

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-7-3 - Compartment



Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours

Maximum Marks: 70

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.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculator is not allowed.

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

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

Column I	Column II
a. Osmotic pressure	i. $\Delta T_f = K_f m$
b. Elevation of boiling point	ii. $\pi = CRT$
c. Depression of freezing point	iii. $(P^\circ_1 - P_1)/P^\circ_1 = W_2 M_1 / M_2 W_1$
d. Relative lowering of vapour pressure	iv. $\Delta T_b = K_b m$

[1 mark]

(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:

- Osmotic pressure obeys $\pi = CRT$, where C is molar concentration, R the gas constant and T absolute temperature.
- For a dilute solution, boiling-point elevation is $\Delta T_b = K_b m$ and freezing-point depression is $\Delta T_f = K_f m$; m denotes molality.

Step 1: Match the first three properties Osmotic pressure matches ii because its expression involves molar concentration and absolute temperature. Elevation of boiling point matches iv, involving the ebullioscopic constant K_b . Depression of freezing point matches i, involving the cryoscopic constant K_f . Thus a-ii, b-iv and c-i.

Step 2: Check the remaining match and options Relative lowering of vapour pressure matches iii: for a dilute solution, $(P^\circ_1 - P_1)/P^\circ_1 = W_2 M_1 / (M_2 W_1)$, where W and M represent masses and molar masses. Only option (D) contains all four matches. Options (A) and (C) mismatch osmotic pressure; option (B) interchanges the temperature-property matches.

Step 3: Conclusion The correct matching is a-ii, b-iv, c-i, d-iii. Hence, the correct option is (D).

Quick Tip to Solve: Identify osmotic pressure first by CRT, then pair the subscripts b and f with boiling and freezing.

2. Functional groups present in amino acids are:

[1 mark]

- (A) -NH_2 and -OH
- (B) -OH and -COOH
- (C) -COOH and -NH_2
- (D) -NH_2 and $\text{-SO}_3\text{H}$

Correct Answer: (C) -COOH and -NH_2

Solution:

Concept:

- An amino acid contains both an amino group, -NH_2 , and a carboxyl group, -COOH .
- The general structure of an alpha-amino acid is $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, where R is the side chain.

Step 1: Identify the defining groups The term amino refers to the amino group and acid refers to the carboxylic acid group. These groups account respectively for basic and acidic behaviour. In an alpha-amino acid, both are attached to the same central carbon, which also carries hydrogen and the side chain.

Step 2: Check all listed pairs Option (C) lists precisely these two groups. Option (A) replaces the carboxyl group with hydroxyl; option (B) omits the amino group. Option (D) substitutes sulphonic acid for carboxylic acid. Some amino-acid side chains may contain other groups, but those are not the pair common to amino acids.

Step 3: Conclusion The functional groups are -COOH and -NH_2 . Hence, the correct option is (C).

Quick Tip to Solve: Read amino acid as amino plus carboxylic acid; do not select groups present only in some side chains.

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

[1 mark]

- (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 concentrated hydrochloric acid with anhydrous ZnCl_2 . It converts alcohols into alkyl chlorides.
- For ordinary saturated alcohols, faster substitution follows greater carbocation stability: tertiary greater than secondary greater than primary.

Step 1: Relate turbidity to the reaction rate The alkyl chloride formed is insoluble in the reaction mixture, producing turbidity. Tertiary alcohols react most rapidly because formation of a tertiary carbocation is favoured. Secondary alcohols react more slowly, while primary alcohols show no

Quick Tip to Solve: For the Lucas test, remember immediate turbidity for tertiary alcohols and delayed turbidity for secondary alcohols.

appreciable turbidity at room temperature under the usual test conditions.

Step 2: Compare the four orders The required order is $3^\circ > 2^\circ > 1^\circ$. Option (A) incorrectly places primary above secondary. Option (B) makes secondary the most reactive and tertiary the least reactive. Option (C) reverses the usual stability-based order. Only option (D) places each class correctly.

Step 3: Conclusion The reactivity order is $3^\circ > 2^\circ > 1^\circ$. Hence, the correct option is (D).

Quick Tip to Solve: For the Lucas test, remember immediate turbidity for tertiary alcohols and delayed turbidity for secondary alcohols.

4. According to Alfred Werner, the secondary valence(s) of the central metal atom/ion in a complex: Identify the *incorrect* statement from the above given statements. [1 mark]

- (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: (B) are ionisable

Solution:

Concept:

- In Werner's theory, primary valence corresponds to oxidation state and is ionisable.
- Secondary valence corresponds to coordination number; it is directional and non-ionisable, and may be satisfied by neutral molecules or anions.

Step 1: Recall the meaning of secondary valence Secondary valences hold ligands within the coordination sphere. These attachments do not simply dissociate as counter-ions on dissolving the complex. Therefore statement (A), which calls secondary valences non-ionisable, is correct. Neutral ligands as well as negatively charged ligands can occupy these positions, so (C) is also correct.

Step 2: Identify the requested incorrect statement The secondary valence is the coordination number and is normally fixed for a metal in Werner's description, making (D) correct. Statement (B) calls secondary valences ionisable, contradicting the theory. The question asks for the incorrect statement, so the correct statements (A), (C) and (D) must be rejected as answers.

Step 3: Conclusion The incorrect statement is (B): secondary valences are ionisable. Hence, the correct option is (B).

Quick Tip to Solve: Underline incorrect before choosing: primary valence is ionisable, whereas secondary valence is non-ionisable.

5. Which of the following statements is true about a galvanic cell consisting of Cu and H₂ electrodes?

[Given: $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $E^\circ_{\text{H}^+/\text{H}_2, \text{Pt}} = +0.00 \text{ V}$]

[1 mark]

- (A) Oxidation occurs at copper electrode
- (B) Reduction occurs at H₂ electrode
- (C) H₂ is cathode and Cu is anode
- (D) H₂ is anode and Cu is cathode

Correct Answer: (D) H₂ is anode and Cu is cathode

Solution:

Concept:

- The half-cell with the higher standard reduction potential undergoes reduction at the cathode of a galvanic cell.
- Oxidation occurs at the anode, and $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

Step 1: Compare the reduction potentials Copper has $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, exceeding the hydrogen-electrode value 0.00 V . Thus copper ions undergo reduction, $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$, at the copper cathode. Hydrogen undergoes oxidation, $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$, at the hydrogen anode.

Step 2: Verify spontaneity and reject the other statements The standard cell potential is $0.34 - 0.00 = +0.34 \text{ V}$, consistent with spontaneous galvanic operation. Option (A) incorrectly assigns oxidation to copper; (B) incorrectly assigns reduction to hydrogen. Option (C) reverses both electrode roles. Option (D) gives the correct roles.

Step 3: Conclusion The hydrogen electrode is the anode and copper is the cathode. Hence, the correct option is (D).

Quick Tip to Solve: Compare reduction potentials first: the more positive electrode is the galvanic cathode.

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

[1 mark]

- (A) $\Delta_r G^\circ = E^\circ_{\text{(cell)}}$
- (B) $\Delta_r G^\circ = nF E^\circ_{\text{(cell)}}$
- (C) $\Delta_r G^\circ = nE^\circ_{\text{cell}}$
- (D) $\Delta_r G^\circ = -nF E^\circ_{\text{(cell)}}$

Correct Answer: (D) $\Delta_r G^\circ = -nF E^\circ_{\text{(cell)}}$

Solution:

Concept:

- The maximum electrical work from a reversible cell equals the decrease in Gibbs energy.
- For transfer of n moles of electrons, the charge magnitude is nF , where F is the Faraday constant.

Step 1: Write the thermodynamic relation Electrical energy delivered by the cell is charge multiplied by potential difference, namely $nF E^\circ_{\text{cell}}$ under standard conditions. Since delivered work corresponds

Quick Tip to Solve: Use the sign check: a positive galvanic cell potential must correspond to a negative Gibbs-energy change.

to a decrease in the reacting system's Gibbs energy,

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

Step 2: Check sign and dimensions against the choices A spontaneous standard galvanic reaction has positive E_{cell}° and negative $\Delta_r G^\circ$. Option (B) has the wrong sign. Options (A) and (C) omit the Faraday constant and therefore do not convert potential into energy per mole of reaction. Option (D) includes the correct sign and both factors.

Step 3: Conclusion $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$. Hence, the correct option is (D).

Quick Tip to Solve: Use the sign check: a positive galvanic cell potential must correspond to a negative Gibbs-energy change.

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

[1 mark]

(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:

- A galvanic cell supplies current through a spontaneous reaction; an electrolytic cell uses external electrical energy to drive the reverse reaction.
- An opposing external potential must exceed the cell potential to reverse the direction of current.

Step 1: Compare the external and cell potentials When an external source is connected in opposition to a galvanic cell, the cell continues to supply current if $E_{\text{cell}} > E_{\text{ext}}$. At equality the two potentials balance, so there is no net current. Neither situation drives the reverse, non-spontaneous chemical reaction.

Step 2: Determine when electrolysis begins If $E_{\text{ext}} > E_{\text{cell}}$, the external source overcomes the cell emf and drives current in the reverse direction. The cell then behaves as an electrolytic cell. Thus (A) describes balance, (B) describes continued galvanic action, and (D) alone does not specify a reverse driving source. Only (C) gives the required inequality.

Step 3: Conclusion The condition is $E_{\text{ext}} > E_{\text{cell}}$. Hence, the correct option is (C).

Quick Tip to Solve: Equality stops the current; an opposing external voltage greater than the cell emf reverses it.

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

[1 mark]

- (A) o-Nitrophenol
- (B) p-Nitrophenol
- (C) Picric acid
- (D) Sodium phenoxide

Correct Answer: (C) Picric acid

Solution:

Concept:

- The hydroxyl group activates phenol towards electrophilic substitution and directs incoming groups to the ortho and para positions.
- Concentrated nitric acid introduces three nitro groups into the activated ring.

Step 1: Identify the nitration conditions Heating phenol with concentrated HNO_3 causes extensive nitration at both ortho positions and the para position. The product is 2,4,6-trinitrophenol, commonly called picric acid.

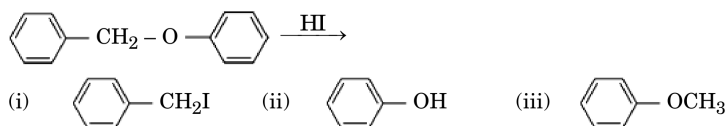
Step 2: Distinguish the other products Mononitration with dilute nitric acid gives a mixture of ortho- and para-nitrophenol, so (A) and (B) do not describe these concentrated-acid conditions. Sodium phenoxide requires a sodium base or sodium metal; nitric acid supplies no sodium, excluding (D).

Step 3: Conclusion Phenol gives picric acid. Hence, the correct option is (C).

Quick Tip to Solve: Link dilute nitric acid with mononitration, but concentrated nitric acid with 2,4,6-trinitration of phenol.

9. The products of the following reaction are:

[1 mark]



- (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:

- In an aryl-alkyl ether, hydrogen iodide cleaves the alkyl-oxygen bond after protonation of oxygen.
- The aryl-oxygen bond has partial double-bond character and resists cleavage by iodide.

Step 1: Locate the cleavable bond The ether is benzyl phenyl ether, $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$. Protonation makes the oxygen-containing group a better leaving group. Iodide attacks at the benzylic carbon, so

Quick Tip to Solve: For an aryl-alkyl ether with HI, retain oxygen on the aromatic ring and put iodine on the alkyl carbon.

the bond between CH_2 and oxygen breaks.

Step 2: Identify the product pair The reaction is



Thus (i) is benzyl iodide and (ii) is phenol. Product (iii), anisole, would require a methyl group absent from the reactant. Every combination containing (iii) is therefore incorrect.

Step 3: Conclusion The products are (i) and (ii). Hence, the correct option is (A).

Quick Tip to Solve: For an aryl-alkyl ether with HI, retain oxygen on the aromatic ring and put iodine on the alkyl carbon.

10. The quantity of electricity in Faraday, required to reduce 1 mol of $\text{Cr}_2\text{O}_7^{2-}$ to Cr^{3+} is: [1 mark]

- (A) 4F
- (B) 3F
- (C) 6F
- (D) 5F

Correct Answer: (C) 6F

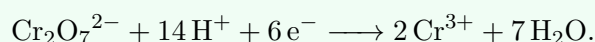
Solution:

Concept:

- One Faraday is the charge carried by one mole of electrons: $F \simeq 96485 \text{ C mol}^{-1}$.
- The required number of Faradays equals the number of moles of electrons accepted by the specified amount of reactant.

Step 1: Find the oxidation-state change In $\text{Cr}_2\text{O}_7^{2-}$, let the chromium oxidation state be x . Then $2x + 7(-2) = -2$, giving $x = +6$. Reduction to Cr^{3+} requires three electrons per chromium atom.

Step 2: Count electrons per dichromate ion Each dichromate ion contains two chromium atoms, so one mole accepts $2 \times 3 = 6$ moles of electrons. The balanced half-reaction is



Hence 3F counts only one chromium atom, while 4F and 5F do not match the electron balance.

Step 3: Conclusion The required quantity of electricity is $6F$. Hence, the correct option is (C).

Quick Tip to Solve: For dichromate, multiply the three-electron change per chromium atom by the two chromium atoms in each ion.

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

[1 mark]

- (A) Scandium
- (B) Zinc
- (C) Manganese
- (D) Cobalt

Correct Answer: (C) Manganese

Solution:

Concept:

- Transition elements show variable oxidation states because both outer s and inner d electrons can participate in bonding.
- The number of accessible oxidation states generally rises towards the middle of the first transition series.

Step 1: Examine manganese Manganese has the electronic configuration $[\text{Ar}] 3d^5 4s^2$. Its seven valence electrons permit a wide range of oxidation states, commonly from +2 to +7, including +2, +3, +4, +5, +6 and +7.

Step 2: Compare the remaining elements Scandium predominantly shows +3, while zinc predominantly shows +2 because its filled $3d^{10}$ shell is especially stable. Cobalt commonly exhibits +2 and +3 and has fewer accessible oxidation states than manganese. Thus none of these three has the breadth shown by manganese.

Step 3: Conclusion Manganese exhibits the maximum number of oxidation states among the given elements. Hence, the correct option is (C).

Quick Tip to Solve: Among first-row transition elements, manganese near the middle has the widest commonly encountered range of oxidation states.

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

[1 mark]

- (A) Reaction of ethanolic NH_3 with $\text{C}_6\text{H}_5\text{Cl}$
- (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:

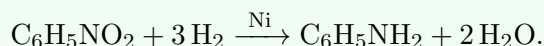
Concept:

- Reduction of a nitro group converts $-\text{NO}_2$ directly into $-\text{NH}_2$ without changing the carbon skeleton.
- Reduction of amides or nitriles by LiAlH_4 retains their carbon atom as a methylene group in the amine.

Step 1: Reduce nitrobenzene Catalytic hydrogenation of nitrobenzene with hydrogen and finely

Quick Tip to Solve: Distinguish aniline, with nitrogen directly on the ring, from benzylamine, which has an intervening methylene group.

divided nickel gives aniline:



The amino group is bonded directly to the benzene ring, as required for aniline.

Step 2: Reject the alternative reactions Chlorobenzene does not undergo ordinary ammonolysis with ethanolic ammonia because its aryl carbon–chlorine bond resists nucleophilic substitution. Reduction of benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, or benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, with LiAlH_4 yields benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, rather than aniline. Therefore (A), (C) and (D) do not provide the stated product under the given conditions.

Step 3: Conclusion Use hydrogen with finely divided nickel to reduce nitrobenzene. Hence, the correct option is (B).

Quick Tip to Solve: Distinguish aniline, with nitrogen directly on the ring, from benzylamine, which has an intervening methylene group.

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

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

[1 mark]

- (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:

- Thermodynamic stability is measured by the overall formation constant: a larger constant means a more stable complex.
- The chelate effect compares suitably similar ligands; it does not by itself rank complexes containing different kinds of donor ligands.

Step 1: Evaluate the assertion For the literal pair given, $[\text{Co}(\text{CN})_6]^{3-}$ is more thermodynamically stable than $[\text{Co}(\text{en})_3]^{3+}$. Cyanide binds cobalt(III) exceptionally strongly, and the overall formation constant of the cyanido complex is larger. Although en forms chelate rings, that advantage does not outweigh the metal–cyanide bonding in this comparison. Thus the assertion is false.

Step 2: Evaluate the reason Ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, contains two nitrogen donor atoms. Each en ligand binds through both nitrogen atoms to the same metal ion, forming a five-membered chelate ring. It is therefore a bidentate, chelating ligand, so the reason is true.

Quick Tip to Solve: Do not rank complexes of different ligands using denticity alone: cyanide can give greater stability despite being monodentate.

Step 3: Check the proposed explanation Chelation enhances stability relative to an appropriate monodentate-ligand comparison, but does not prove greater stability than every monodentate-ligand complex. Here cyanide and en differ in their bonding properties. The true statement about en cannot explain the false stability ranking; codes (A), (B) and (C) all require a true assertion.

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is (D).

Quick Tip to Solve: Do not rank complexes of different ligands using denticity alone: cyanide can give greater stability despite being monodentate.

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.

[1 mark]

- (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:

- Thionyl chloride converts an alcohol into an alkyl chloride while producing gaseous sulfur dioxide and hydrogen chloride.
- Gaseous by-products escape from the reaction mixture, simplifying purification of the organic product.

Step 1: Evaluate the assertion The assertion reverses the usual preference. Thionyl chloride is preferred for preparing alkyl chlorides from alcohols because its by-products can leave as gases. Phosphorus halides are therefore not preferred over thionyl chloride for this preparation; the assertion is false.

Step 2: Evaluate the reason The conversion is



Escape of SO_2 and HCl leaves the alkyl chloride readily separable in a pure form. Thus the reason is true in the context of alkyl chloride preparation.

Step 3: Select the assertion–reason code A true reason cannot make the reversed preference in the assertion correct. Codes (A) and (B) require a true assertion, and code (C) requires a false reason. The appropriate combination is a false assertion with a true reason.

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is (D).

Quick Tip to Solve: For alcohol to alkyl chloride, remember that thionyl chloride is preferred because both side products escape as gases.

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. [1 mark]

- (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 alkylation and acylation are electrophilic aromatic substitution reactions and require a sufficiently electron-rich aromatic ring.
- The carboxyl group, $-\text{COOH}$, withdraws electron density by inductive and resonance effects; its oxygen atoms can coordinate to the Lewis acid AlCl_3 .

Step 1: Judge the assertion Aromatic carboxylic acids such as benzoic acid do not undergo the usual Friedel-Crafts reaction. Their aromatic rings are strongly deactivated towards electrophilic substitution by the electron-withdrawing carboxyl group. Thus Assertion (A) is true.

Step 2: Judge the reason The carboxyl group is deactivating. In addition, the Lewis-acid catalyst AlCl_3 forms a complex with an oxygen atom of the carboxyl group, so it becomes bonded to that group. Both statements in Reason (R) are true.

Step 3: Check the explanatory link The reason identifies both the reduced reactivity of the ring and the interaction of the functional group with the catalyst. These account for the failure of the usual Friedel-Crafts reaction. Hence R directly explains A; the alternatives claiming a false statement or no explanatory connection do not apply.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is (A).

Quick Tip to Solve: For Friedel-Crafts reactions, check both ring deactivation and complex formation with AlCl_3 .

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

Reason (R): The intermolecular forces of attraction between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. [1 mark]

- (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:

- For an ideal solution, unlike and like intermolecular attractions are comparable: $A - B \approx A - A \approx B - B$.
- Ideal mixing has $\Delta_{\text{mix}}V = 0$, where $\Delta_{\text{mix}}V = V_{\text{solution}} - (V_A + V_B)$.

Step 1: Judge the assertion An ideal solution shows no expansion or contraction on mixing. Therefore its final volume equals the sum of the component volumes measured at the same temperature and pressure: $V_{\text{solution}} = V_A + V_B$. Assertion (A) is true.

Step 2: Judge the reason In an ideal solution, solute-solvent attractions have approximately the same strength as solute-solute and solvent-solvent attractions. They are not weaker, as the printed reason claims. Weaker unlike attractions instead favour positive deviation from Raoult's law. Reason (R) is false.

Step 3: Check the explanatory link The proposed reason cannot explain ideal volume additivity because it contradicts the intermolecular condition for ideal mixing. Options requiring both statements to be true or the assertion to be false are therefore excluded.

Step 4: Conclusion A is true and R is false. Hence, the correct option is (C).

Quick Tip to Solve: Associate an ideal solution with similar like and unlike attractions and zero volume change on mixing.

Section B (10 marks)

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

(ii) 'E° for Mn³⁺/Mn²⁺ couple is more positive than that for Fe³⁺/Fe²⁺.' Justify the statement.

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

[2 marks]

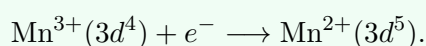
Solution:

Concept:

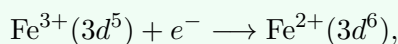
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids because 4f electrons shield nuclear charge poorly.
- A more positive standard reduction potential means a greater thermodynamic tendency for reduction under standard conditions. A half-filled 3d⁵ subshell has additional stability.

Step 1: (i) Compare zirconium and hafnium Hafnium follows the lanthanoids in the periodic table. Poor shielding by the intervening 4f electrons increases the effective nuclear attraction and contracts its size. Consequently, Zr and Hf have almost the same atomic and ionic radii despite belonging to successive periods. Together with their similar outer electronic configurations and common +4 oxidation state, this gives very similar chemical properties.

Step 2: (ii) Compare the two reduction processes For manganese, Mn³⁺ is 3d⁴, whereas Mn²⁺ is the particularly stable half-filled 3d⁵:



Reduction therefore gains half-filled-subshell stability. For iron,



reduction starts from the stable half-filled configuration and loses that special stability. Thus manganese(III) has a stronger tendency to accept an electron than iron(III), accounting for the more positive reduction potential of the manganese couple.

Step 3: Conclusion (i) Zr and Hf resemble each other because of lanthanoid contraction. (ii) Reduction of Mn³⁺ produces stable 3d⁵, while reduction of Fe³⁺ destroys 3d⁵ stability, so $E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^\circ > E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ$.

Quick Tip to Solve: Write the d-electron counts on both sides of each reduction before comparing half-filled-shell stability.

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

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

[2 marks]

Solution:

Concept:

- Variable oxidation states in transition elements arise because both the outer ns and inner $(n - 1)d$ electrons can participate in bonding.
- Visible colour in ordinary aqueous transition-metal ions commonly arises from electronic transitions between ligand-field-split, partially occupied d orbitals.

Step 1: (i) Identify the element and its electronic configuration Scandium, Sc, does not exhibit variable oxidation states in its usual compounds. Its ground-state configuration is $[\text{Ar}]3d^14s^2$. It loses the two $4s$ electrons and the single $3d$ electron to form Sc^{3+} , with the stable noble-gas configuration $[\text{Ar}]$. Removing another electron would disrupt the inner closed shell and requires very high energy. Hence its characteristic oxidation state is +3.

Step 2: (ii) Compare the copper ions Copper has configuration $[\text{Ar}]3d^{10}4s^1$. Accordingly, Cu^+ has $[\text{Ar}]3d^{10}$, a completely filled d subshell. No $d-d$ transition is available within that filled subshell, so the ion is colourless. In contrast, Cu^{2+} has $[\text{Ar}]3d^9$, an incompletely filled d subshell. In its aqueous complex, water ligands split the d -orbital energies; absorption of visible light promotes d electrons between these levels, giving the observed colour.

Step 3: Conclusion (i) Scandium: its usual oxidation state is +3, giving stable $[\text{Ar}]$. (ii) Cu^+ is $3d^{10}$ and colourless; Cu^{2+} is $3d^9$ and coloured because $d-d$ transitions are possible.

Quick Tip to Solve: Count d electrons in the ion, after removing $4s$ electrons first, before predicting its aqueous colour.

18. A reaction $\text{A} \rightarrow \text{B}$ 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?

[2 marks]

Solution:

Concept:

- For a second-order reaction involving a single reactant A, the instantaneous rate is $r = k[A]^2$, with rate constant k .
- At constant temperature, the same k applies before and after changing concentration, so $r_2/r_1 = ([A]_2/[A]_1)^2$.

Step 1: Establish the reference rate Let the original concentration be $[A]_1 = c$, so the original rate is $r_1 = kc^2$. Only the concentration is changed, and the temperature is held fixed. Each stated change is compared separately with this original concentration and rate.

Step 2: (i) Increase the concentration threefold The new concentration is $[A]_2 = 3c$. Substitution

Quick Tip to Solve: For a second-order rate law, square the concentration multiplier: $3^2 = 9$ and $(1/2)^2 = 1/4$.

into the second-order rate law gives

$$r_2 = k(3c)^2 = 9kc^2 = 9r_1.$$

Thus tripling the concentration multiplies the rate by the square of three. The order refers to the exponent on concentration; the rate does not merely triple.

Step 3: (ii) Reduce the concentration to half The new concentration is $[A]_3 = c/2$. Hence

$$r_3 = k\left(\frac{c}{2}\right)^2 = \frac{kc^2}{4} = \frac{r_1}{4}.$$

The new rate is one-fourth of the original rate, corresponding to a fourfold reduction. These factors follow from the rate law, without needing a numerical value of k or an elapsed reaction time.

Step 4: Conclusion (i) The rate becomes 9 times the original rate. (ii) The rate becomes $\frac{1}{4}$ of the original rate.

Quick Tip to Solve: For a second-order rate law, square the concentration multiplier: $3^2 = 9$ and $(1/2)^2 = 1/4$.

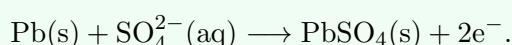
19. Write the reactions taking place at anode and cathode in a lead storage battery, when it is in use. [2 marks]

Solution:

Concept:

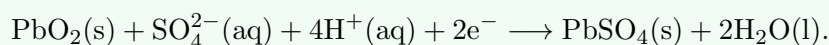
- A lead storage battery supplies current by a spontaneous redox reaction during discharge. Oxidation occurs at the lead anode and reduction at the lead dioxide cathode.
- The electrolyte is aqueous sulphuric acid. Sulphate ions convert both electrode materials to insoluble lead sulphate, PbSO_4 .

Step 1: Anode reaction during use The lead plate is the negative electrode. Lead loses two electrons and changes from oxidation state zero to +2. Its balanced oxidation half-reaction is



The electrons released pass through the external circuit to the cathode.

Step 2: Cathode reaction during use At the positive electrode, lead in PbO_2 is reduced from +4 to +2. In the acidic electrolyte, the balanced reduction half-reaction is



Both atoms and net charge balance. Adding the two half-reactions cancels the two electrons; sulphuric acid is consumed as the battery discharges.

Step 3: Conclusion During discharge, lead is oxidised at the anode and lead dioxide is reduced at the cathode, according to the balanced half-reactions above. Both electrodes form lead sulphate.

Quick Tip to Solve: For a battery in use, write oxidation at Pb and reduction at PbO_2 ; both electrodes form lead sulphate.

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]

[2 marks]

Solution:

Concept:

- For an ideal solution containing a non-volatile solute, Raoult's law gives $p = x_1 p^0$. Thus the relative lowering $(p^0 - p)/p^0 = x_2$, the solute mole fraction.
- If the solute is dilute, $x_2 \simeq n_2/n_1$, where $n_1 = w_1/M_1$ is the amount of water and $n_2 = w_2/M_2$ is the amount of solute.

Step 1: Calculate relative lowering Here $p^0 = 32$ mm Hg, $p = 31.84$ mm Hg, $w_2 = 10$ g and $w_1 = 200$ g. Therefore

$$\frac{p^0 - p}{p^0} = \frac{32 - 31.84}{32} = 0.005.$$

The two pressures have the same units, so their ratio is dimensionless. Take the molar mass of water as $M_1 = 18 \text{ g mol}^{-1}$.

Step 2: Obtain the molar mass Using the dilute-solution expression,

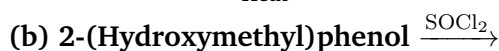
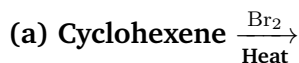
$$0.005 = \frac{w_2 M_1}{M_2 w_1} = \frac{10 \times 18}{M_2 \times 200}, \quad M_2 = 180 \text{ g mol}^{-1}.$$

The dilution approximation is justified by the small solute mole fraction. If the exact mole-fraction denominator is retained, $0.005 = (10/M_2)/(200/18 + 10/M_2)$, which gives $M_2 = 179.1 \text{ g mol}^{-1}$, consistent with the usual dilute-solution result.

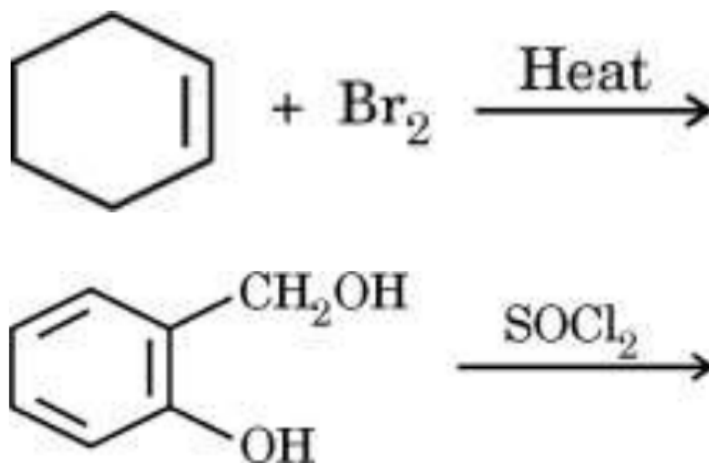
Step 3: Conclusion The molar mass of the solute is approximately 180 g mol^{-1} using the dilute-solution formula (exact mole-fraction calculation: 179.1 g mol^{-1}).

Quick Tip to Solve: Compute the small pressure difference first: 0.16 mm Hg, then divide by the pure-solvent pressure 32 mm Hg.

21. Draw the structures of major monohalo products in each of the following:



[2 marks]



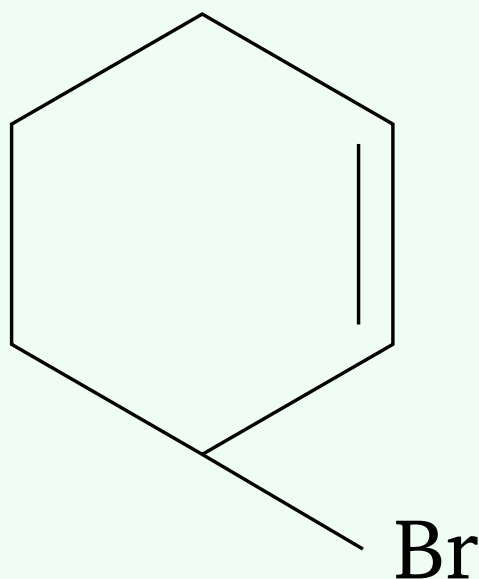
Solution:

Concept:

- Heating bromine with an alkene under allylic substitution conditions replaces an allylic hydrogen while retaining the carbon-carbon double bond.
- Thionyl chloride replaces the hydroxyl group of a benzylic alcohol by chlorine. The phenolic C(sp²) – OH group does not undergo the corresponding substitution.

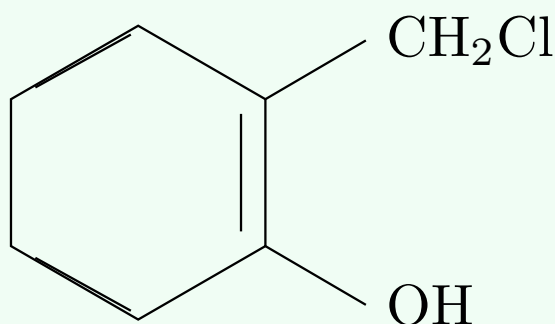
Step 1: Product from cyclohexene In cyclohexene the carbons next to the double bond are allylic. Heating with Br₂, as specified, favours allylic radical substitution for the requested monohalo product. Replacement of one allylic hydrogen gives 3-bromocyclohex-1-ene, together with HBr. The symmetry-related allylic positions give the same constitutional product. Addition across the double bond would instead give a dibromo product and does not answer the requested monohalo transformation.

Quick Tip to Solve: Keep the double bond for heated allylic bromination; with SOCl₂ replace only the benzylic CH₂OH group.



Product (a): 3-bromocyclohex-1-ene

Step 2: Product from the benzylic alcohol The starting compound has adjacent $-\text{CH}_2\text{OH}$ and phenolic $-\text{OH}$ groups. Reaction with SOCl_2 converts $-\text{CH}_2\text{OH}$ to $-\text{CH}_2\text{Cl}$, releasing SO_2 and HCl . The aryl carbon–oxygen bond has partial double-bond character, so the phenolic hydroxyl remains unchanged. The major product is 2-(chloromethyl)phenol, shown below with the substituents in the required ortho positions.



Product (b): 2-(chloromethyl)phenol

Step 3: Conclusion (a) 3-Bromocyclohex-1-ene. (b) 2-(Chloromethyl)phenol, $o\text{-HOC}_6\text{H}_4\text{CH}_2\text{Cl}$.

Quick Tip to Solve: Keep the double bond for heated allylic bromination; with SOCl_2 replace only the benzylic CH_2OH group.

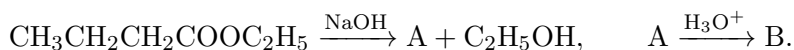
Section C (21 marks)

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

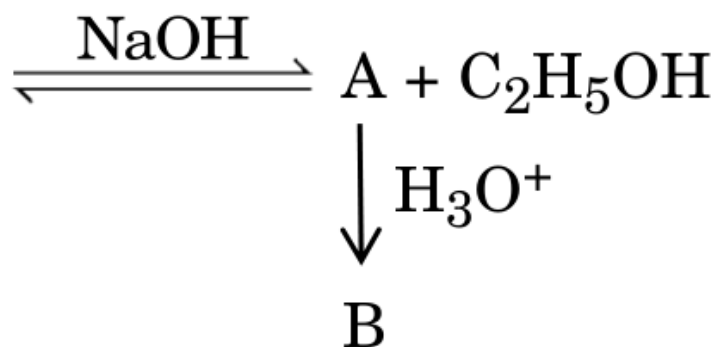
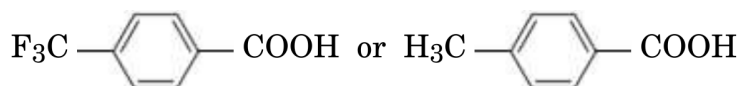
(ii) Which of the given acids is stronger and why?

$p\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}$ or $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$.

(iii) Complete the given reaction sequence:



[3 marks]

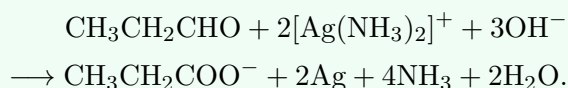


Solution:

Concept:

- Tollens'reagent, ammoniacal silver(I), oxidises an aldehyde to a carboxylate while silver(I) is reduced to metallic silver. Ordinary ketones do not respond.
- Electron-withdrawing groups stabilise a carboxylate ion and increase acidity; electron-donating groups have the opposite effect.
- Alkaline hydrolysis of an ester forms the carboxylate salt and an alcohol. Acidification subsequently gives the free carboxylic acid.

Step 1: (i) Distinguish propanal and propanone Warm separate samples with freshly prepared Tollens'reagent in a water bath. Propanal gives a silver mirror, while propanone gives no silver mirror. The aldehyde oxidation can be represented by



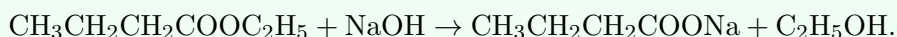
Thus a positive silver-mirror test identifies propanal.

Step 2: (ii) Compare the two aromatic acids $p\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}$ is stronger than $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$. The $-\text{CF}_3$ group has a strong electron-withdrawing inductive effect and stabilises the negative charge of the benzoate conjugate base. The $-\text{CH}_3$ group is electron donating and destabilises the

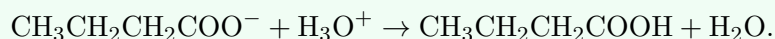
Quick Tip to Solve: For ester hydrolysis, follow the acyl chain: NaOH gives its sodium salt, and H_3O^+ then gives the acid.

carboxylate relative to the trifluoromethyl-substituted compound. Greater conjugate-base stability favours dissociation of the first acid.

Step 3: (iii) Identify A and B Ethyl butanoate undergoes saponification:



Therefore A is sodium butanoate. Acidification protonates its carboxylate group:



Hence B is butanoic acid; the four-carbon acyl chain is retained in both stages.

Step 4: Conclusion (i) Propanal gives Tollens' silver mirror; propanone does not. (ii) The para-trifluoromethyl acid is stronger. (iii) A = $\text{CH}_3\text{CH}_2\text{CH}_2\text{COONa}$; B = $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$.

Quick Tip to Solve: For ester hydrolysis, follow the acyl chain: NaOH gives its sodium salt, and H_3O^+ then gives the acid.

OR

22(b). An organic compound with the molecular formula $\text{C}_9\text{H}_{10}\text{O}$ 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.

[3 marks]

Solution:

Concept:

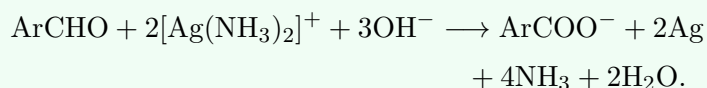
- A positive 2,4-DNP test establishes a carbonyl group; reduction of Tollens' reagent identifies the compound as an aldehyde.
- Cannizzaro disproportionation occurs for an aldehyde without an α -hydrogen: one molecule is oxidised to carboxylate and another is reduced to alcohol.
- Vigorous oxidation converts an alkyl side chain containing a benzylic hydrogen into a carboxyl group. Phthalic acid has adjacent carboxyl groups.

Step 1: Identify the carbon skeleton The molecular formula is $\text{C}_9\text{H}_{10}\text{O}$. Since both carbonyl and Tollens tests are positive, the oxygen belongs to an aldehyde group. An aromatic aldehyde has no α -hydrogen on the carbon attached to $-\text{CHO}$, allowing Cannizzaro reaction. The remaining two carbons form an ethyl substituent on the benzene ring. Formation of phthalic acid on vigorous oxidation places the ethyl and aldehyde groups ortho to each other. Thus the compound is 2-ethylbenzaldehyde, $o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{CHO}$. Both side chains oxidise to adjacent $-\text{COOH}$ groups.

Step 2: Reaction with Tollens reagent Let $\text{Ar} = o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4$. The aldehyde is oxidised to carboxylate

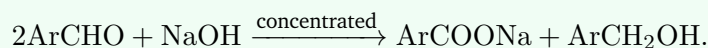
Quick Tip to Solve: Use the oxidation product to locate the substituents: phthalic acid fixes their positions as ortho.

while silver(I) is reduced to metallic silver, producing a silver mirror:



The immediate organic product in alkaline Tollens reagent is 2-ethylbenzoate; acidification yields 2-ethylbenzoic acid.

Step 3: Cannizzaro reaction With concentrated aqueous alkali, two molecules disproportionate:



The products are sodium 2-ethylbenzoate and (2-ethylphenyl)methanol. The ethyl group remains unchanged; the aldehyde carbon in one molecule is oxidised, while that in the other is reduced. Benzylic hydrogens on the ethyl group are not alpha-hydrogens of the aldehyde group.

Step 4: Conclusion The compound is 2-ethylbenzaldehyde. It gives a silver mirror with Tollens reagent and sodium 2-ethylbenzoate plus (2-ethylphenyl)methanol with concentrated NaOH.

Quick Tip to Solve: Use the oxidation product to locate the substituents: phthalic acid fixes their positions as ortho.

23. (a) Arrange the following compounds in the decreasing order of their acidic strength: Phenol, 4-Nitrophenol, 2,4,6-Trinitrophenol

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

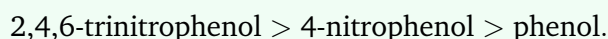
(c) Name the reagent used in the oxidation of a primary unsaturated alcohol to an aldehyde. [3 marks]

Solution:

Concept:

- Phenol acidity depends on the stability of the phenoxide ion formed on losing H^+ . Electron-withdrawing substituents stabilise this conjugate base.
- Alcohols form intermolecular hydrogen bonds with water through the hydroxyl group.
- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde under anhydrous conditions.

Step 1: (a) Compare the acidic strengths The decreasing order is



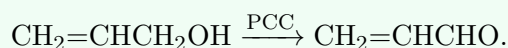
Nitro groups withdraw electron density by their inductive effect and, at ortho and para positions, by resonance. They stabilise the negative charge of the phenoxide conjugate base. The three nitro groups in 2,4,6-trinitrophenol provide greater stabilisation than the single para nitro group in 4-nitrophenol, so proton loss is most favourable for trinitrophenol. Unsubstituted phenol has no such additional stabilisation.

Step 2: (b) Explain water solubility The polar $-\text{OH}$ group of an alcohol forms hydrogen bonds

Quick Tip to Solve: Count electron-withdrawing nitro groups for acidity; choose PCC when oxidation must stop at an aldehyde.

with water molecules: the oxygen can accept a hydrogen bond and the hydroxyl hydrogen can donate one. These favourable alcohol-water interactions help the molecules enter the aqueous phase. Hydrocarbons of comparable molecular masses are essentially nonpolar and cannot form hydrogen bonds with water, so their solubility is lower. For alcohols, increasing the size of the nonpolar alkyl portion generally decreases solubility.

Step 3: (c) Select the oxidation reagent The reagent is pyridinium chlorochromate, PCC, commonly used in anhydrous dichloromethane. It converts the primary alcohol group into an aldehyde while retaining the carbon-carbon double bond. For example,



Controlled, anhydrous conditions prevent further oxidation of the aldehyde to the carboxylic acid.

Step 4: Conclusion (a) 2,4,6-Trinitrophenol > 4-nitrophenol > phenol. (b) Alcohols hydrogen-bond with water. (c) Use PCC.

Quick Tip to Solve: Count electron-withdrawing nitro groups for acidity; choose PCC when oxidation must stop at an aldehyde.

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.

[Given: Molar mass of $\text{Na}_2\text{SO}_4 = 142 \text{ g mol}^{-1}$, K_f for water = $1.86 \text{ K kg mol}^{-1}$]

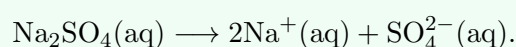
[3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f the molal depression constant, and m the molality.
- Molality is moles of solute per kilogram of solvent; use the mass of water, not the mass of solution.
- Complete dissociation of Na_2SO_4 gives two sodium ions and one sulfate ion per formula unit, so $i = 3$.

Step 1: Determine the particle factor The assumed complete dissociation is



Thus one mole of salt yields three moles of dissolved particles. The van't Hoff factor is therefore $i = 3$. The ions are counted as particles irrespective of the magnitudes of their charges; sulfate counts as one ion, not two.

Step 2: Calculate the molality The amount of sodium sulfate and the mass of solvent are

$$n = \frac{2 \text{ g}}{142 \text{ g mol}^{-1}} = 0.0140845 \text{ mol}, \quad w = \frac{50}{1000} = 0.050 \text{ kg}.$$

Quick Tip to Solve: Count all three ions first, convert 50 g water to 0.050 kg, and subtract the depression from zero Celsius.

Hence the molality of salt before applying the particle factor is

$$m = \frac{n}{w} = \frac{2/142}{0.050} = 0.28169 \text{ mol kg}^{-1}.$$

Using the solvent mass in kilograms is essential because K_f is expressed in molality units.

Step 3: Find the depression and the freezing point Substitution gives

$$\begin{aligned}\Delta T_f &= iK_fm \\ &= 3 \times 1.86 \times 0.28169 \\ &= 1.57183 \text{ K.}\end{aligned}$$

Pure water freezes at 0°C . Since dissolved nonvolatile solute lowers the freezing point,

$$T_f = T_f^\circ - \Delta T_f = 0 - 1.57183 = -1.57183^\circ\text{C}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius; the absolute freezing temperature is approximately 271.58 K.

Step 4: Conclusion The freezing point of the solution is -1.57°C (approximately 271.58 K).

Quick Tip to Solve: Count all three ions first, convert 50 g water to 0.050 kg, and subtract the depression from zero Celsius.

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

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

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

[3 marks]

Solution:

Concept:

- Nucleic acids are polynucleotides whose nucleotide units contain a pentose sugar, a nitrogenous base and phosphate.
- Starch contains amylose and amylopectin. Interchain bonds in proteins are distinct from the peptide bonds within a chain.

Step 1: (a) Compare DNA and RNA DNA contains 2-deoxy-D-ribose, whereas RNA contains D-ribose. At the 2' carbon DNA has H instead of the OH group found in RNA. Secondly, DNA contains the pyrimidine base thymine, while RNA contains uracil in its place. Adenine, guanine and cytosine occur in both. These give two structural differences in their nucleotide constituents.

Step 2: (b) Identify the branched starch component The component is amylopectin. Its characteristic feature is its branched structure. The α -D-(+)-glucose units form chains through $\alpha(1 \rightarrow 4)$ glycosidic linkages, while the branch points contain $\alpha(1 \rightarrow 6)$ glycosidic linkages. Amylose, in contrast, is predominantly linear.

Quick Tip to Solve: For two DNA–RNA differences, compare the sugar and thymine versus uracil; distinguish interchain bonds from peptide bonds.

Step 3: (c) State the bonds holding the chains The polypeptide chains in fibrous proteins are held together by hydrogen bonds and disulphide bonds. Hydrogen bonds involve suitable polar groups on the chains; disulphide bridges are covalent $-S-S-$ links between cysteine residues. Peptide bonds join amino-acid residues within a polypeptide chain and should not replace these interchain bonds in the answer.

Step 4: Conclusion (a) DNA has deoxyribose and thymine; RNA has ribose and uracil. (b) Amylopectin has a branched structure. (c) Hydrogen and disulphide bonds hold the chains together.

Quick Tip to Solve: For two DNA–RNA differences, compare the sugar and thymine versus uracil; distinguish interchain bonds from peptide bonds.

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

(b) Explain the Finkelstein reaction.

[3 marks]

Solution:

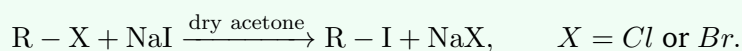
Concept:

- Reactivity towards nucleophilic substitution depends on the strength and nature of the carbon–halogen bond.
- Finkelstein reaction is halogen exchange: an alkyl chloride or bromide reacts with sodium iodide in dry acetone to form an alkyl iodide.

Step 1: (a) Explain the resonance effect In a haloarene, a lone pair of the halogen overlaps with the aromatic ring and participates in resonance. Consequently the carbon–halogen bond acquires partial double-bond character. It is shorter and stronger than the ordinary single carbon–halogen bond in a haloalkane, so its cleavage by a nucleophile is more difficult.

Step 2: (a) Explain the hybridisation effect The carbon bonded to halogen in a haloarene is sp^2 -hybridised, whereas that in a haloalkane is sp^3 -hybridised. The sp^2 carbon has greater s-character and holds the bonding electron pair more tightly. The resulting shorter, stronger carbon–halogen bond is harder to break. These two effects account for the lower substitution reactivity of haloarenes.

Step 3: (b) Explain Finkelstein reaction An alkyl chloride or alkyl bromide is heated with sodium iodide in dry acetone to replace chlorine or bromine by iodine:



Sodium chloride or sodium bromide precipitates because it is insoluble in acetone. Removal of this salt drives the halogen-exchange reaction towards the alkyl iodide. For example, bromoethane gives iodoethane with sodium iodide.

Step 4: Conclusion Haloarenes resist nucleophilic substitution because resonance gives partial double-bond character and the halogen-bearing carbon is sp^2 -hybridised. Finkelstein reaction converts alkyl chlorides/bromides into alkyl iodides using NaI in dry acetone.

Quick Tip to Solve: For haloarenes, connect both resonance and hybridisation to a stronger C–X bond; remember dry acetone and salt precipitation for Finkelstein.

27. Conductivity of 2.5×10^{-4} M methanoic acid solution is $5.25 \times 10^{-5} \text{ S cm}^{-1}$.

(a) Calculate its molar conductivity.

(b) Calculate its degree of dissociation.

[Given: $\lambda^\circ_{(\text{H}^+)} = 349.5 \text{ S cm}^2 \text{ mol}^{-1}$ and $\lambda^\circ_{(\text{HCOO}^-)} = 50.5 \text{ S cm}^2 \text{ mol}^{-1}$]

[3 marks]

Solution:

Concept:

- Molar conductivity is conductivity multiplied by the volume containing one mole. With concentration in mol per litre, use $\Lambda_m = 1000\kappa/c$ when conductivity is in S per centimetre.
- By Kohlrausch's law, limiting molar conductivity is the sum of the limiting ionic contributions. For a weak electrolyte, $\alpha = \Lambda_m/\Lambda_m^\circ$.

Step 1: (a) Calculate molar conductivity The given conductivity is $\kappa = 5.25 \times 10^{-5} \text{ S cm}^{-1}$, and concentration is $c = 2.5 \times 10^{-4} \text{ mol L}^{-1}$. The factor 1000 converts litres into cubic centimetres:

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{c} \\ &= \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}} \\ &= 210 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

The units are consistent because conductivity is expressed per centimetre.

Step 2: (b) Find limiting molar conductivity Methanoic acid dissociates as $\text{HCOOH} \rightleftharpoons \text{H}^+ + \text{HCOO}^-$. At infinite dilution its molar conductivity is the sum of the ionic contributions:

$$\begin{aligned}\Lambda_m^\circ &= \lambda_{\text{H}^+}^\circ + \lambda_{\text{HCOO}^-}^\circ \\ &= 349.5 + 50.5 \\ &= 400.0 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

Each mole of dissociated acid supplies one mole of each ion.

Step 3: (b) Calculate the degree of dissociation For this weak acid, the ratio of the molar conductivity at the given concentration to its limiting value gives the fraction dissociated:

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

Thus 52.5 percent of the acid is dissociated. The result lies between zero and one, as required for a degree of dissociation; the observed molar conductivity is correspondingly below its limiting value.

Step 4: Conclusion $\Lambda_m = 210 \text{ S cm}^2 \text{ mol}^{-1}$ and $\alpha = 0.525 = 52.5\%$.

Quick Tip to Solve: When conductivity is in S per centimetre and concentration in mol per litre, include the factor 1000 before dividing by concentration.

28. (a) Define 'Denatured Protein' with an example.

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

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

[3 marks]

Solution:

Concept:

- Denaturation disrupts the secondary and tertiary structures of a protein, causing loss of its biological activity; the primary peptide chain remains intact.
- The open-chain aldehyde group of glucose undergoes nucleophilic addition with hydrogen cyanide, HCN. Vitamin C is ascorbic acid.

Step 1: (a) Define denaturation and give an example A denatured protein is a protein whose native secondary and tertiary structures have been disrupted by heat or a change in pH, so that it loses its characteristic biological activity. The peptide bonds of its primary structure are not broken in this process. For example, on boiling an egg, the soluble albumin in the egg white denatures and coagulates into an insoluble white mass.

Step 2: (b) React glucose with hydrogen cyanide Glucose reacts with HCN to form glucose cyanohydrin. Cyanide attacks the carbonyl carbon of the open-chain aldehyde form, followed by protonation of oxygen. The reaction is



The aldehyde carbon becomes a carbon bearing both the hydroxyl and cyanide groups. This addition reaction supports the presence of a carbonyl group in glucose.

Step 3: (c) Identify the deficiency disease Deficiency of vitamin C causes scurvy. Its characteristic symptoms include bleeding gums and impaired wound healing, associated with defective collagen formation.

Step 4: Conclusion (a) Denatured protein: a protein with disrupted native folding and lost biological activity, e.g. boiled egg albumin. (b) Glucose forms its cyanohydrin with HCN. (c) Vitamin C deficiency causes scurvy.

Quick Tip to Solve: For glucose plus HCN, replace the terminal $-\text{CHO}$ by $-\text{CH}(\text{OH})\text{CN}$; retain the rest of the chain.

Section D (8 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

29(a). Case Study: 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 α -hydrogen. Aldehydes and ketones having at least one α -hydrogen atom undergo a reaction in the presence of dilute alkali as a catalyst to form β -hydroxy aldehydes or β -hydroxy ketones. On the other hand, aldehydes which do not possess an α -hydrogen undergo self-oxidation and reduction in the presence of concentrated alkali.

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

Cyclohexanone, Benzaldehyde, Methanal, 2-Methylpentanal

[2 marks]

Solution:

Concept:

- Aldol condensation requires at least one α -hydrogen on a carbon adjacent to the carbonyl carbon.
- Cannizzaro reaction is the disproportionation of an aldehyde lacking α -hydrogen in concentrated alkali.

Step 1: Identify compounds with alpha-hydrogen Cyclohexanone has methylene groups adjacent to its carbonyl group, so it contains α -hydrogens and undergoes aldol condensation. In 2-methylpentanal, $\text{CHO} - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$, carbon 2 bears one hydrogen. This hydrogen is adjacent to the aldehyde carbonyl, so 2-methylpentanal also undergoes aldol condensation.

Step 2: Identify aldehydes without alpha-hydrogen Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no hydrogen on the ring carbon directly attached to the aldehyde group. Methanal, HCHO , has no adjacent carbon at all. Neither therefore has an α -hydrogen. Both undergo Cannizzaro reaction in concentrated alkali, forming an alcohol and a carboxylate salt by self-reduction and self-oxidation, respectively.

Step 3: Conclusion Aldol condensation: cyclohexanone and 2-methylpentanal. Cannizzaro reaction: benzaldehyde and methanal.

Quick Tip to Solve: Count hydrogen on the carbon next to $\text{C}=\text{O}$, not on the aldehyde carbon itself; one alpha-hydrogen suffices.

29(b). Arrange the following compounds in increasing order of reactivity towards nucleophilic addition reactions: Butanone, Propanone, Propanal, Ethanal [1 mark]

Solution:

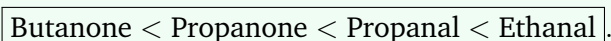
Concept:

- Reactivity increases when the carbonyl carbon is more electrophilic and less sterically hindered. Alkyl groups donate electron density by the +I effect.

Step 1: Compare ketones and aldehydes Butanone and propanone have two alkyl groups attached to the carbonyl carbon; propanal and ethanal have only one. The two alkyl groups reduce electrophilicity and hinder nucleophile approach, so the ketones are less reactive than the aldehydes.

Step 2: Compare members of each class Butanone has an ethyl group in place of one methyl group of propanone and is less reactive. Likewise, propanal has an ethyl group instead of the methyl group in ethanal and is less reactive because of greater electron donation and steric hindrance.

Step 3: Conclusion The increasing order is



Quick Tip to Solve: First place both ketones before both aldehydes; within each pair, the smaller alkyl group favours addition.

OR

29(b). Draw the structure of the semicarbazone of cyclohexanone. [1 mark]

Solution:

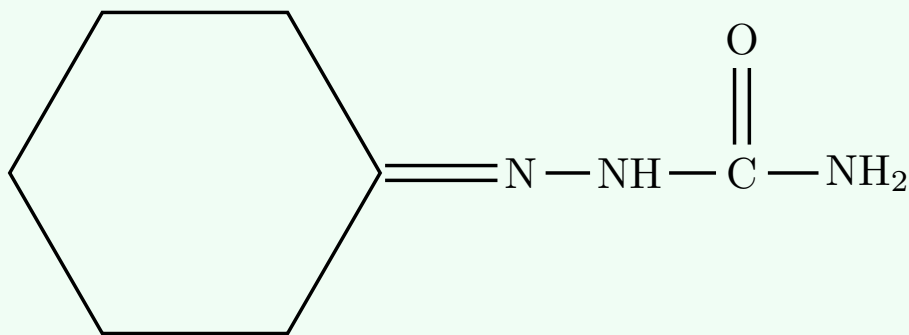
Concept:

- Semicarbazide, $\text{H}_2\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, reacts through its terminal hydrazino $-\text{NH}_2$ group with a carbonyl compound.

Step 1: Replace the carbonyl oxygen Cyclohexanone condenses with semicarbazide, eliminating water. Its ring carbonyl group $>\text{C}=\text{O}$ is converted into $>\text{C}=\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, while the six-membered carbon ring is retained.

Step 2: Identify the product linkage The exocyclic double bond joins the former carbonyl carbon to nitrogen. The remainder of the attached chain is $-\text{NH} - \text{C}(=\text{O}) - \text{NH}_2$; the amide carbonyl of semicarbazide remains unchanged. The labelled skeletal structure below shows this connectivity.

Quick Tip to Solve: Keep the six-carbon ring intact and replace only its $\text{C}=\text{O}$ oxygen by $\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$.



Semicarbazone of cyclohexanone

Step 3: Conclusion The semicarbazone of cyclohexanone is the six-membered ring bearing the exocyclic group $>C = N - NH - C(=O) - NH_2$.

Quick Tip to Solve: Keep the six-carbon ring intact and replace only its C=O oxygen by N-NH-C(=O)-NH₂.

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

[1 mark]

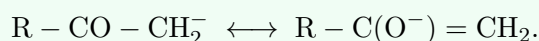
Solution:

Concept:

- Removal of an α -hydrogen as a proton from a carbonyl compound gives an enolate ion, whose negative charge is delocalised by resonance.

Step 1: Form the conjugate base A base removes a proton from the carbon adjacent to the carbonyl carbon. The resulting carbanion is an enolate ion; its electrons can interact with the neighbouring carbonyl π system.

Step 2: Explain resonance stabilisation The resonance forms are



Thus the negative charge is distributed over carbon and oxygen, with oxygen accommodating negative charge particularly well. Stabilisation of this conjugate base favours loss of the proton and explains the acidity of the α -hydrogen.

Step 3: Conclusion The α -hydrogen is acidic because its removal produces a resonance-stabilised enolate ion.

Quick Tip to Solve: Explain acidity through stability of the conjugate base: draw the carbon-charge and oxygen-charge enolate forms.

30(a). Case Study: 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.

(a) Give reasons for the following:

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

(ii) Transition metals show variable oxidation states.

[2 marks]

Solution:

Concept:

- Atomic and ionic radii influence the chemical properties of transition elements. Lanthanoid contraction is the decrease in size caused by poor shielding by the filling 4f electrons.
- The ns and $(n - 1)d$ subshells have comparable energies, so both can contribute electrons to bonding.

Step 1: Explain the resemblance of the second and third series The second and third transition series are the 4d and 5d series. Before the 5d series, the 4f subshell fills across the lanthanoids. The 4f electrons shield the nuclear charge poorly, so the effective nuclear attraction increases and the atomic and ionic sizes contract. This lanthanoid contraction largely compensates for the extra shell of the 5d elements. Corresponding 4d and 5d elements consequently have nearly equal radii and similar chemical properties; the corresponding 3d elements are appreciably smaller.

Step 2: Explain variable oxidation states In a transition metal, the energies of the outer ns and inner $(n - 1)d$ electrons are close. Different numbers of these electrons can therefore participate in bond formation or be removed, producing several oxidation states. For example, iron forms Fe^{2+} and Fe^{3+} , involving loss of its two 4s electrons and, for the latter ion, one additional 3d electron.

Step 3: Conclusion (i) Lanthanoid contraction makes corresponding 4d and 5d radii nearly equal. (ii) Comparable ns and $(n - 1)d$ energies allow different numbers of electrons to participate in bonding.

Quick Tip to Solve: Link the resemblance specifically to lanthanoid contraction, and variable oxidation states to the small energy gap between the two subshells.

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

[1 mark]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.
- A completely filled d subshell contains ten electrons, written d^{10} .

Step 1: Check the zinc atom Zinc has atomic number 30 and electronic configuration $[\text{Ar}] 3d^{10}4s^2$. Its $3d$ subshell is therefore completely filled, rather than partially filled.

Step 2: Check its common ion Zinc loses the two $4s$ electrons to form its common ion Zn^{2+} , with configuration $[\text{Ar}] 3d^{10}$. The ion also has a completely filled d subshell, so zinc fails the defining condition even though it lies in the d -block.

Step 3: Conclusion Zn is a non-transition element because both Zn and its common ion Zn^{2+} have a completely filled $3d^{10}$ subshell.

Quick Tip to Solve: Check the d -electron count in both the neutral atom and its common ion before classifying an element as a transition element.

OR

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

[1 mark]

Solution:

Concept:

- The standard enthalpy of atomisation, $\Delta_a H^\circ$, is the enthalpy required to form one mole of gaseous atoms from the element in its standard state.
- Stronger metallic bonding requires more energy to separate a metallic solid into isolated atoms.

Step 1: Identify the bonding electrons Transition metals generally have several unpaired $(n-1)d$ electrons as well as outer ns electrons available for participation in metallic bonding. The involvement of these electrons produces strong interatomic attractions in the metal lattice.

Step 2: Relate bonding to atomisation Atomisation separates the atoms completely and therefore requires the metallic bonds to be overcome. Stronger metallic bonding demands a larger energy input, explaining the generally high positive enthalpies of atomisation of transition metals.

Step 3: Conclusion Transition metals generally have high $\Delta_a H^\circ$ because participation of unpaired d electrons and outer s electrons produces strong metallic bonding.

Quick Tip to Solve: Connect the number of electrons participating in metallic bonding to the energy needed to separate the metal into gaseous atoms.

30(c). Why is there not much change in the atomic radius of the transition metals with the increase in atomic number? [1 mark]

Solution:

Concept:

- Atomic radius depends on nuclear attraction and on shielding of that attraction by other electrons.
- Across a transition series, successive electrons enter the inner $(n - 1)d$ subshell while the nuclear charge increases.

Step 1: Consider increasing nuclear charge As atomic number increases across a transition series, the nucleus gains protons. The resulting greater attraction tends to draw the electron cloud closer and decrease the atomic radius.

Step 2: Include shielding by the added d electrons The additional electrons enter the inner $(n - 1)d$ subshell. Their increasing shielding partially offsets the effect of increasing nuclear charge on the outer electrons. After an initial small decrease, the competing effects are nearly balanced, so the radii change only slightly across much of the series.

Step 3: Conclusion The increasing shielding by added $(n - 1)d$ electrons largely offsets increasing nuclear charge, so transition-metal atomic radii show only a small change across a series.

Quick Tip to Solve: State both competing effects: increasing nuclear attraction contracts the atom, while added inner d electrons increase shielding.

Section E (15 marks)

- 31(a).** (i) (I) The pK_b value of aniline is higher than that of methylamine. Explain why.
(II) Arrange the following compounds in decreasing order of their basic strength in the gaseous phase: NH_3 , $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{C}_2\text{H}_5\text{NH}_2$
(III) What is Hinsberg's reagent? Mention its one use.
(ii) How will you convert the following:
(I) Nitrobenzene to Benzenediazonium chloride?
(II) Iodomethane to Ethanamine?

[5 marks]

Solution:

Concept:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton. A larger K_b means a stronger base, whereas $pK_b = -\log K_b$ decreases as basicity increases.
- Alkyl groups donate electron density through the positive inductive effect. In the gaseous phase, aqueous solvation does not determine the order.
- Diazotisation converts a primary aromatic amine into a diazonium salt at 273–278 K. Cyanide substitution followed by reduction increases an alkyl chain by one carbon.

Step 1: (i)(I) Compare aniline and methylamine In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance. It is therefore less available for accepting H^+ . Protonation also

Quick Tip to Solve: For a one-carbon increase ending in a primary amine, use alcoholic KCN followed by nitrile reduction.

removes this lone pair from conjugation. In methylamine, the methyl group has a +I effect and increases electron density on nitrogen, making its lone pair more readily available. Hence aniline is the weaker base: its K_b is smaller and its pK_b is higher than that of methylamine.

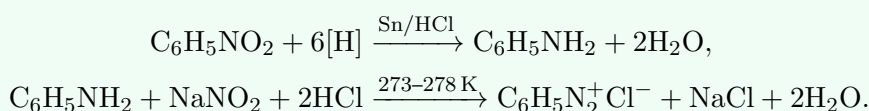
Step 2: (i)(II) Order of basic strength in the gas phase The electron-releasing effect increases with the number of ethyl groups attached to nitrogen. Since there is no aqueous hydration effect in the gaseous phase, the order is



The tertiary amine has three donating ethyl groups, the secondary has two, and the primary has one; ammonia has none.

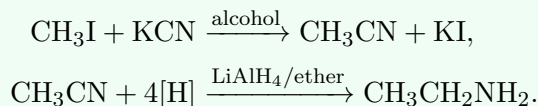
Step 3: (i)(III) Hinsberg reagent and its use Hinsberg's reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. It is used to distinguish primary, secondary and tertiary amines. A primary amine gives a sulphonamide containing an acidic N–H bond, soluble in alkali; a secondary amine gives a sulphonamide without N–H, insoluble in alkali. A tertiary amine does not form such a sulphonamide.

Step 4: (ii)(I) Nitrobenzene to benzenediazonium chloride First reduce the nitro group using tin and hydrochloric acid, then liberate aniline by alkaline work-up. Treat aniline with freshly generated nitrous acid at low temperature:



The low temperature is necessary because the diazonium salt decomposes on warming.

Step 5: (ii)(II) Iodomethane to ethanamine Treat iodomethane with alcoholic potassium cyanide to obtain ethanenitrile; reduce the nitrile using lithium aluminium hydride in dry ether, followed by hydrolysis:

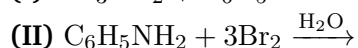
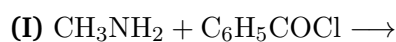


The carbon atom of the cyanide group becomes the methylene carbon attached to the amino group. Thus the product contains two carbons, as required.

Step 6: Conclusion Aniline has higher pK_b because of lone-pair delocalisation; gas-phase basicity follows tertiary > secondary > primary > ammonia. Hinsberg reagent is $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. The conversions proceed through aniline and ethanenitrile, respectively.

Quick Tip to Solve: For a one-carbon increase ending in a primary amine, use alcoholic KCN followed by nitrile reduction.

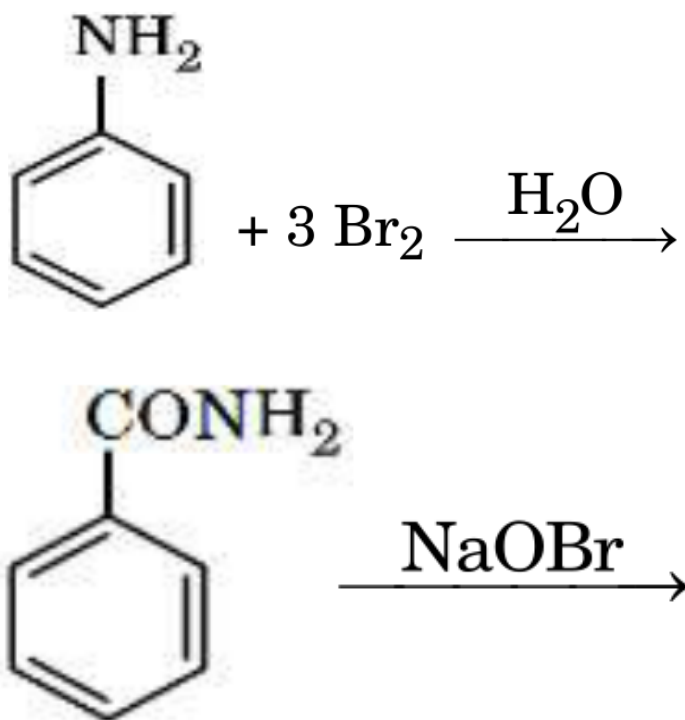
31(b). (i) Complete the following equations:



(ii) (I) Explain the carbylamine reaction.

(II) Why can aromatic primary amines not be prepared by the Gabriel phthalimide synthesis?

[5 marks]

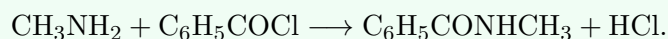


Solution:

Concept:

- Primary amines undergo acylation and the carbylamine test. The nitrogen lone pair also activates the ortho and para positions of aniline strongly towards electrophilic substitution.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon. Gabriel synthesis requires nucleophilic substitution on a suitable carbon halide.

Step 1: (i)(I) Acylation of methylamine Methylamine reacts with benzoyl chloride to form N-methylbenzamide:

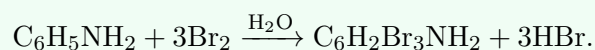


One hydrogen attached to nitrogen is replaced by the benzoyl group $\text{C}_6\text{H}_5\text{CO}-$. A base such as pyridine can absorb the hydrogen chloride produced and prevent protonation of the amine.

Step 2: (i)(II) Bromination of aniline Aniline reacts readily with bromine water to give a white

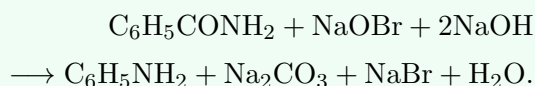
Quick Tip to Solve: In Hofmann degradation remove only the amide carbonyl carbon; benzamide consequently gives aniline, not benzylamine.

precipitate of 2,4,6-tribromoaniline:



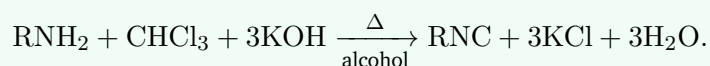
The $-\text{NH}_2$ group donates its lone pair into the ring, greatly increasing electron density at both ortho positions and the para position. Bromination therefore occurs at positions 2, 4 and 6 without a Lewis-acid catalyst.

Step 3: (i)(III) Hofmann degradation of benzamide Benzamide on treatment with sodium hypobromite gives aniline, containing one carbon fewer than the starting amide. The balanced alkaline equation is



The phenyl group remains intact while the carbonyl carbon is removed as carbonate in the alkaline medium.

Step 4: (ii)(I) Carbylamine reaction On heating a primary aliphatic or aromatic amine with chloroform and alcoholic potassium hydroxide, a foul-smelling isocyanide (carbylamine) is formed:



For example, aniline gives phenyl isocyanide $\text{C}_6\text{H}_5\text{NC}$. Secondary and tertiary amines do not give this reaction, so it is a test for primary amines. The connectivity in the product is $\text{R}-\text{N}\equiv\text{C}$, not the nitrile connectivity $\text{R}-\text{C}\equiv\text{N}$.

Step 5: (ii)(II) Limitation of Gabriel phthalimide synthesis Gabriel synthesis first uses the phthalimide anion as a nucleophile to replace halide in an alkyl halide; hydrolysis of the N-alkyl product then releases a primary amine. To prepare an aromatic primary amine by this route, an aryl halide would have to undergo the corresponding substitution. Ordinary aryl halides do not undergo this nucleophilic displacement with the phthalimide anion. Their halogen is bonded to an sp^2 carbon, and resonance gives the aryl carbon-halogen bond partial double-bond character. Thus N-arylphthalimide is not obtained by the usual Gabriel reaction, and aromatic primary amines cannot be prepared by this method.

Step 6: Conclusion The products are N-methylbenzamide, 2,4,6-tribromoaniline and aniline, respectively. Carbylamine formation identifies primary amines; the resistance of ordinary aryl halides to substitution prevents Gabriel preparation of aromatic primary amines.

Quick Tip to Solve: In Hofmann degradation remove only the amide carbonyl carbon; benzamide consequently gives aniline, not benzylamine.

32(a). (i) A first order reaction is 20% complete in 10 minutes. Calculate the time taken when 80% of the reaction will be completed.

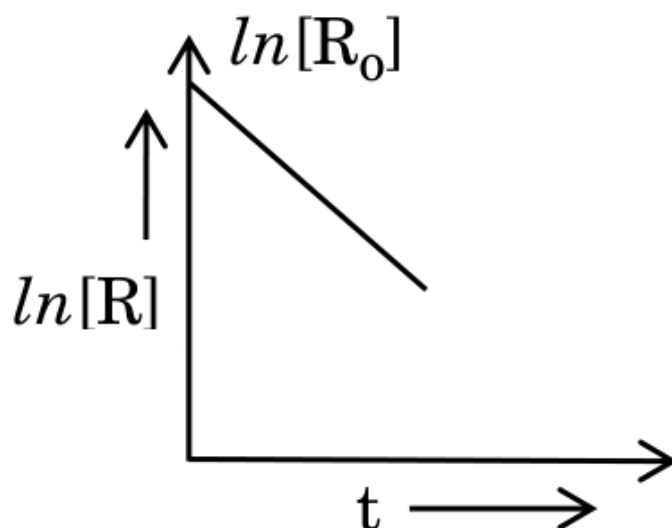
[Given: $\log 5 = 0.7$, $\log 4 = 0.6$]

(ii) For a chemical reaction $R \rightarrow P$, variation in $\ln[R]$ vs. time (t) graph is given below:

(I) Predict the order of the reaction.

(II) Write the slope of the curve.

[5 marks]



Solution:

Concept:

- For a first order reaction, the integrated rate equation is $kt = \ln([R]_0/[R]_t) = 2.303 \log([R]_0/[R]_t)$, where k is the rate constant and $[R]_0$, $[R]_t$ are the initial and remaining reactant concentrations.
- A plot of $\ln[R]_t$ against time obeys $\ln[R]_t = \ln[R]_0 - kt$. Comparing this with $y = c + mx$ identifies its intercept and slope.

Step 1: (i) Use the extent after 10 minutes to obtain the rate constant Let the initial concentration be a . At 20% completion, $0.80a$ remains; the concentration in the integrated equation is the amount remaining, not the amount consumed. Therefore,

$$k = \frac{2.303}{10} \log \frac{a}{0.80a} = \frac{2.303}{10} \log \frac{5}{4}.$$

With the supplied logarithms, $\log(5/4) = 0.7 - 0.6 = 0.1$, so $k = 0.02303 \text{ min}^{-1}$. The initial concentration cancels because the reaction is first order.

Step 2: (i) Calculate the total time for 80 percent completion At 80% completion, only $0.20a$ remains. Thus

$$t_{80} = \frac{2.303}{k} \log \frac{a}{0.20a} = \frac{2.303}{0.02303} \log 5 = 100(0.7) = 70 \text{ min}.$$

This is the time measured from the start of the reaction, as requested. It is longer than the first ten minutes because the rate decreases as the reactant concentration falls. The given rounded logarithms must be used consistently in both calculations.

Quick Tip to Solve: Convert percent completed into percent remaining before taking the logarithm; for a natural-log concentration plot, the slope is directly $-k$.

Step 3: (ii)(I) Identify the reaction order The printed graph is a straight line when the natural logarithm of the remaining reactant concentration is plotted against time. Rearranging the first order integrated law gives $\ln[R]_t = \ln[R]_0 - kt$, exactly the displayed linear relation. Hence the graph identifies first order kinetics. A zero order reaction instead gives a straight line for $[R]$ against t , so it does not match these axes.

Step 4: (ii)(II) Read the slope from the integrated equation In $y = c + mx$, take $y = \ln[R]_t$ and $x = t$. The coefficient of time is $-k$, so

$$\text{slope} = \frac{\Delta \ln[R]}{\Delta t} = -k.$$

The negative sign agrees with the decreasing line, while the intercept is $\ln[R]_0$. Since these axes use natural logarithms, no factor of 2.303 belongs in the slope.

Step 5: Conclusion (i) The time for 80% completion is 70 min, using the given logarithms. (ii)(I) The reaction is first order; (II) the slope is $-k$.

Quick Tip to Solve: Convert percent completed into percent remaining before taking the logarithm; for a natural-log concentration plot, the slope is directly $-k$.

OR

32(b). (i) For first order reaction, calculate the ratio between the time taken to complete 3/4th of the reaction and the time taken to complete half of the reaction.

(ii) (I) What is meant by a complex reaction?

(II) Give an example of a pseudo first order reaction.

[5 marks]

Solution:

Concept:

- For a first order reaction, $t = (1/k) \ln([R]_0/[R]_t)$, where k is the first order rate constant. Its half-life is $t_{1/2} = \ln 2/k$, independent of the initial concentration.
- A complex reaction proceeds through two or more elementary steps. In a pseudo first order reaction, an excess reactant has practically constant concentration, so the observed rate law becomes first order in the other reactant.

Step 1: (i) Express the time for three-fourths completion Let the initial reactant concentration be a . Completion of three-fourths of the reaction leaves $a/4$ unreacted. Substitute the remaining concentration into the first order integrated rate equation:

$$t_{3/4} = \frac{1}{k} \ln \frac{a}{a/4} = \frac{\ln 4}{k} = \frac{2 \ln 2}{k}.$$

The fraction in this expression is the fraction remaining. Using $3a/4$ as the final concentration would instead calculate the time for only one-fourth completion.

Step 2: (i) Compare with the half-life For half completion, the remaining concentration is $a/2$.

Quick Tip to Solve: Three-fourths completion leaves one-quarter of the reactant, which is reached after two successive half-lives; excess water can be absorbed into the observed rate constant.

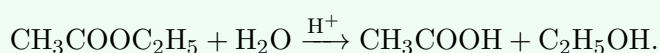
Therefore

$$t_{1/2} = \frac{1}{k} \ln \frac{a}{a/2} = \frac{\ln 2}{k}, \quad \frac{t_{3/4}}{t_{1/2}} = \frac{2 \ln 2/k}{\ln 2/k} = 2.$$

This also follows from successive half-lives: after one half-life, one-half remains, and after two half-lives, one-quarter remains. Thus three-fourths completion requires exactly two half-lives for a first order reaction.

Step 3: (ii)(I) Explain a complex reaction A complex reaction is a reaction that occurs through a sequence of two or more elementary reactions rather than in a single elementary step. The individual steps together constitute its mechanism and may involve intermediates, which are formed in one step and consumed in another. Its overall balanced chemical equation represents the net change and does not necessarily describe the molecular event controlling the rate.

Step 4: (ii)(II) Give and explain a pseudo first order example Acid-catalysed hydrolysis of ethyl acetate in a large excess of water is an example:



At fixed acid concentration, write the rate as $v = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$. Water is the solvent and is present in such large excess that its concentration changes negligibly during the reaction. Absorb this practically constant factor into $k_{\text{obs}} = k[\text{H}_2\text{O}]$. The observed law becomes $v = k_{\text{obs}}[\text{CH}_3\text{COOC}_2\text{H}_5]$, which is first order in ester. It is called pseudo first order because the simple observed dependence results from keeping the other reactant effectively constant.

Step 5: Conclusion (i) $t_{3/4} : t_{1/2} = 2 : 1$. (ii)(I) A complex reaction proceeds through two or more elementary steps. (II) Acid-catalysed ethyl acetate hydrolysis in excess water is a pseudo first order reaction.

Quick Tip to Solve: Three-fourths completion leaves one-quarter of the reactant, which is reached after two successive half-lives; excess water can be absorbed into the observed rate constant.

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

(II) Write the formula of the given complex: Hexaamminenickel(II) chloride

(ii) $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green in colour, whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain. [Atomic number: Ni = 28]

[5 marks]

Solution:

Concept:

- The oxidation state fixes the metal-ion configuration. Iron has configuration $[\text{Ar}]3d^64s^2$, so Fe^{3+} is $3d^5$; nickel(II) is $3d^8$.
- A strong-field ligand produces a large crystal-field splitting and can cause pairing. In valence bond theory, octahedral inner-orbital and outer-orbital complexes use d^2sp^3 and sp^3d^2 hybrid orbitals, respectively.
- A complex appears coloured when it absorbs visible light selectively. The energy of a d -orbital

Quick Tip to Solve: First find the oxidation state, then the d-electron count; use ligand strength for pairing and absorption energy for colour.

transition is determined by the splitting of the orbitals in the ligand field, rather than by the presence of unpaired electrons alone.

Step 1: (i)(I) Determine the iron(III) configuration In both complexes the six ligands carry a total charge of -6 , while the complex ion has charge -3 . Thus iron has oxidation state $+3$:

$$x - 6 = -3 \Rightarrow x = +3.$$

Removal of the two $4s$ electrons and one $3d$ electron gives $\text{Fe}^{3+} : 3d^5$. The different orbital arrangements therefore arise from the different field strengths of the ligands, not from different oxidation states.

Step 2: Compare cyanide and fluoride ligands In $[\text{Fe}(\text{CN})_6]^{3-}$, CN^- is a strong-field ligand. Its large octahedral splitting causes the five $3d$ electrons to occupy the lower t_{2g} set as $t_{2g}^5 e_g^0$. Two $3d$ orbitals are vacant and combine with one $4s$ and three $4p$ orbitals to give $d^2 sp^3$ hybridisation. Since the participating d orbitals belong to the inner $3d$ shell, it is an inner-orbital octahedral complex, with one unpaired electron.

In $[\text{FeF}_6]^{3-}$, F^- is a weak-field ligand. It does not cause pairing of the five $3d$ electrons; the high-spin arrangement is $t_{2g}^3 e_g^2$. No $3d$ orbital is empty. The metal therefore uses one $4s$, three $4p$ and two outer $4d$ orbitals, giving $sp^3 d^2$ hybridisation. It is an outer-orbital octahedral complex with five unpaired electrons.

Step 3: (i)(II) Translate the complex name into a formula Ammine denotes the neutral ligand NH_3 , and hexammine specifies six such ligands around nickel. Nickel(II) has charge $+2$; hence the coordination entity is $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Two chloride counterions are required for electrical neutrality, so the compound is $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. The chlorides lie outside the coordination sphere.

Step 4: (ii) Explain the different colours of the nickel complexes In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, nickel(II) has the octahedral $3d^8$ arrangement $t_{2g}^6 e_g^2$. Water produces a ligand-field splitting for which electronic transitions absorb light in the visible region. The remaining transmitted light makes the solution appear green.

Cyanide is much stronger-field than water. In square-planar $[\text{Ni}(\text{CN})_4]^{2-}$, the eight d electrons are paired in the four lower-energy d orbitals; the empty $d_{x^2-y^2}$ orbital is separated from the occupied orbitals by a large energy gap. The relevant absorption lies outside the visible region, at higher energy, so the solution is colourless. Merely saying that all electrons are paired is insufficient: colour depends on the energies of allowed absorptions, whereas pairing accounts for its diamagnetism.

Step 5: Conclusion $[\text{Fe}(\text{CN})_6]^{3-}$ is inner-orbital $d^2 sp^3$, while $[\text{FeF}_6]^{3-}$ is outer-orbital $sp^3 d^2$. Hexamminenickel(II) chloride is $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. The aqua nickel(II) complex absorbs visible light and appears green; the larger splitting in the cyanide complex places the relevant absorption outside the visible region, making it colourless.

Quick Tip to Solve: First find the oxidation state, then the d-electron count; use ligand strength for pairing and absorption energy for colour.

33(b). (i) (I) Write IUPAC name of the given complexes: $[\text{Ag}(\text{CN})_2][\text{Ag}(\text{NH}_3)_2]$

(II) What is the coordination number of the central metal ion in the following complexes? $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$

(III) Draw a geometrical isomer of the complex $[\text{CoCl}_2(\text{en})_2]^+$, which is optically active.

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

[5 marks]

Solution:

Concept:

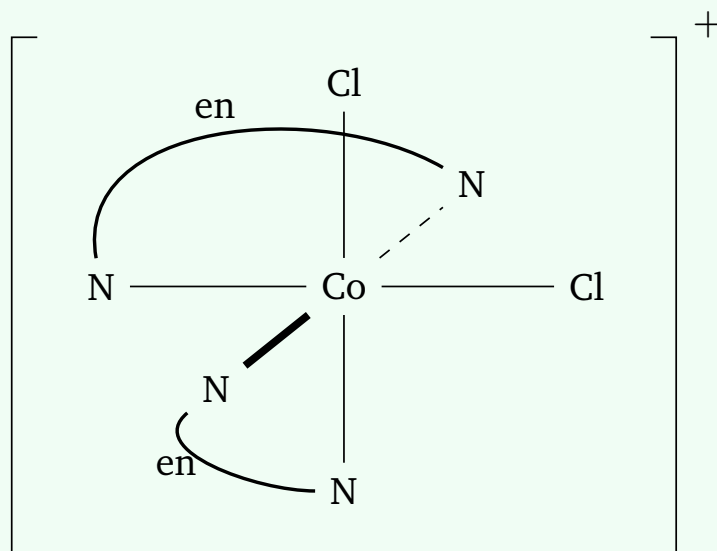
- A coordination salt is named with the cation first and the anion second. An anionic silver complex uses the metal name argentate; neutral ammonia and anionic cyanide ligands are named ammine and cyanido.
- Coordination number counts donor atoms directly bonded to the central metal. Oxalato and ethane-1,2-diamine (en) are bidentate ligands, while ammonia and chlorido are monodentate.
- Optical isomers are non-superimposable mirror images. In valence bond theory, the number and type of vacant metal orbitals accepting ligand electron pairs determine hybridisation; unpaired electrons determine magnetic behaviour.

Step 1: (i)(I) Name the complex salt The ions are $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$. Ammonia is neutral, so silver in the cation has oxidation state +1. In the anion, if the silver oxidation state is x , then $x + 2(-1) = -1$, giving $x = +1$. Although the anion is written first in the given formula, the cation is named first. The name is **diamminesilver(I) dicyanidoargentate(I)**.

Step 2: (i)(II) Count the donor atoms In $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, each oxalato ligand bonds through two oxygen donor atoms. Three such ligands therefore give the iron coordination number $3 \times 2 = 6$. In $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$, three ammonia molecules each donate through one nitrogen atom and three chlorido ligands each donate through one chlorine atom. Thus chromium has coordination number $3 + 3 = 6$. Count the metal–donor bonds, not merely the number of ligand molecules.

Step 3: (i)(III) Draw the optically active cis isomer The required geometrical isomer is cis- $[\text{CoCl}_2(\text{en})_2]^+$. Its two chlorido ligands occupy adjacent octahedral positions, making a 90° angle at cobalt. The four remaining positions are occupied by the four nitrogen donor atoms of two en ligands, each joining the indicated pair of nitrogen atoms. The drawing shows one member of the non-superimposable mirror-image pair. The trans isomer has opposite chlorido ligands and is optically inactive.

Quick Tip to Solve: Count two donor atoms per oxalato ligand; for nickel carbonyl, first obtain the paired $3d^{10}$ arrangement before choosing the four hybrid orbitals.



One optically active cis isomer; each curved N–N link represents one en ligand.

Step 4: (ii) Apply valence bond theory to nickel tetracarbonyl Carbon monoxide is neutral, so nickel has oxidation state zero in $[\text{Ni}(\text{CO})_4]$. The free Ni atom has configuration $[\text{Ar}]3d^84s^2$. Under the influence of the strong-field CO ligands, the two $4s$ electrons enter the $3d$ subshell and pair, producing the arrangement $3d^{10}$. The five $3d$ orbitals are then fully occupied and the $4s$ and three $4p$ orbitals are vacant. These four orbitals hybridise to form four equivalent sp^3 orbitals. Each accepts a lone pair from the carbon end of one CO ligand, giving four coordinate bonds and a **tetrahedral** complex. All electrons are paired, so there are zero unpaired electrons and the complex is **diamagnetic**. The four-coordinate formula by itself does not imply square-planar geometry: here the filled $3d$ subshell leads to sp^3 , rather than dsp^2 , hybridisation.

Step 5: Conclusion (i) Diamminesilver(I) dicyanidoargentate(I); coordination numbers 6 and 6; the optically active isomer is $\text{cis-}[\text{CoCl}_2(\text{en})_2]^+$, drawn above. (ii) $[\text{Ni}(\text{CO})_4]$ is sp^3 -hybridised, tetrahedral and diamagnetic.

Quick Tip to Solve: Count two donor atoms per oxalato ligand; for nickel carbonyl, first obtain the paired $3d^{10}$ arrangement before choosing the four hybrid orbitals.