H_5NO_2 + 6[H] \xrightarrow{\text{Sn / HCl}} C_6H_5NH_2 + 2H_2O$$

Step 2: Diazotization of Aniline.

Aniline is treated with nitrous acid (HNO_2, prepared *in situ* using $NaNO_2 + HCl$) at an ice-cold temperature ($273 - 278$ K or $0 - 5°C$) to form benzenediazonium chloride.

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273-278\ K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O$$

Overall Conversion Scheme:

$$\text{Nitrobenzene} \xrightarrow{\text{Sn / HCl}} \text{Aniline} \xrightarrow{NaNO_2+HCl,\ 0-5°C} \text{Benzenediazonium Chloride}$$

Quick Tip: To convert $-NO_2 \rightarrow -N_2^+Cl^-$: First reduce with Fe/HCl or Sn/HCl to $-NH_2$, then apply diazotization ($NaNO_2 + HCl$ at $0 - 5°C$).

31.(a)(ii)(II) How will you convert Iodomethane to Ethanamine?

Solution:

Concept: Converting iodomethane (CH_3I, a 1-carbon compound) to ethanamine ($CH_3CH_2NH_2$, a 2-carbon compound) requires stepping up the carbon chain using potassium cyanide followed by reduction.

Step 1: Nucleophilic Substitution (Stepping up the chain).

Iodomethane is treated with ethanolic potassium cyanide (KCN). The cyanide ion (^-CN) replaces iodide ($-I$) to form acetonitrile (ethanenitrile), increasing the carbon chain length by one carbon atom.

$$CH_3I + KCN\ (alc.) \xrightarrow{\Delta} CH_3CN + KI$$

Step 2: Reduction of Nitrile to Primary Amine.

Acetonitrile (CH_3CN) is reduced using lithium aluminium hydride ($LiAlH_4$) or sodium and alcohol (Na/C_2H_5OH) or catalytic hydrogenation (H_2/Ni) to produce ethanamine.

$$CH_3CN + 4[H] \xrightarrow{LiAlH_4/\text{ether or } Na/EtOH} CH_3CH_2NH_2$$

Overall Conversion Scheme:

$$CH_3I \xrightarrow{KCN\ (alc.)} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$$

Quick Tip: To increase the carbon chain by 1 carbon and form an amine: React alkyl halide with KCN (alc.) $\rightarrow$ Nitrile $\xrightarrow{LiAlH_4 \text{ or } Na/EtOH}$ 1° Amine.

31.(b)(i)(I) Complete the following equation:

$$CH_3NH_2 + C_6H_5COCl \longrightarrow$$

Solution:

Concept: This reaction is the **Benzoylation** (Schotten-Baumann reaction) of primary aliphatic amines. The amino group acts as a nucleophile and attacks the carbonyl carbon of benzoyl chloride, displacing the chloride ion.

Step 1: Reaction Mechanism / Equation.

Methanamine (CH_3NH_2) reacts with benzoyl chloride (C_6H_5COCl) in the presence of a base

like aqueous NaOH or pyridine to neutralize the eliminated HCl:

$$CH_3NH_2 + C_6H_5COCl \xrightarrow{\text{Base}} C_6H_5CONHCH_3 + HCl$$

Step 2: Product Identification.

- **Main Product:** *N*-Methylbenzamide ($C_6H_5CONHCH_3$).
- **Side Product:** Hydrochloric acid (HCl).

Completed Reaction:

$$CH_3NH_2 + C_6H_5COCl \longrightarrow C_6H_5CONHCH_3 + HCl$$

Quick Tip: Acylation/Benzoylation replaces an —H on the amine nitrogen with the acyl/benzoyl group ($-COC_6H_5$).

31.(b)(i)(II) Complete the following equation:

$$\text{Aniline} + 3Br_2 \xrightarrow{H_2O}$$

Solution:

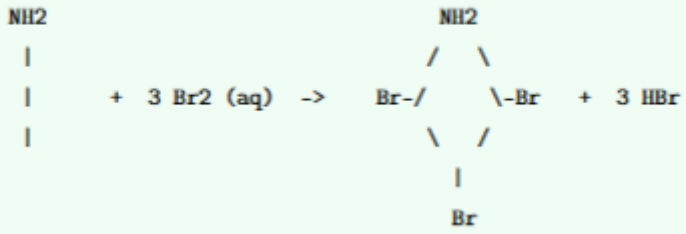
Concept: The $-NH_2$ group in aniline is an extremely strong activating group towards electrophilic aromatic substitution due to resonance delocalization of nitrogen's lone pair into the ring.

Step 1: Effect of Polar Solvent (Water).

When aniline is treated with bromine water (Br_2/H_2O), water polarizes the bromine molecule completely. Furthermore, aniline undergoes slight ionization in water to form a highly reactive species, leading to polybromination at all available ortho and para positions simultaneously.

Step 2: Reaction Equation and Products.

$$C_6H_5NH_2 + 3Br_2(aq) \longrightarrow C_6H_2Br_3NH_2 \downarrow + 3HBr$$



Products:

- **Main Product:** 2,4,6-Tribromoaniline (White precipitate).
- **Side Product:** Hydrogen bromide (HBr).

Quick Tip: Aniline + Bromine water → White precipitate of 2,4,6-Tribromoaniline . To get monobromo derivative, protection of $-NH_2$ by acetylation with $(CH_3CO)_2O$ is required first!

31.(b)(i)(III) Complete the following equation:

$$\text{Benzamide } (C_6H_5CONH_2) \xrightarrow{\text{NaOBr}}$$

Solution:

Concept: This reaction is the **Hofmann Bromamide Degradation Reaction**. Sodium hypobromite (NaOBr) is formed *in situ* by reacting bromine with sodium hydroxide ($Br_2 + NaOH$).

Step 1: Mechanism / Reaction Behavior.

In the Hofmann bromamide reaction, an primary acid amide is treated with bromine in an aqueous or ethanolic solution of sodium hydroxide (NaOBr), leading to degradation of the carbonyl carbon and forming a primary amine containing one carbon atom less than the starting amide.

Step 2: Reaction Equation.

$$C_6H_5CONH_2 + NaOBr \longrightarrow C_6H_5NH_2 + Na_2CO_3 + NaBr + H_2O$$

(Or simplified as: $C_6H_5CONH_2 + Br_2 + 4NaOH \rightarrow C_6H_5NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$)

Products:

- **Main Product:** Aniline ($C_6H_5NH_2$).

Completed Reaction:

$$C_6H_5CONH_2 \xrightarrow{NaOBr} C_6H_5NH_2$$

Quick Tip: Hofmann Bromamide Degradation: $-CONH_2 \xrightarrow{NaOBr \text{ or } Br_2/NaOH} -NH_2$. Removes the $C=O$ group, reducing the carbon count by 1!

32.(a)(i)(I) Explain why $[Fe(CN)_6]^{3-}$ is an inner orbital complex, whereas $[FeF_6]^{3-}$ is an outer orbital complex. [Atomic number: Fe = 26]

Solution:

Concept: According to Valence Bond Theory (VBT), the type of hybridization (d^2sp^3 vs sp^3d^2) depends on the field strength of the ligands involved. Strong field ligands cause pairing of d-electrons, yielding inner orbital complexes, whereas weak field ligands cannot cause pairing, yielding outer orbital complexes.

Step 1: Oxidation state and electronic configuration of Fe.

In both complexes, Iron is in the +3 oxidation state (Fe^{3+}).

$$Fe\ (Z=26) : [Ar]\,3d^6\,4s^2$$

$$Fe^{3+} : [Ar]\,3d^5\,4s^0\,4p^0$$

Step 2: Case 1: $[Fe(CN)_6]^{3-}$ complex.

- Cyanide ion (CN^-) is a **strong field ligand**.
- It forces the unpaired $3d$ electrons of Fe^{3+} to pair up against Hund's rule:

$$3d^5 \text{ (unpaired)} \xrightarrow{\text{pairing by } CN^-} \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \_\_\ \_\_$$

- This leaves two inner $3d$ orbitals vacant.
- Hybridization involves two inner $3d$, one $4s$, and three $4p$ orbitals → **d^2sp^3** hybridization.

- Thus, $[Fe(CN)_6]^{3-}$ forms an **inner orbital complex** (low spin).

Step 3: Case 2: $[FeF_6]^{3-}$ complex.

- Fluoride ion (F^-) is a **weak field ligand**.
- It cannot force pairing of the $3d$ electrons. All five $3d$ electrons remain unpaired:

$$3d^5 : \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}\ \underline{\uparrow}$$

- To accommodate 6 lone pairs from F^-, outer $4d$ orbitals are used: $4s, 4p_3$, and two outer $4d$ orbitals → **sp^3d^2** hybridization.
- Thus, $[FeF_6]^{3-}$ forms an **outer orbital complex** (high spin).

Quick Tip: Strong field ligands (CN^-, CO, en, NH_3) → Forced electron pairing → Inner orbital complex (d^2sp^3).
Weak field ligands (F^-, Cl^-, H_2O) → No pairing → Outer orbital complex (sp^3d^2).

32.(a)(i)(II) Write the formula of the given complex: Hexaamminenickel(II) chloride

Solution:

Concept: To write the chemical formula from IUPAC name: 1. Identify the central metal cation and its charge. 2. Identify ligands and their numbers. 3. Balance the charge using counter ions.

Step 1: Identify central metal and ligands.

- **Central metal ion:** Nickel (Ni) in +2 oxidation state → Ni^{2+}.
- **Ligand:** "Hexaammine" indicates 6 ammine (NH_3) neutral ligands.
- **Coordination Entity:** $[Ni(NH_3)_6]^{2+}$.

Step 2: Balancing charge with counter ions.

- The coordination entity carries a charge of +2.
- Counter ion is chloride (Cl^-), which carries a charge of -1.
- To neutralize +2 charge, two chloride ions are required ($2 \times -1 = -2$).

Step 3: Final Chemical Formula.

$$[Ni(NH_3)_6]Cl_2$$

Quick Tip: Formula Structure: $[\text{Metal(Ligand)}_n]\text{Counter-Ion}_m$. Ensure total overall charge sums to zero!

32.(a)(ii) A solution of $[Ni(H_2O)_6]^{2+}$ is green in colour while a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain. [Atomic number: Ni = 28]

Solution:

Concept: The color of transition metal complexes is caused by $d-d$ transitions of unpaired electrons in the presence of ligands, which absorb specific wavelengths of visible light.

Step 1: Electronic setup of Ni^{2+} ($Z = 28$).

$$Ni^{2+} : [Ar]\, 3d^8\, 4s^0$$

Step 2: Analyzing $[Ni(H_2O)_6]^{2+}$.

- H_2O is a weak field ligand .
- It forms an octahedral complex where $3d^8$ electrons remain unpaired in the t_{2g} and e_g orbitals:

$$t_{2g}^6\ e_g^2 \quad \text{(2 unpaired electrons)}$$

- Due to the presence of unpaired electrons, $d-d$ electronic transitions are allowed when visible light falls on it. Red light is absorbed, and its complementary green color is transmitted/reflected. Hence, it is green .

Step 3: Analyzing $[Ni(CN)_4]^{2-}$.

- CN^- is a strong field ligand .
- It forms a square planar complex (dsp^2 hybridization) and forces all 8 d-electrons to pair up completely:

$$3d^8 \xrightarrow{\text{pairing}} \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \_\_ \quad \text{(0 unpaired electrons)}$$

- Since there are no unpaired d-electrons available for $d-d$ transition, no absorption of visible light takes place.
- Hence, the solution is colourless .

Quick Tip: Unpaired d-electrons present → $d-d$ transition possible → Colored solution.
No unpaired d-electrons (fully paired d^8 or d^{10}) → No $d-d$ transition → Colourless.

32.(b)(i)(I) Write IUPAC name of the given complex: $[Ag(CN)_2][Ag(NH_3)_2]$

Solution:

Concept: For a coordination compound containing both complex cation and complex anion, write the cationic complex name first followed by the anionic complex name. Note that silver is named "argentate" in anionic complex.

Step 1: Identify cation, anion, and oxidation state.

- Cationic complex: $[Ag(NH_3)_2]^+$ (Diaqmmine silver(I))
- Anionic complex: $[Ag(CN)_2]^-$ (Dicyanidoargentate(I))
- Oxidation state of Ag in both species: Let oxidation state of both Ag be x:

$$(x+2\times 0)+(x+2\times(-1))=0 \implies 2x-2=0 \implies x=+1$$

Step 2: Formulate standard IUPAC Name.

Naming cationic complex first, then anionic complex:

$$\text{Diamminesilver(I) dicyanidoargentate(I)}$$

Quick Tip: In salt complexes, Cation named first, Anion second. Metal name ends in "-ate" inside the anionic complex (Silver → Argentate).

32.(b)(i)(II) What is the coordination number of the central metal ion in the following complexes?

$[Fe(C_2O_4)_3]^{3-}$ and $[Cr(NH_3)_3Cl_3]$

Solution:

Concept: Coordination number is the total number of ligand donor atoms directly bonded to the central metal ion.

$$\text{Coordination Number} = \sum(\text{Number of ligands} \times \text{Denticity of ligand})$$

Step 1: Complex 1: $[Fe(C_2O_4)_3]^{3-}$

- Ligand: Oxalate ion ($C_2O_4^{2-}$).
- Denticity: Bidentate (each oxalate ligand provides 2 donor oxygen atoms).
- Calculation:

$$\text{Coordination Number} = 3 \times 2 = \mathbf{6}$$

Step 2: Complex 2: $[Cr(NH_3)_3Cl_3]$

- Ligands: 3 Ammine (NH_3) ligands and 3 Chloride (Cl^-) ligands.
- Denticity: Both are monodentate ligands (each provides 1 donor atom).
- Calculation:

$$\text{Coordination Number} = (3 \times 1) + (3 \times 1) = \mathbf{6}$$

Summary:

- Coordination number of Fe^{3+} in $[Fe(C_2O_4)_3]^{3-}$ is **6**.
- Coordination number of Cr^{3+} in $[Cr(NH_3)_3Cl_3]$ is **6**.

Quick Tip: Don't just count the number of ligands! Multiply the number of ligands by their denticity (Oxalate is bidentate → count = 2 per ligand).

32.(b)(i)(III) Draw a geometrical isomer of the complex $[CoCl_2(en)_2]^+$, which is optically active.

Solution:

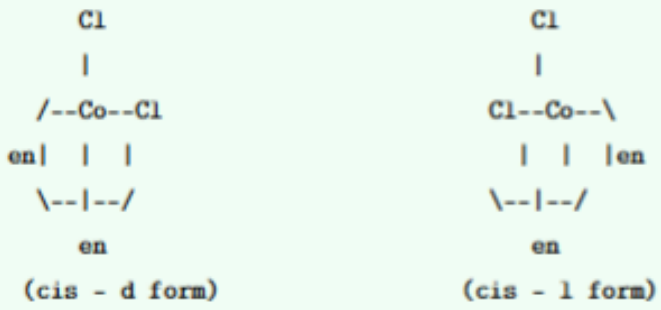
Concept: The complex $[CoCl_2(en)_2]^+$ exhibits geometrical isomerism (cis and trans forms).

- **Trans-isomer:** Symmetrical (possesses a plane of symmetry), superimposable on its mirror image, hence optically inactive .
- **Cis-isomer:** Unsymmetrical (lacks plane of symmetry), non-superimposable on its mirror image, hence optically active .

Step 1: Identifying the Optically Active Isomer.

The cis-isomer of $[CoCl_2(en)_2]^+$ is non-superimposable on its mirror image and therefore optically active.

Step 2: Drawing Cis-Isomer (and its enantiomer).



In the *cis*-isomer, the two chloride ligands are adjacent (at a 90° angle to each other), which creates chirality.

Quick Tip: For $[M(a)_2(b\text{-}b)_2]$ type complexes: - *Cis*-isomer is chiral (optically active). - *Trans*-isomer has a plane of symmetry, making it achiral (optically inactive).

32.(b)(ii) Using valence bond theory, explain the hybridization of $[Ni(CO)_4]$ and its magnetic behaviour. [Atomic number: Ni = 28]

Solution:

Concept: Valence Bond Theory (VBT) explains bond formation in coordination complexes by considering the hybridization of metal ion atomic orbitals to accommodate electron pairs donated by ligands.

Step 1: Oxidation State and Ground State Configuration.

In tetracarbonylnickel(0), Ni is in the zero oxidation state (Ni^0).

$$\text{Ni } (Z = 28) \text{ Ground State Configuration: } [Ar]\,3d^8\,4s^2\,4p^0$$

$$3d \text{ orbitals: } \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow} \quad 4s \text{ orbital: } \underline{\uparrow\downarrow} \quad 4p \text{ orbitals: } \_\_\ \_\_\ \_\_$$

Step 2: Effect of Ligand and Rearrangement.

CO (Carbon monoxide) is a very strong field ligand . In its presence, the two $4s$ electrons are forced to pair up into the $3d$ orbitals:

$$3d \text{ orbitals (after rearrangement): } \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow} \quad (3d^{10} \text{ configuration})$$

Now, the $4s$ orbital and three $4p$ orbitals become completely vacant.

Step 3: Hybridization and Geometry.

- One $4s$ and three $4p$ orbitals hybridize to form four equivalent $\mathbf{sp^3}$ hybrid orbitals .
- The geometry of the complex is Tetrahedral .
- Four lone pairs of electrons from four CO ligands fill these four sp^3 hybrid orbitals.

Step 4: Magnetic Behaviour.

Since all electrons in the complex are completely paired up (there are zero unpaired electrons, $n = 0$), $[Ni(CO)_4]$ is Diamagnetic in nature.

Quick Tip: $[Ni(CO)_4]$ Summary: - Oxidation state of Ni $= 0$ - Hybridization $= sp^3$ - Geometry $=$ Tetrahedral - Unpaired electrons $= 0$ - Magnetic property $=$ Diamagnetic

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