

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-7-1 - 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. 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

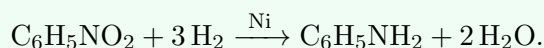
Correct Answer: (B) Reaction of Nitrobenzene with Hydrogen gas in presence of finely divided Nickel

Solution:

Concept:

- Reduction of an aromatic nitro group converts $-\text{NO}_2$ into $-\text{NH}_2$, retaining the carbon skeleton.
- Aniline is $\text{C}_6\text{H}_5\text{NH}_2$, with nitrogen directly bonded to the benzene ring.

Step 1: Reduce nitrobenzene Hydrogen in the presence of finely divided nickel reduces nitrobenzene to aniline:



Thus the reaction in option (B) gives the required aromatic primary amine.

Step 2: Check the alternatives Chlorobenzene does not undergo ordinary ammonolysis with ethanolic ammonia because its aryl carbon–chlorine bond resists nucleophilic substitution. Reduction of either benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, or benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, with LiAlH_4 gives benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$; the intervening carbon remains, so this is not aniline.

Step 3: Conclusion Nitrobenzene reduced with hydrogen over finely divided nickel gives aniline. Hence, the correct option is (B).

Quick Tip to Solve: Count the carbons between the ring and nitrogen: aniline has none, whereas reduction of benzamide or benzonitrile leaves a $-\text{CH}_2-$ group.

2. 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 metals exhibit variable oxidation states because both the $(n-1)d$ and ns electrons can participate in bonding.

Quick Tip to Solve: For this comparison, recall the middle-of-series element manganese: its $3d^5 4s^2$ configuration allows oxidation states up to +7.

- A larger number of accessible valence electrons can produce a wider range of oxidation states.

Step 1: Examine manganese Manganese has electronic configuration $[\text{Ar}] 3d^5 4s^2$. It commonly exhibits oxidation states from +2 to +7, including +2, +3, +4, +5, +6, +7. The availability of its seven valence electrons accounts for this broad range.

Step 2: Compare the other elements Scandium predominantly exhibits +3, while zinc predominantly exhibits +2 because Zn^{2+} has a stable filled $3d^{10}$ subshell. Cobalt commonly shows +2 and +3, a smaller range than manganese. Therefore none of options (A), (B), and (D) exceeds 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: For this comparison, recall the middle-of-series element manganese: its $3d^5 4s^2$ configuration allows oxidation states up to +7.

3. 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 and is satisfied by ligands directly bound to the metal.

Step 1: Apply secondary-valence properties Secondary valences are non-ionisable because their ligands belong to the coordination sphere. They are satisfied by neutral molecules, such as NH_3 , or negative ions, such as Cl^- . Thus statements (A) and (C) correctly describe secondary valence.

Step 2: Identify the incorrect statement Secondary valence equals coordination number and, in Werner's description, is normally fixed for a given metal, as stated in (D). Ionisability is a property of primary valence, not secondary valence. Therefore statement (B), which calls secondary valences ionisable, contradicts the theory.

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

Quick Tip to Solve: Underline "incorrect" first: secondary means coordination sphere and non-ionisable; primary means oxidation state and ionisable.

4. 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 drives a spontaneous reaction using its own cell emf E_{cell} .
- An external potential E_{ext} , connected to oppose the cell emf, can reverse the cell reaction.

Step 1: Compare the opposing potentials When the opposing external potential is smaller than the cell emf, $E_{\text{ext}} < E_{\text{cell}}$, the cell continues to supply current as a galvanic cell. At equality, the net driving potential is zero and the current stops; equality does not produce electrolysis.

Step 2: Reverse the spontaneous reaction If $E_{\text{ext}} > E_{\text{cell}}$, the external source forces current through the cell in the reverse direction. The non-spontaneous reverse reaction then occurs, so the cell behaves as an electrolytic cell. Simply specifying $E_{\text{cell}} = 0$ does not provide a source to drive that reverse reaction.

Step 3: Conclusion The opposing external potential must exceed the cell emf: $E_{\text{ext}} > E_{\text{cell}}$. Hence, the correct option is (C).

Quick Tip to Solve: Use the three cases for an opposing voltage: smaller means discharge, equal means no current, and larger means reverse reaction.

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

[1 mark]

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

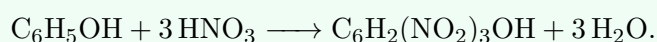
Correct Answer: (C) Picric acid

Solution:

Concept:

- The $-\text{OH}$ group strongly activates the benzene ring of phenol towards electrophilic substitution.
- This group directs incoming nitro groups to the ortho and para positions.

Step 1: Apply vigorous nitration conditions On heating phenol with concentrated nitric acid, nitration occurs at both ortho positions and at the para position. The product is 2,4,6-trinitrophenol, commonly called picric acid:



Quick Tip to Solve: Link dilute nitric acid with mono-nitrophenols and hot concentrated nitric acid with nitration at all three activated positions, 2, 4 and 6.

Step 2: Distinguish the alternative products Ortho-nitrophenol and para-nitrophenol are the mononitration products associated with dilute nitric acid, rather than the vigorous conditions stated here. Sodium phenoxide requires reaction with a sodium-containing base or metal; concentrated nitric acid cannot supply sodium. Thus (A), (B), and (D) do not describe the stated reaction.

Step 3: Conclusion Phenol heated with concentrated nitric acid gives picric acid (2,4,6-trinitrophenol). Hence, the correct option is (C).

Quick Tip to Solve: Link dilute nitric acid with mono-nitrophenols and hot concentrated nitric acid with nitration at all three activated positions, 2, 4 and 6.

6. 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:

- For a dilute solution, osmotic pressure is $\pi = CRT$, where C is molar concentration, R the gas constant and T absolute temperature.
- The temperature changes are $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$, where m is molality and K_b, K_f are the respective solvent constants.

Step 1: Match pressure and temperature relations Osmotic pressure matches relation (ii), so a-ii. Elevation of boiling point uses the subscript b , giving b-iv. Depression of freezing point uses the subscript f , giving c-i. These three direct matches already distinguish the correct option from the alternatives.

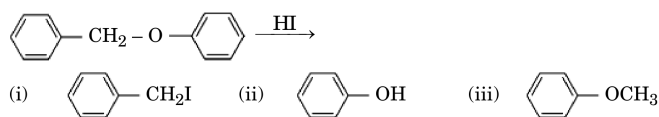
Step 2: Check relative lowering of vapour pressure For a dilute solution of a non-volatile solute, Raoult's law gives $(P^\circ_1 - P_1)/P^\circ_1 \simeq n_2/n_1 = W_2 M_1 / (M_2 W_1)$, matching (iii), so d-iii. Here W_1, W_2 are solvent and solute masses and M_1, M_2 their molar masses. Options (A), (B), and (C) each mismatch at least one pressure or temperature relation.

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

Quick Tip to Solve: Match b with boiling and f with freezing first; then assign $\pi = CRT$ to osmotic pressure and the pressure ratio to vapour-pressure lowering.

7. 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:

- An aryl-alkyl ether undergoes cleavage with HI at the alkyl-oxygen bond.
- The aryl-oxygen bond resists cleavage because it has partial double-bond character and involves an sp^2 -hybridised ring carbon.

Step 1: Identify the cleavable bond The reactant is benzyl phenyl ether, $C_6H_5CH_2OC_6H_5$. After protonation of oxygen, iodide attacks the benzylic carbon and the bond between CH_2 and oxygen breaks. This produces benzyl iodide and leaves the aryl oxygen as phenol.

Step 2: Compare with the listed products The overall reaction is



Benzyl iodide is product (i), and phenol is product (ii). Anisole, product (iii), would require a methyl group that is absent from the reactant; it is not formed. Therefore every option including (iii) is excluded.

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

Quick Tip to Solve: In benzyl phenyl ether, cut the CH_2-O bond: iodine goes to the benzyl group and hydrogen goes to the phenoxy oxygen.

8. 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.
- The usual reactivity order follows carbocation stability: tertiary is more stable than secondary, which is more stable than primary.

Step 1: Compare alcohol classes A tertiary alcohol produces immediate turbidity at room temperature as the insoluble alkyl chloride separates. A secondary alcohol gives turbidity after a few minutes. A primary alcohol normally shows no turbidity at room temperature and requires heating for appreciable reaction.

Step 2: Check the options The order is $3^\circ > 2^\circ > 1^\circ$. Option (A) incorrectly places primary above secondary. Options (B) and (C) incorrectly place tertiary last. Only option (D) places all three classes in the experimentally observed order.

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

Quick Tip to Solve: Rank Lucas-test turbidity from immediate to delayed to absent at room temperature: tertiary, secondary, primary.

9. Functional groups present in amino acids are:

[1 mark]

- (A) $-\text{NH}_2$ and $-\text{OH}$
- (B) $-\text{OH}$ and $-\text{COOH}$
- (C) $-\text{COOH}$ and $-\text{NH}_2$
- (D) $-\text{NH}_2$ and $-\text{SO}_3\text{H}$

Correct Answer: (C) $-\text{COOH}$ and $-\text{NH}_2$

Solution:

Concept:

- An amino acid contains both an amino group, $-\text{NH}_2$, and a carboxyl group, $-\text{COOH}$.
- An α -amino acid has the general structure $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, where R denotes the side chain.

Step 1: Identify the defining groups The amino group is basic and the carboxyl group is acidic. Their simultaneous presence accounts for the amphoteric behaviour of amino acids. In a zwitterion, these groups are present as $-\text{NH}_3^+$ and $-\text{COO}^-$, respectively.

Quick Tip to Solve: Expand the name amino acid into amino plus carboxylic acid to identify the required pair of groups.

Step 2: Check all alternatives Options (A) and (B) each replace a required group with a hydroxyl group. Option (D) replaces the carboxyl group with a sulphonic acid group. Some amino acids have additional groups in their side chains, but these do not replace the defining amino and carboxyl groups. The required pair appears in option (C).

Step 3: Conclusion The groups are $-\text{COOH}$ and $-\text{NH}_2$. Hence, the correct option is (C).

Quick Tip to Solve: Expand the name amino acid into amino plus carboxylic acid to identify the required pair of groups.

10. 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:

- Maximum electrical work delivered by a reversible cell is nFE_{cell} , where n is the number of electrons transferred in the balanced reaction and F is the Faraday constant.
- At constant temperature and pressure, maximum useful work delivered equals $-\Delta_r G$.

Step 1: Relate Gibbs energy and electrical work Equating the two expressions gives $-\Delta_r G = nFE_{\text{cell}}$. For standard-state conditions this becomes $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$.

Step 2: Check sign and dimensions A spontaneous standard cell has positive potential and negative Gibbs energy change, so the minus sign is essential. Option (B) has the opposite sign. Options (A) and (C) omit the Faraday constant and therefore do not convert voltage into molar energy. Only (D) has both the required sign and factors.

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

Quick Tip to Solve: Check the sign by spontaneity: positive cell potential must give a negative Gibbs energy change.

11. 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

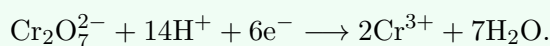
Solution:

Concept:

- One Faraday, 1 F, is the charge carried by one mole of electrons.
- The total electron requirement equals the decrease in oxidation number summed over all the chromium atoms being reduced.

Step 1: Calculate the change per chromium atom For $\text{Cr}_2\text{O}_7^{2-}$, $2x + 7(-2) = -2$, so chromium is in oxidation state +6. Reduction to Cr^{3+} decreases its oxidation number by three. Each chromium atom therefore accepts three electrons.

Step 2: Include both chromium atoms Each dichromate ion contains two chromium atoms, requiring six electrons in total. The balanced acidic half-reaction is



Thus one mole of dichromate requires six moles of electrons, or 6 F. Option (B) counts only one chromium atom; (A) and (D) do not satisfy electron balance.

Step 3: Conclusion The electricity required is $\boxed{6\text{ F}}$. Hence, the correct option is (C).

Quick Tip to Solve: Multiply the three-electron reduction per chromium atom by the two chromium atoms in each dichromate ion.

12. Which of the following statements is true about a galvanic cell consisting of Cu and H_2 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 H_2 electrode
- (C) H_2 is cathode and Cu is anode
- (D) H_2 is anode and Cu is cathode

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

Solution:

Concept:

- Reduction occurs at the cathode and oxidation occurs at the anode of a galvanic cell.
- The electrode with the higher standard reduction potential is the cathode for spontaneous standard cell operation.

Quick Tip to Solve: Compare reduction potentials first: the higher value gives the cathode; reverse the other half-reaction for the anode.

Step 1: Compare the given potentials The copper reduction potential, $+0.34\text{ V}$, is higher than the hydrogen reduction potential, 0.00 V . Thus copper ions are reduced at the copper cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$.

Step 2: Identify the anode and check the choices Hydrogen is oxidised according to $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$, so its electrode is the anode. The standard cell potential is $E_{\text{cell}}^\circ = 0.34 - 0.00 = +0.34\text{ V}$, consistent with galvanic operation. Options (A), (B) and (C) incorrectly assign oxidation to copper or reduction to hydrogen, or reverse both roles.

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

Quick Tip to Solve: Compare reduction potentials first: the higher value gives the cathode; reverse the other half-reaction for the anode.

13. 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:

- Ideal solutions have zero volume change on mixing: $\Delta_{\text{mix}}V = 0$.
- Unlike-molecule attractions in an ideal solution are comparable to the corresponding like-molecule attractions.

Step 1: Judge Assertion (A) The volume of an ideal solution equals the sum of the initial volumes of its components. Neither contraction nor expansion occurs on mixing, so $V_{\text{solution}} = V_1 + V_2$ and $\Delta_{\text{mix}}V = 0$. The assertion is true.

Step 2: Judge Reason (R) The reason states that solute-solvent attractions are weaker than solute-solute and solvent-solvent attractions. This is not the ideal-solution condition. Weaker unlike attractions lead to positive deviation from Raoult's law, whereas comparable attractions characterise an ideal solution. The reason is false.

Step 3: Check the explanatory link A false reason cannot explain the true assertion. Options (A) and (B) require both statements to be true; option (D) requires the assertion to be false. The combination given by option (C) is therefore the appropriate one.

Quick Tip to Solve: For ideal solutions, pair comparable intermolecular attractions with zero volume change on mixing.

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

Quick Tip to Solve: For ideal solutions, pair comparable intermolecular attractions with zero volume change on mixing.

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

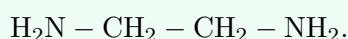
Solution:

Concept:

- Complex stability depends on the overall metal-ligand interactions as well as on ligand denticity. Chelation alone does not establish an order between different donor ligands.
- Ethane-1,2-diamine, en, is a neutral bidentate ligand; cyanide is a strong-field monodentate ligand with very strong bonding to cobalt(III).

Step 1: Judge the assertion The assertion is false. Hexacyanidocobaltate(III), $[\text{Co(CN)}_6]^{3-}$, is more stable thermodynamically than $[\text{Co(en)}_3]^{3+}$. The overall formation constants illustrate the comparison: $\log_{10} \beta$ is approximately 64 for the cyanide complex and 48.7 for the ethane-1,2-diamine complex. A larger formation constant indicates greater stability against dissociation into metal ion and free ligands.

Step 2: Judge the reason The reason is true. Ethane-1,2-diamine has the structure



Its two nitrogen atoms each donate a lone pair to the same cobalt ion, forming a five-membered chelate ring. Thus en is a chelating ligand.

Step 3: Check the claimed explanation Chelation gives additional stability, particularly in comparisons involving similar donor groups, but it cannot override every difference in metal-ligand bonding. Here the ligands being compared are chemically different, and the cyanide complex has the greater overall formation constant. Therefore the true statement about en does not make the assertion true. Codes (A), (B) and (C) all require a true assertion and are rejected.

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 with different ligands by denticity alone; compare overall formation constants when available.

15. 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]

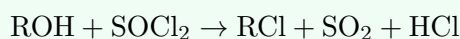
- (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).
- (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (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 the corresponding alkyl chloride:



- The gaseous by-products SO_2 and HCl escape, facilitating isolation of a pure alkyl chloride.

Step 1: Judge Assertion (A) The assertion reverses the usual preference. Thionyl chloride is preferred for preparing alkyl chlorides from alcohols because its by-products are gases and are readily removed. Hence Assertion (A) is false.

Step 2: Judge Reason (R) The reason is true: reaction with thionyl chloride gives the alkyl chloride in a relatively pure form as sulphur dioxide and hydrogen chloride escape. Phosphorus halides leave non-gaseous phosphorus-containing by-products, which require separation.

Step 3: Check the assertion-reason relation Although the reason is true, it supports the preference for thionyl chloride, opposite to the assertion. Thus neither option (A) nor (B), which requires a true assertion, applies; option (C) also reverses the truth values.

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 both by-products of SOCl_2 escape as gases.

16. 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 reactions are electrophilic aromatic substitution reactions requiring a sufficiently reactive aromatic ring and an available Lewis acid catalyst.
- The $-\text{COOH}$ group withdraws electron density from the ring and can coordinate with the Lewis acid AlCl_3 .

Step 1: Judge Assertion (A) Aromatic carboxylic acids such as benzoic acid do not undergo the usual Friedel-Crafts alkylation or acylation. The aromatic ring bearing a carboxyl group is strongly deactivated towards electrophilic substitution. Therefore Assertion (A) is true.

Step 2: Judge Reason (R) The carboxyl group is electron withdrawing and deactivating. In addition, an oxygen atom of the carboxyl group coordinates with aluminium chloride, binding the Lewis acid catalyst. Both statements in Reason (R) are true.

Step 3: Check whether R explains A Ring deactivation makes electrophilic attack difficult, while coordination of the carboxyl group with the catalyst interferes with the catalyst needed for the reaction. These are precisely the reasons for the failure of Friedel-Crafts reaction. Options (B), (C) and (D) therefore do not describe the stated relation.

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

Quick Tip to Solve: When a carboxyl group is directly attached to benzene, check both ring deactivation and binding of AlCl_3 .

Section B (10 marks)

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

(ii) ' E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than that for $\text{Fe}^{3+}/\text{Fe}^{2+}$.' Justify the statement.

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

[2 marks]

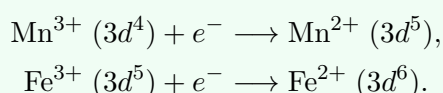
Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids, caused by ineffective shielding of increasing nuclear charge by $4f$ electrons.
- A more positive standard reduction potential E° indicates a greater tendency for the oxidised species to gain an electron. A half-filled d^5 configuration has extra stability.

Step 1: (i) Compare zirconium and hafnium Hafnium follows the lanthanoids in the periodic table. Because of lanthanoid contraction, the expected increase in size from Zr to Hf is almost cancelled. Consequently Zr and Hf have almost identical atomic and ionic radii, especially for their common $+4$ ions. Their similar sizes and the same valence-shell pattern give them very similar chemical properties.

Step 2: (ii) Compare the reductions of manganese and iron The relevant configurations and reductions are



Reduction of Mn^{3+} produces the especially stable half-filled $3d^5$ configuration. In contrast, reduction of Fe^{3+} destroys its half-filled $3d^5$ configuration. Thus Mn^{3+} has a greater tendency to be reduced, so its E° is more positive.

Step 3: Conclusion (i) Zr and Hf are similar because lanthanoid contraction makes their sizes almost equal. (ii) $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}} > E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ because manganese reduction forms stable $3d^5$, whereas iron reduction removes that stability.

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

OR

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 when both the outer ns and inner $(n-1)d$ electrons can participate in bonding.
- In aqueous transition-metal ions, visible absorption commonly results from $d-d$ transitions between

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons when writing configurations of first-row transition-metal ions.

ligand-field-split, partially filled d orbitals.

Step 1: (i) Identify the element and explain its oxidation state Scandium, Sc, does not exhibit variable oxidation states in its normal compounds. Its atomic configuration is $[\text{Ar}] 3d^1 4s^2$. Loss of the two $4s$ electrons and one $3d$ electron produces Sc^{3+} , with the stable noble-gas configuration $[\text{Ar}]$. Removing another electron would disrupt this closed shell and require much more energy; thus its characteristic oxidation state is +3.

Step 2: (ii) Explain the difference in colour Copper has configuration $[\text{Ar}] 3d^{10} 4s^1$. Therefore Cu^+ is $[\text{Ar}] 3d^{10}$: its d subshell is completely filled, so no $d-d$ transition is possible and it is colourless. In contrast, Cu^{2+} is $[\text{Ar}] 3d^9$. In its aqueous complex, the d orbitals split in energy, and absorption of visible light promotes an electron between these levels. The transmitted light gives the solution its characteristic colour.

Step 3: Conclusion (i) Scandium shows essentially only +3, giving the stable $[\text{Ar}]$ configuration. (ii) Cu^+ is colourless because it is $3d^{10}$; Cu^{2+} is coloured because its $3d^9$ configuration permits visible-light $d-d$ transitions.

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons when writing configurations of first-row transition-metal ions.

18. A reaction is of first order with respect to A and of second order with respect to B. What will happen to the rate of reaction if (i) only the concentration of B is increased to three times, and (ii) A is taken in excess? [2 marks]

Solution:

Concept:

- For a reaction first order in A and second order in B, the rate law is $r = k[\text{A}][\text{B}]^2$, where k is the rate constant at a fixed temperature.
- When one reactant is present in large excess, its concentration changes negligibly during the reaction and can be incorporated into an observed rate constant.

Step 1: (i) Triple only the concentration of B Let the original concentrations be $[\text{A}] = a$ and $[\text{B}] = b$. The original rate is $r = kab^2$. On tripling only B, A and the temperature remain unchanged, so

$$r_1 = ka(3b)^2 = 9kab^2 = 9r.$$

Thus the rate becomes nine times its original value, because the exponent on B is two.

Step 2: (ii) Take A in large excess If A is taken in a sufficiently large excess, its fractional consumption is negligible, so $[\text{A}] \approx [\text{A}]_0$ throughout the reaction. The rate law can then be written

$$r = k[\text{A}]_0[\text{B}]^2 = k_{\text{obs}}[\text{B}]^2, \quad k_{\text{obs}} = k[\text{A}]_0.$$

The reaction therefore behaves as a pseudo-second-order reaction with respect to B, although the underlying overall order remains three. At a fixed B concentration, increasing A increases the instantaneous rate in direct proportion to A. No particular numerical rate multiplier follows from

Quick Tip to Solve: Raise the concentration multiplier to its rate-law exponent; an excess reactant is absorbed into k_{obs} .

saying only that A is in excess.

Step 3: Conclusion (i) The rate increases ninefold. (ii) With A in large excess, $r = k_{\text{obs}}[\text{B}]^2$; the reaction exhibits pseudo-second-order kinetics.

Quick Tip to Solve: Raise the concentration multiplier to its rate-law exponent; an excess reactant is absorbed into k_{obs} .

19. Write the reactions taking place at anode and cathode in a dry cell.

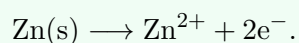
[2 marks]

Solution:

Concept:

- A dry cell is a primary galvanic cell: oxidation occurs at the zinc-container anode, while reduction occurs at the cathode mixture surrounding the graphite rod.
- The moist electrolyte contains NH_4Cl and ZnCl_2 . Manganese dioxide is reduced during discharge; the graphite rod acts as a current collector.

Step 1: Anode: oxidation of zinc The zinc container supplies electrons to the external circuit and is gradually consumed. The anode half-reaction is



Thus zinc is oxidised from oxidation state zero to +2.

Step 2: Cathode: reduction of manganese dioxide Ammonium ions participate in the cathodic process, and manganese dioxide is reduced from manganese(IV) to manganese(III). The commonly used cathode half-reaction is



It may be multiplied by two to match the two electrons released at the zinc anode. The ammonia produced can form a complex with zinc ions.

Step 3: Conclusion Anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. Cathode: $\text{MnO}_2 + \text{NH}_4^+ + \text{e}^- \rightarrow \text{MnO(OH)} + \text{NH}_3$.

Quick Tip to Solve: Write oxidation at the zinc container first; the graphite rod collects current while manganese dioxide undergoes reduction.

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 a non-volatile solute, Raoult's law gives relative lowering of solvent vapour pressure: $(p^0 - p)/p^0 = x_2$, where x_2 is the solute mole fraction.
- For a dilute solution, $x_2 \simeq n_2/n_1$, with $n = w/M$. Here w , M and n denote mass, molar mass and amount in moles, respectively.

Step 1: Calculate the relative lowering The solute is non-volatile, so it does not contribute to the vapour pressure. Given $p^0 = 32$ mm Hg and $p = 31.84$ mm Hg,

$$\frac{p^0 - p}{p^0} = \frac{32 - 31.84}{32} = \frac{0.16}{32} = 0.005.$$

Both vapour pressures are at the same temperature, 308 K, as required for applying Raoult's law.

Step 2: Obtain the solute molar mass Taking the molar mass of water as 18 g mol^{-1} , the dilute-solution relation gives

$$0.005 \simeq \frac{10/M_2}{200/18},$$
$$M_2 \simeq \frac{10 \times 18}{200 \times 0.005} = 180 \text{ g mol}^{-1}.$$

The small mole fraction justifies this standard dilute-solution approximation. If the exact mole fraction $x_2 = n_2/(n_1 + n_2)$ is retained instead, the value is 179.1 g mol^{-1} , consistent with the approximate result.

Step 3: Conclusion The molar mass of the solute is approximately 180 g mol^{-1} using the dilute-solution formula.

Quick Tip to Solve: Use the pressure difference 0.16 in the numerator and pure-water pressure 32 in the denominator; keep the two masses in the same units.

21. (a) What happens when chlorobutane is treated with Na metal in the presence of dry ether?

(b) Arrange the following compounds in increasing order of their boiling points:

1-Bromobutane, 1-Iodobutane, Butane, 1-Chlorobutane

[2 marks]

Solution:

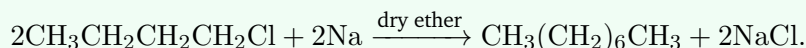
Concept:

- In the Wurtz reaction, two alkyl halide molecules react with sodium in dry ether to form a higher alkane: $2\text{RCl} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaCl}$.
- For the same straight-chain alkyl group, boiling points of alkyl halides generally increase from

Quick Tip to Solve: For Wurtz coupling count carbons in both alkyl groups; for this boiling-point comparison keep the butyl group fixed and compare the halogens.

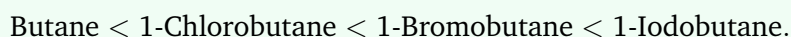
chloride to bromide to iodide as polarizability and dispersion forces increase.

Step 1: (a) Reaction with sodium in dry ether Chlorobutane undergoes Wurtz coupling. Taking chlorobutane in its usual straight-chain form, two butyl groups join to give *n*-octane:



The product contains eight carbon atoms because coupling joins two four-carbon chains. Dry ether provides the anhydrous reaction medium.

Step 2: (b) Compare intermolecular attractions Butane is the lightest molecule in the list and has the weakest intermolecular attractions, so it boils first. Among the three 1-halo derivatives, increasing halogen size and polarizability strengthen London dispersion forces. Thus the chloride has a lower boiling point than the bromide, and the iodide has the highest boiling point:



Step 3: Conclusion (a) Chlorobutane forms *n*-octane by Wurtz reaction. (b) Increasing boiling point: Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane.

Quick Tip to Solve: For Wurtz coupling count carbons in both alkyl groups; for this boiling-point comparison keep the butyl group fixed and compare the halogens.

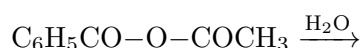
Section C (21 marks)

22(a). (i) Give a chemical test to distinguish between ethanal and propanal.

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



(iii) Complete the given equation:



[3 marks]

Solution:

Concept:

- The iodoform test detects the $\text{CH}_3\text{CO}-$ group; ethanal also responds positively, forming yellow CHI_3 .
- An electron-withdrawing substituent increases carboxylic-acid strength through the negative inductive effect by stabilising the carboxylate conjugate base.
- An acid anhydride undergoes hydrolysis with water to yield the carboxylic acids corresponding to its two acyl groups.

Step 1: (i) Distinguish ethanal and propanal Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 , while propanal does not give this

Quick Tip to Solve: Use iodoform rather than Tollens for this aldehyde pair; split the mixed anhydride at its bridging oxygen to identify its two acid products.

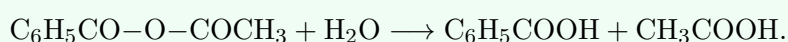
precipitate:



Ethanal has the required methyl carbonyl arrangement; propanal has an ethyl group attached to the aldehyde carbonyl. Tollens' reagent is unsuitable for distinguishing this pair because both are aldehydes and give a positive test.

Step 2: (ii) Compare the strengths of the two acids CH_2FCOOH is the stronger acid. Fluorine is more electronegative than chlorine and exerts a stronger $-I$ effect at the same position. It withdraws electron density through sigma bonds and stabilises the negatively charged conjugate base, CH_2FCOO^- , more effectively than chlorine stabilises $\text{CH}_2\text{ClCOO}^-$. Greater conjugate-base stability favours ionisation and increases acid strength.

Step 3: (iii) Complete the hydrolysis reaction The given compound is the mixed anhydride of benzoic acid and ethanoic acid. Hydrolysis cleaves the anhydride linkage, producing one molecule of each acid:



The two carbonyl groups remain present, each becoming part of a carboxylic acid group.

Step 4: Conclusion (i) Ethanal gives a yellow iodoform precipitate; propanal does not. (ii) CH_2FCOOH is stronger owing to the greater $-I$ effect of fluorine. (iii) The products are $\text{C}_6\text{H}_5\text{COOH}$ and CH_3COOH .

Quick Tip to Solve: Use iodoform rather than Tollens for this aldehyde pair; split the mixed anhydride at its bridging oxygen to identify its two acid products.

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:

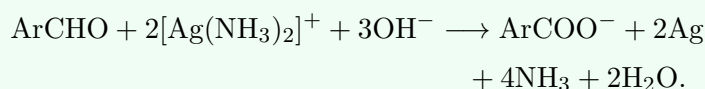
- A 2,4-DNP derivative identifies a carbonyl group, while reduction of Tollens' reagent identifies an aldehyde. Cannizzaro reaction is the disproportionation of an aldehyde without an α -hydrogen in concentrated alkali.
- Vigorous oxidation converts an aromatic aldehyde group and an alkyl side chain having a benzylic hydrogen into carboxyl groups. Phthalic acid is benzene-1,2-dicarboxylic acid.

Step 1: Identify the functional group and substitution pattern The compound contains a carbonyl group because it forms a 2,4-DNP derivative. Its positive Tollens' test establishes that this group is an aldehyde, rather than a ketone. Cannizzaro reaction further indicates that the aldehyde has no α -hydrogen. In an aromatic aldehyde, the carbon adjacent to the aldehydic carbon is a substituted ring carbon and bears no hydrogen. The formula $\text{C}_9\text{H}_{10}\text{O}$ is consistent with $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)\text{CHO}$. Vigorous

Quick Tip to Solve: Use phthalic acid to fix the ortho positions; the extra two carbons beyond benzaldehyde identify an ethyl side chain.

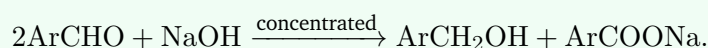
oxidation gives two adjacent carboxyl groups, so the ethyl and aldehyde groups must occupy adjacent ring positions. Thus the compound is 2-ethylbenzaldehyde (*o*-ethylbenzaldehyde).

Step 2: Write the Tollens reaction Let $\text{Ar} = o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4$. The aldehyde is oxidised to the corresponding carboxylate ion in alkaline Tollens' reagent, while silver(I) is reduced to metallic silver:



A silver mirror is obtained. The organic product is 2-ethylbenzoate, which gives 2-ethylbenzoic acid on acidification.

Step 3: Write the Cannizzaro reaction With concentrated sodium hydroxide, one aldehyde molecule is reduced to the benzyl alcohol derivative and another is oxidised to the carboxylate salt:



The products are (2-ethylphenyl)methanol and sodium 2-ethylbenzoate. The ring ethyl group remains unchanged in both of these reactions; vigorous oxidation is a separate identification test.

Step 4: Conclusion The compound is *o*-ethylbenzaldehyde, $o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{CHO}$. Tollens' reagent gives 2-ethylbenzoate and silver; concentrated NaOH gives the corresponding benzyl alcohol and sodium carboxylate.

Quick Tip to Solve: Use phthalic acid to fix the ortho positions; the extra two carbons beyond benzaldehyde identify an ethyl side chain.

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?

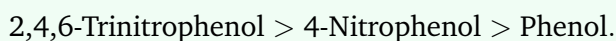
(c) Name the reagent used in the oxidation of a primary unsaturated alcohol to an aldehyde. [3 marks]

Solution:

Concept:

- Acid strength increases when the conjugate base is stabilised. Nitro groups withdraw electron density and stabilise phenoxide ions through inductive and resonance effects.
- Hydrogen bonding with water favours dissolution. A mild selective oxidant converts a primary alcohol to an aldehyde without requiring cleavage of a carbon-carbon double bond.

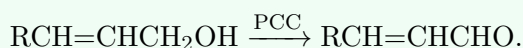
Step 1: (a) Compare the acidic strengths On losing H^+ , each phenol produces a phenoxide ion. The para nitro group withdraws electron density by its $-I$ and $-R$ effects and stabilises the negative charge of the conjugate base. Hence 4-nitrophenol is more acidic than phenol. In 2, 4, 6-trinitrophenol, three nitro groups produce a much greater electron-withdrawing effect and stabilise its conjugate base still further. The decreasing order is



Quick Tip to Solve: Count the nitro groups to rank phenol acidity; for an unsaturated primary alcohol, choose PCC to retain the double bond.

Step 2: (b) Explain the water solubility Alcohol molecules contain a polar –OH group. Its oxygen can accept hydrogen bonds from water, and its hydroxyl hydrogen can form hydrogen bonds with water oxygen atoms. These favourable alcohol-water interactions help the molecules enter aqueous solution. Hydrocarbons of comparable molecular masses have no such polar group and cannot form hydrogen bonds with water. Their interactions with water are therefore much weaker, so alcohols are more soluble.

Step 3: (c) Name the selective oxidising reagent Use pyridinium chlorochromate (PCC), commonly in an anhydrous medium such as dichloromethane. It oxidises the primary –CH₂OH group to –CHO while retaining the carbon-carbon double bond of an unsaturated alcohol:



The mild, anhydrous conditions allow the oxidation to stop at the aldehyde stage.

Step 4: Conclusion (a) 2, 4, 6-Trinitrophenol > 4-nitrophenol > phenol. (b) Alcohols form hydrogen bonds with water. (c) Pyridinium chlorochromate (PCC).

Quick Tip to Solve: Count the nitro groups to rank phenol acidity; for an unsaturated primary alcohol, choose PCC to retain the double bond.

24. 2 g of Na₂SO₄ is dissolved in 50 g of water to form a solution. Calculate the freezing point of this solution, assuming Na₂SO₄ undergoes complete dissociation.

[Given: Molar mass of Na₂SO₄ = 142 g mol⁻¹, K_f for water = 1.86 K kg mol⁻¹]

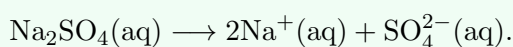
[3 marks]

Solution:

Concept:

- Freezing point depression is $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the molal depression constant and m is moles of solute formula units per kilogram of solvent.
- Complete dissociation of one formula unit of Na₂SO₄ gives three ions. Hence $i = 3$. The freezing point of pure water is 0 °C or 273.15 K.

Step 1: Find the number of solute particles The complete dissociation specified in the question is



Thus one mole of sodium sulphate produces three moles of ions and the van't Hoff factor is $i = 2+1 = 3$. The factor is based on the number of independently moving particles, not their charges. There is no need to calculate a partial degree of dissociation because complete dissociation is given.

Step 2: Calculate the molality The amount of sodium sulphate and mass of water are

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

Quick Tip to Solve: For fully dissociated sodium sulphate use $i = 3$, divide by 0.050 kg of water, and subtract the depression from zero Celsius.

Molality uses the mass of the solvent, so

$$m = \frac{0.0140845}{0.050} = 0.28169 \text{ mol kg}^{-1}.$$

The solution mass of 52 g must not be used in this denominator.

Step 3: Calculate the depression and the freezing point Substituting into the colligative-property relation gives

$$\begin{aligned}\Delta T_f &= iK_f m \\ &= 3 \times 1.86 \times 0.28169 \\ &= 1.57183 \text{ K} \approx 1.57 \text{ K}.\end{aligned}$$

A depression lowers the freezing point below that of pure water. Since a temperature difference of one kelvin equals one degree Celsius,

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

Equivalently, $T_f = 273.15 - 1.57183 = 271.57817 \text{ K}$.

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

Quick Tip to Solve: For fully dissociated sodium sulphate use $i = 3$, divide by 0.050 kg of water, and subtract the depression from zero Celsius.

25. (a) Mention any two types of RNA molecules.

(b) How is glycogen different from starch?

(c) Explain the β -pleated sheet structure of proteins.

[3 marks]

Solution:

Concept:

- RNA molecules perform different functions in protein synthesis; messenger RNA and transfer RNA are two distinct types.
- Starch and glycogen are storage polysaccharides made from α -D-glucose units, but differ in biological source and extent of branching.
- The β -pleated sheet is a secondary structure of proteins, stabilised by hydrogen bonds between peptide groups of neighbouring extended chains or chain segments.

Step 1: (a) Name two types of RNA Two types are **messenger RNA (mRNA)** and **transfer RNA (tRNA)**. Messenger RNA carries genetic information from DNA to the site of protein synthesis, whereas transfer RNA brings the appropriate amino acids to the ribosome. Ribosomal RNA is another type, but only two names are required here.

Step 2: (b) Compare glycogen with starch Glycogen is the chief storage carbohydrate of animals and is stored mainly in liver and muscles. Starch is the storage carbohydrate of plants. Both contain α -glucose units, but glycogen is **more highly branched** than starch. Starch contains relatively unbranched amylose together with branched amylopectin; glycogen resembles amylopectin with more

Quick Tip to Solve: For the beta-sheet, name both the extended zigzag arrangement and the hydrogen bonds between neighbouring peptide groups.

frequent branches.

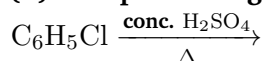
Step 3: (c) Describe the beta-pleated sheet In a β -pleated sheet, polypeptide chains or segments are stretched out in an extended, zigzag arrangement and lie side by side. Hydrogen bonds form between the C = O group of one peptide bond and the N – H group of a neighbouring chain or segment. These bonds hold the chains together in a sheet resembling the pleated folds of a fabric. Thus, hydrogen bonding stabilises the sheet without changing the amino-acid sequence.

Step 4: Conclusion (a) mRNA and tRNA. (b) Glycogen is an animal storage polysaccharide and is more highly branched than plant starch. (c) The β -pleated sheet consists of neighbouring extended polypeptide chains held together by hydrogen bonds.

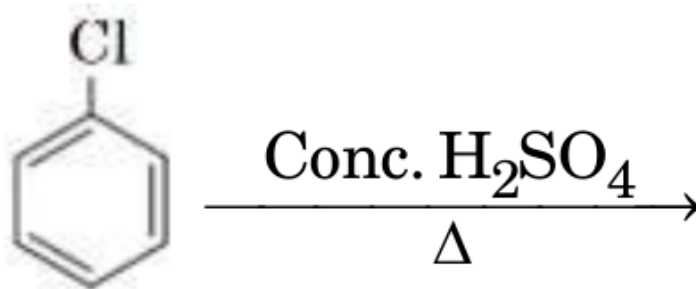
Quick Tip to Solve: For the beta-sheet, name both the extended zigzag arrangement and the hydrogen bonds between neighbouring peptide groups.

26. (a) “Haloalkanes react with KCN to form alkyl cyanides as the main product, whereas with AgCN, they form isocyanides as the main product.” Explain the statement.

(b) Complete the given equation:



[3 marks]

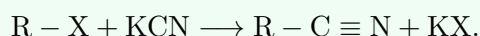


Solution:

Concept:

- Cyanide is an ambident nucleophile: it can form a bond through its carbon atom or its nitrogen atom, giving different connectivity in the products.
- Chlorine deactivates the benzene ring by its inductive effect but directs electrophilic substitution to the ortho and para positions through resonance donation.

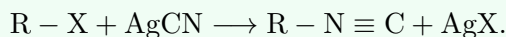
Step 1: (a) Explain the reaction with KCN Potassium cyanide is predominantly ionic and supplies free CN^- ions in solution. Although cyanide can attack through either end, attack through carbon is favoured and produces the more stable carbon–carbon bond. Consequently, nucleophilic substitution of the halogen in an alkyl halide gives an alkyl cyanide (nitrile) as the main product:



The group attached directly to the alkyl carbon is therefore the carbon atom of cyanide.

Quick Tip to Solve: Track the bonded atom: carbon attack gives R-CN, nitrogen attack gives R-NC; chlorine still directs ring substitution ortho and para.

Step 2: (a) Explain the reaction with AgCN Silver cyanide is predominantly covalent; its carbon end is bonded to silver and is not freely available for attack in the same way as in ionic KCN. The nitrogen end is available to form the new bond with the alkyl group. Thus, the main product is an alkyl isocyanide:



The difference between the two products is the atom through which the cyanide group is attached to R, rather than any change in the alkyl skeleton.

Step 3: (b) Complete the sulphonation reaction Heating chlorobenzene with concentrated sulphuric acid introduces the $-SO_3H$ group at the ortho and para positions. The para product predominates because it has less steric crowding than the ortho product:



The two equations represent the alternative ortho and para substitutions, respectively. In each case one ring hydrogen is replaced by the sulphonic acid group.

Step 4: Conclusion KCN mainly gives $R - CN$, whereas covalent AgCN mainly gives $R - NC$. Sulphonation gives the ortho and para isomers of chlorobenzenesulphonic acid; the para isomer is the major product.

Quick Tip to Solve: Track the bonded atom: carbon attack gives $R-CN$, nitrogen attack gives $R-NC$; chlorine still directs ring substitution ortho and para.

27. The resistance and conductivity of a conductivity cell containing 0.1 mol L^{-1} KCl solution are 100 ohms and $1.29 \times 10^{-2} \text{ S cm}^{-1}$, respectively. If the resistance of the same cell filled with 0.02 mol L^{-1} KCl solution is 520 ohms, calculate conductivity and molar conductivity of 0.02 mol L^{-1} KCl solution. [3 marks]

Solution:

Concept:

- For a conductivity cell, conductivity $\kappa = G(l/A) = (l/A)/R$, where R is resistance, $G = 1/R$ is conductance and l/A is the cell constant.
- The cell constant depends on the geometry of the cell and remains unchanged when the solution is replaced in the same cell.
- When κ is in S cm^{-1} and concentration c is in mol L^{-1} , molar conductivity is $\Lambda_m = 1000\kappa/c$ in $\text{S cm}^2 \text{ mol}^{-1}$.

Step 1: Find the cell constant using the first solution The first solution has $R_1 = 100 \Omega$ and

Quick Tip to Solve: In the same cell, first calculate the fixed product κR ; divide it by the new resistance before finding molar conductivity.

$\kappa_1 = 1.29 \times 10^{-2} \text{ S cm}^{-1}$. Therefore,

$$\begin{aligned}\frac{l}{A} &= \kappa_1 R_1 \\ &= (1.29 \times 10^{-2})(100) \\ &= 1.29 \text{ cm}^{-1}.\end{aligned}$$

Multiplying conductivity by resistance cancels siemens against inverse ohms, leaving inverse centimetres for the cell constant.

Step 2: Calculate the conductivity of the dilute solution For the same cell, $l/A = 1.29 \text{ cm}^{-1}$ and the new resistance is $R_2 = 520 \Omega$. Hence,

$$\begin{aligned}\kappa_2 &= \frac{l/A}{R_2} = \frac{1.29}{520} \\ &= 2.48077 \times 10^{-3} \text{ S cm}^{-1} \\ &\simeq 2.48 \times 10^{-3} \text{ S cm}^{-1}.\end{aligned}$$

This is smaller than the conductivity of the concentrated solution, as expected from the larger measured resistance in the unchanged cell.

Step 3: Calculate the molar conductivity With $c_2 = 0.02 \text{ mol L}^{-1}$, use the unrounded conductivity:

$$\begin{aligned}\Lambda_{m,2} &= \frac{1000\kappa_2}{c_2} \\ &= \frac{1000(1.29/520)}{0.02} \\ &= 124.038 \text{ S cm}^2 \text{ mol}^{-1} \\ &\simeq 124.04 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

The factor 1000 converts the litre in the concentration unit into cubic centimetres, making the units consistent with the conductivity used.

Step 4: Conclusion The dilute KCl solution has

$$\kappa = 2.48 \times 10^{-3} \text{ S cm}^{-1}$$

and

$$\Lambda_m = 124.04 \text{ S cm}^2 \text{ mol}^{-1}.$$

Quick Tip to Solve: In the same cell, first calculate the fixed product κR ; divide it by the new resistance before finding molar conductivity.

28. (a) What is meant by invert sugar?

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

(c) Name the disease caused by the deficiency of Vitamin B₁.

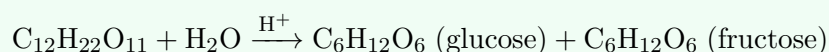
[3 marks]

Solution:

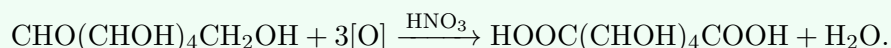
Concept:

- Sucrose undergoes hydrolysis to give equimolar amounts of glucose and fructose. Their mixture is called invert sugar because the direction of optical rotation is reversed.
- An oxidising agent can oxidise both the aldehyde group and the primary alcoholic group of open-chain glucose. Vitamin deficiency diseases depend on the particular vitamin lacking.

Step 1: Explain invert sugar (a) On hydrolysis, dextrorotatory sucrose produces an equimolar mixture of D-(+)-glucose and D-(-)-fructose. This mixture is laevorotatory because the negative rotation of fructose exceeds the positive rotation of glucose. The change from positive to negative optical rotation is called inversion, and the product mixture is invert sugar.



Step 2: Oxidise glucose with nitric acid (b) Nitric acid oxidises both the aldehyde group, $-\text{CHO}$, and the terminal primary alcohol group, $-\text{CH}_2\text{OH}$, of glucose to carboxyl groups. The product is the dicarboxylic acid saccharic acid (glucaric acid). Using $[\text{O}]$ for an oxidising oxygen equivalent, the balanced reaction is



The four intervening secondary alcoholic groups remain in the product.

Step 3: Identify the deficiency disease (c) Vitamin B₁, also called thiamine, is required for normal metabolism and nerve function. Its deficiency causes beri-beri.

Step 4: Conclusion (a) Invert sugar is the laevorotatory glucose-fructose mixture obtained by sucrose hydrolysis. (b) Nitric acid converts glucose to saccharic acid. (c) Vitamin B₁ deficiency causes beri-beri.

Quick Tip to Solve: For glucose oxidation, inspect both terminal groups: nitric acid converts both ends to $-\text{COOH}$.

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: 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:

- Lanthanoid contraction is the progressive reduction in atomic and ionic sizes across the lanthanoids due to poor shielding by the added 4f electrons.
- The outer ns and inner $(n-1)d$ orbitals in transition metals have comparable energies, so electrons from both can participate in bonding.

Step 1: Explain the resemblance of the second and third series (i) The filling of 4f orbitals between the second (4d) and third (5d) transition series causes lanthanoid contraction. Since 4f electrons shield nuclear charge poorly, the increasing effective nuclear attraction contracts the atoms. This largely offsets the size increase expected from adding a new shell. Consequently corresponding 4d and 5d elements have almost equal atomic radii, unlike their appreciably smaller 3d counterparts. Their similar sizes lead to closely similar chemical properties; zirconium and hafnium are a familiar example.

Step 2: Explain variable oxidation states (ii) The energy difference between the ns and $(n-1)d$ orbitals is small. Depending on the bonding environment, different numbers of ns and $(n-1)d$ electrons may be used or removed. Thus transition metals can exhibit several oxidation states. For example, iron commonly forms Fe^{2+} and Fe^{3+} .

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

Quick Tip to Solve: Link the 4d-5d similarity to poor 4f shielding; link variable oxidation states to similar ns and d energies.

29(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 usual oxidation states.
- A completely filled d subshell contains ten electrons and is written d^{10} .

Step 1: Examine the zinc atom Zinc has atomic number 30 and electronic configuration $[\text{Ar}] 3d^{10}4s^2$. Its $3d$ subshell is completely filled, so the neutral atom does not have a partially filled d subshell.

Step 2: Examine its usual ion Zinc forms Zn^{2+} by losing the two $4s$ electrons. The ion has configuration $[\text{Ar}] 3d^{10}$, which is also completely filled. Merely belonging to the d -block does not fulfil the definition of a transition element.

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

Quick Tip to Solve: Check both Zn and Zn^{2+} : losing $4s^2$ leaves $3d^{10}$ unchanged.

OR

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

[1 mark]

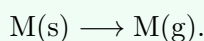
Solution:

Concept:

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

Step 1: Identify the source of strong metallic bonding Transition metals generally possess several unpaired $(n - 1)d$ electrons as well as outer ns electrons. Participation of these electrons in metallic bonding gives strong interatomic attraction and high cohesive energy.

Step 2: Relate bonding to atomisation enthalpy Atomisation breaks the metallic bonding by separating the solid into individual gaseous atoms:



Because the bonding is strong, a large energy input is needed. Hence transition metals generally have high positive standard enthalpies of atomisation.

Step 3: Conclusion Transition metals generally have high $\Delta_a H^\circ$ because strong metallic bonding involving d and s electrons requires considerable energy to break.

Quick Tip to Solve: Connect atomisation with separating metal atoms: more unpaired bonding electrons generally means stronger cohesion.

29(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 the effective nuclear attraction felt by electrons, which reflects both nuclear charge and shielding.
- Across a transition series, added electrons enter the inner $(n - 1)d$ subshell while the principal outer shell remains the same.

Step 1: Identify the competing effects With each increase in atomic number, the nuclear charge increases and tends to pull the electrons inward, reducing atomic size. At the same time, the additional electron enters the $(n - 1)d$ subshell and increases shielding of the outer electrons.

Step 2: Explain the small net change The increasing shielding by the added d electrons partly counterbalances the increased nuclear charge. Thus the effective inward pull changes only moderately and the atomic radii change relatively little across the transition series, particularly in its middle region. A small initial decrease is therefore consistent with the nearly constant trend.

Step 3: Conclusion The increase in nuclear charge is largely counterbalanced by the increased shielding from added $(n - 1)d$ electrons, so transition-metal atomic radii change only slightly across a series.

Quick Tip to Solve: For radius across one transition series, compare increased nuclear attraction with the shielding added by each new d electron.

30(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:

- Aldehydes and ketones containing at least one α -hydrogen undergo aldol condensation: the hydrogen on a carbon adjacent to the carbonyl carbon permits enolate formation in dilute alkali.
- An aldehyde without any α -hydrogen undergoes Cannizzaro reaction in concentrated alkali,

Quick Tip to Solve: Inspect the carbon next to $C=O$: an H there permits aldol; an aldehyde without such an H gives Cannizzaro.

producing an alcohol and a carboxylate salt by disproportionation.

Step 1: Identify compounds with alpha-hydrogen In cyclohexanone, both ring carbons adjacent to the carbonyl carbon are CH_2 groups, so α -hydrogens are present. In 2-methylpentanal, $\text{CHO} - \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$, carbon 2 bears one hydrogen. Hence both compounds can form an enolate and undergo aldol condensation.

Step 2: Identify aldehydes without alpha-hydrogen Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no hydrogen on the aromatic carbon directly attached to CHO . Methanal, HCHO , has no α -carbon at all; its hydrogens are attached to the carbonyl carbon. Both are aldehydes lacking α -hydrogen, so both undergo Cannizzaro reaction.

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

Quick Tip to Solve: Inspect the carbon next to $\text{C}=\text{O}$: an H there permits aldol; an aldehyde without such an H gives Cannizzaro.

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

Solution:

Concept:

- Nucleophilic addition is favoured by a more electrophilic, less sterically hindered carbonyl carbon.
- Alkyl groups donate electron density by the $+I$ effect and hinder approach; aldehydes are generally more reactive than ketones.

Step 1: Compare the two ketones Butanone has an ethyl and a methyl group attached to its carbonyl carbon, whereas propanone has two methyl groups. The larger ethyl group causes greater steric hindrance and electron donation. Thus butanone is less reactive than propanone.

Step 2: Compare the aldehydes and combine Propanal has an ethyl group and ethanal has a methyl group next to CHO ; the smaller methyl group makes ethanal more reactive. Both aldehydes have only one alkyl group at the carbonyl carbon and are more reactive than the two ketones.

Step 3: Conclusion Butanone < Propanone < Propanal < Ethanal.

Quick Tip to Solve: Place ketones before aldehydes, then place the compound with the bulkier alkyl group first within each pair.

30(b). Draw the structure of the semicarbazone of cyclohexanone.

[1 mark]

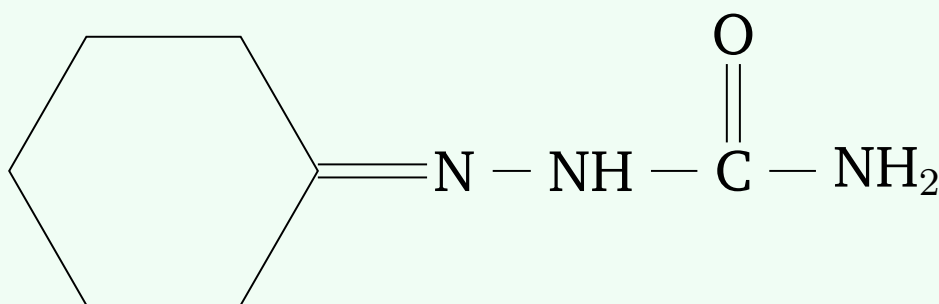
Solution:

Concept:

- Semicarbazide has the structure $\text{H}_2\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$. Its terminal hydrazino $-\text{NH}_2$ group condenses with the carbonyl group.
- Semicarbazone formation replaces the carbonyl $\text{C} = \text{O}$ bond by $\text{C} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, with elimination of water.

Step 1: Identify the reacting group Cyclohexanone contains a carbonyl carbon within a six-membered ring. Condensation occurs at this carbon and the terminal $-\text{NH}_2$ group of semicarbazide; the ring skeleton is retained. The amide $-\text{CONH}_2$ group remains intact.

Step 2: Write the product structure The original ring carbonyl carbon is now double-bonded to nitrogen and remains single-bonded to its two neighbouring ring carbons. The exocyclic chain is $=\text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$, as shown in the structure below. Each unlabelled vertex of the ring represents a carbon atom with the required hydrogens.



Structure of cyclohexanone semicarbazone

Step 3: Conclusion The product is cyclohexanone semicarbazone, with the ring carbonyl group converted into $\text{C} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$.

Quick Tip to Solve: Attach $=\text{N}-\text{NH}-\text{CONH}_2$ to the original carbonyl carbon; retain all six ring carbons.

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

[1 mark]

Solution:

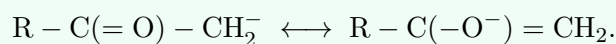
Concept:

- An α -hydrogen is bonded to the carbon adjacent to a carbonyl group.
- Acidity increases when removal of H^+ gives a resonance-stabilised conjugate base.

Step 1: Remove an alpha-proton The electron-withdrawing carbonyl group facilitates removal of an α -hydrogen as a proton by a base. The electron pair left behind forms an enolate ion rather than a localised, unstable carbanion.

Quick Tip to Solve: Explain acidity by drawing the conjugate base and delocalising its negative charge onto carbonyl oxygen.

Step 2: Show stabilisation of the conjugate base The negative charge is delocalised between the α -carbon and oxygen through resonance:



The contributor with charge on electronegative oxygen stabilises the enolate. This stabilisation makes loss of the α -proton favourable relative to an ordinary alkane hydrogen.

Step 3: Conclusion The α -hydrogen is acidic because its removal forms a resonance-stabilised enolate ion; the electron-withdrawing carbonyl group also assists proton removal.

Quick Tip to Solve: Explain acidity by drawing the conjugate base and delocalising its negative charge onto carbonyl oxygen.

Section E (15 marks)

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

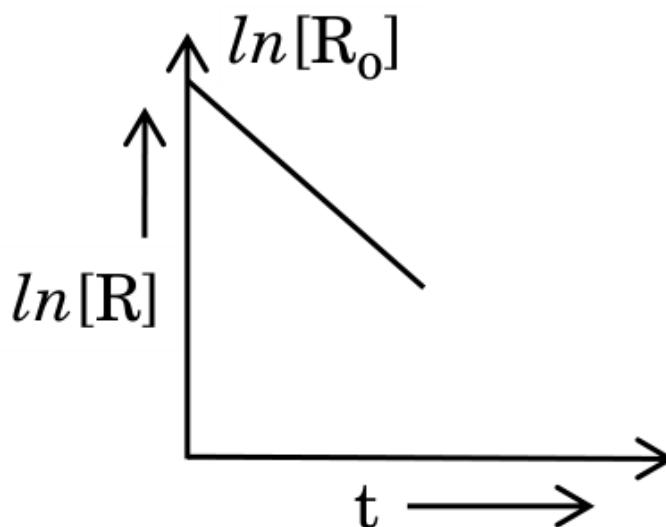
[Given: $\log 5 = 0.7$, $\log 4 = 0.6$]

(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, rate is proportional to reactant concentration: $-d[R]/dt = k[R]$, where k is the rate constant.
- The integrated rate equation is $kt = 2.303 \log([R]_0/[R]_t)$, where the subscripts denote initial

Quick Tip to Solve: Convert percent completion into percent remaining first; distinguish natural-log and common-log plots when identifying the slope.

concentration and concentration remaining at time t .

- Equivalently, $\ln[R]_t = \ln[R]_0 - kt$; a plot of natural logarithm of concentration against time has slope $-k$.

Step 1: (i) Calculate the rate constant Take the initial amount as 100 units. After 10 minutes, 20 units have reacted and 80 units remain. Use the unreacted amount in the integrated rate equation:

$$k = \frac{2.303}{10} \log \frac{100}{80} = \frac{2.303}{10} \log \frac{5}{4}.$$

With the supplied logarithms, $\log(5/4) = \log 5 - \log 4 = 0.7 - 0.6 = 0.1$. Thus,

$$k = 0.02303 \text{ min}^{-1}.$$

Step 2: (i) Find the total time for 80 percent completion When 80 percent has reacted, only 20 percent remains. The ratio of initial to remaining amount is therefore $100/20 = 5$. Using the same rate constant,

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

This is the total time measured from the start, as required. Both calculations use the logarithmic values supplied in the question consistently. Equal percentages do not react in equal time intervals in a first order reaction because the rate decreases with the amount remaining.

Step 3: (ii)(I) Identify the reaction order The graph shows a linear decrease of $\ln[R]$ with time. The first order integrated rate law,

$$\ln[R]_t = \ln[R]_0 - kt,$$

has precisely this form. The intercept is $\ln[R]_0$, consistent with the printed graph. A zero order reaction would instead give a straight line for concentration itself against time.

Step 4: (ii)(II) Determine the slope Compare the integrated equation with $y = c + mx$, taking $y = \ln[R]$ and $x = t$. The coefficient of time is $-k$, hence

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

The negative sign represents decreasing reactant concentration. Since the vertical axis uses the natural logarithm, there is no factor of 2.303 in the slope; that factor is used when expressing the integrated equation with common logarithms.

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

Quick Tip to Solve: Convert percent completion into percent remaining first; distinguish natural-log and common-log plots when identifying the slope.

31(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, $t = (2.303/k) \log(a/(a-x))$, where a is the initial amount, x the amount reacted and k the rate constant.
- The half-life is $t_{1/2} = 0.693/k$, independent of the initial concentration for a first order reaction.
- A complex reaction proceeds through two or more elementary steps. A pseudo first order reaction has first order observed kinetics under conditions that keep other reacting species effectively constant.

Step 1: (i) Express the time for three-fourths completion Let the initial reactant amount be a . On completion of 3/4 of the reaction, the amount remaining is $a/4$. Substitution in the first order rate equation gives

$$t_{3/4} = \frac{2.303}{k} \log \frac{a}{a/4} = \frac{2.303}{k} \log 4.$$

The concentration ratio is dimensionless, and the same rate constant applies throughout at a fixed temperature. The fraction in the logarithm must use the amount remaining rather than the amount already consumed.

Step 2: (i) Form the ratio with half-life For half completion, the amount remaining is $a/2$, so

$$t_{1/2} = \frac{2.303}{k} \log 2.$$

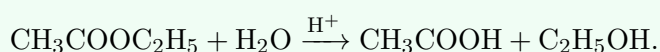
Dividing the two times cancels the common factor:

$$\frac{t_{3/4}}{t_{1/2}} = \frac{\log 4}{\log 2} = \frac{2 \log 2}{\log 2} = 2.$$

This can also be checked by successive half-lives: after one half-life, $a/2$ remains; after two half-lives, $a/4$ remains. Thus three-fourths consumption takes two half-lives.

Step 3: (ii)(I) Define a complex reaction A complex reaction is a reaction that occurs through a sequence of two or more elementary steps rather than a single elementary event. The individual steps constitute its reaction mechanism and may involve intermediates. Their sum gives the overall chemical equation. Consequently, the observed rate law cannot in general be inferred simply from the stoichiometric coefficients of the overall equation; the mechanism determines the kinetics.

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



Quick Tip to Solve: Three-fourths completion leaves one-fourth, which requires two successive half-lives; always state the excess-water condition for pseudo first order hydrolysis.

At fixed acid concentration, its rate may be written as $r = k[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$. Since water is present in large excess, its concentration changes negligibly and can be incorporated into the observed constant $k' = k[\text{H}_2\text{O}]$. Hence

$$r = k'[\text{CH}_3\text{COOC}_2\text{H}_5].$$

The reaction therefore behaves as first order with respect to the changing ester concentration under these experimental conditions.

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

Quick Tip to Solve: Three-fourths completion leaves one-fourth, which requires two successive half-lives; always state the excess-water condition for pseudo first order hydrolysis.

32(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

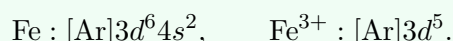
(ii) A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green in colour while a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. Explain. [Atomic number : Ni = 28] [5 marks]

Solution:

Concept:

- The oxidation state fixes the metal-ion configuration: iron(III) is $3d^5$, whereas nickel(II) is $3d^8$. Ligand field strength determines whether pairing occurs before hybridisation.
- An octahedral inner orbital complex uses two $3d$ orbitals in d^2sp^3 hybridisation; an outer orbital complex uses two $4d$ orbitals in sp^3d^2 hybridisation.
- A complex is coloured when it absorbs visible light for an electronic transition. The separation of the split d orbitals depends on both the ligand and the geometry.

Step 1: (i)(I) Find the configuration of iron(III) In both complexes the six ligands each carry charge -1 , and the complex has charge -3 . Hence the oxidation state of iron is $+3$. For $Z = 26$,



The free ion has five singly occupied $3d$ orbitals. Whether two of these orbitals become vacant depends on the strength of the approaching ligands.

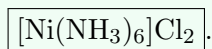
Step 2: Compare cyanide and fluoride ligands CN^- is a strong field ligand. Its octahedral splitting is large enough to favour pairing of the five $3d$ electrons in the three lower-energy orbitals, giving $t_{2g}^5e_g^0$. Thus two inner $3d$ orbitals are available to combine with one $4s$ and three $4p$ orbitals. Consequently $[\text{Fe}(\text{CN})_6]^{3-}$ has d^2sp^3 hybridisation and is an inner orbital octahedral complex, with one unpaired electron.

F^- is a weak field ligand. Its splitting is insufficient to overcome the pairing energy, so the $3d$ electrons remain unpaired, with configuration $t_{2g}^3e_g^2$. No two $3d$ orbitals are vacant. The metal therefore uses

Quick Tip to Solve: First obtain the metal oxidation state; then use ligand strength to decide pairing. Explain colour through absorption energy, rather than equating diamagnetism with colourlessness.

one $4s$, three $4p$ and two outer $4d$ orbitals for sp^3d^2 hybridisation. Thus $[\text{FeF}_6]^{3-}$ is an outer orbital octahedral complex with five unpaired electrons.

Step 3: (i)(II) Write the formula from the name Hexaammine denotes six neutral NH_3 ligands. Nickel(II) gives the coordination entity charge $+2$, so two chloride counterions are required outside the coordination sphere:



Chloride is the counterion; it is not one of the six ligands bound to nickel.

Step 4: (ii) Explain the difference in colour Nickel has configuration $[\text{Ar}]3d^84s^2$, so Ni^{2+} is $3d^8$. In octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, water produces a splitting that permits absorption of visible light in $d-d$ transitions. The transmitted light gives the solution its green colour.

Cyanide is a much stronger field ligand. In square planar $[\text{Ni}(\text{CN})_4]^{2-}$, the $3d$ electrons pair and the complex has dsp^2 hybridisation. The relevant orbital energy separation is much greater, so the electronic absorption lies outside the visible region, at higher energy. The solution therefore appears colourless. Pairing alone is not the criterion for absence of colour; the decisive point is that visible light is not absorbed appreciably.

Step 5: Conclusion $[\text{Fe}(\text{CN})_6]^{3-}$ is inner orbital (d^2sp^3), whereas $[\text{FeF}_6]^{3-}$ is outer orbital (sp^3d^2). Hexaamminenickel(II) chloride is $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. The aqua nickel(II) complex absorbs visible light and is green, whereas the stronger cyanide field in the square planar complex shifts absorption outside the visible region, making it colourless.

Quick Tip to Solve: First obtain the metal oxidation state; then use ligand strength to decide pairing. Explain colour through absorption energy, rather than equating diamagnetism with colourlessness.

OR

32(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: $\text{Ni} = 28$]

[5 marks]

Solution:

Concept:

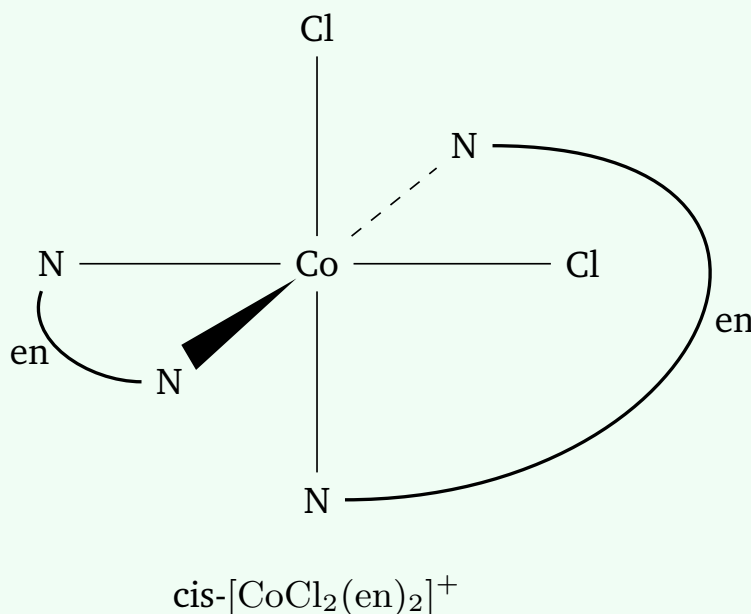
- Name a complex salt with the complex cation first and the complex anion second. The ligands NH_3 and CN^- are named ammine and cyanido; an anionic silver complex uses argentate.
- Coordination number counts the donor atoms directly bonded to the metal. Oxalato, $\text{C}_2\text{O}_4^{2-}$, and ethane-1,2-diamine, abbreviated en, are bidentate ligands.
- The octahedral cis form of $[\text{CoCl}_2(\text{en})_2]^+$ has two non-superimposable mirror-image forms. In valence bond theory, four equivalent sp^3 orbitals give tetrahedral coordination; paired electrons give diamagnetism.

Quick Tip to Solve: Count donor atoms rather than ligands: three oxalato ligands give six donors. For this cobalt complex draw adjacent Cl groups, then connect each en pair at adjacent sites.

Step 1: (i)(I) Name the complex salt In $[\text{Ag}(\text{NH}_3)_2]^+$, ammonia is neutral, so silver is in oxidation state +1. Its cation name is diamminesilver(I). In $[\text{Ag}(\text{CN})_2]^-$, each cyanido ligand has charge -1 ; if the silver oxidation state is x , then $x - 2 = -1$, giving $x = +1$. Its anion name is dicyanidoargentate(I). Although the formula prints the anion before the cation, the name must put the cation first: **diamminesilver(I) dicyanidoargentate(I)**.

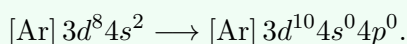
Step 2: (i)(II) Count the directly attached donor atoms In $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, each of the three oxalato ligands coordinates through two oxygen donor atoms. Therefore, the coordination number of iron is $3 \times 2 = 6$. In $[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$, the three ammine ligands and the three chlorido ligands are all monodentate. Therefore, the coordination number of chromium is $3 + 3 = 6$. Coordination number counts donor atoms, so the three bidentate ligands in the first complex do not give coordination number three.

Step 3: (i)(III) Draw the optically active cis isomer Place the two chlorido ligands at adjacent positions of an octahedron, with $\angle \text{Cl} - \text{Co} - \text{Cl} = 90^\circ$. Each en ligand supplies two nitrogen donor atoms at adjacent sites, joined by its $-\text{CH}_2\text{CH}_2-$ backbone. The drawing shows one optical form of the cis isomer; the curved links labelled en identify the two separate chelate rings. Solid wedge and dashed bonds distinguish the front and rear coordination sites. Its mirror image cannot be superimposed on it, so the cis isomer is optically active. The trans geometrical isomer, with opposite chlorido ligands, is optically inactive.



One optically active cis form; each curved en link joins the two N donors of one ethane-1,2-diamine ligand.

Step 4: (ii) Explain the bonding and magnetism of nickel tetracarbonyl Carbon monoxide is neutral, so nickel has oxidation state zero in $[\text{Ni}(\text{CO})_4]$. The ground-state configuration of the free nickel atom is $[\text{Ar}] 3d^8 4s^2$. In the presence of the strong-field CO ligands, the electrons rearrange to give a completely filled $3d^{10}$ subshell, leaving the $4s$ and $4p$ orbitals empty:



Quick Tip to Solve: Count donor atoms rather than ligands: three oxalato ligands give six donors. For this cobalt complex draw adjacent Cl groups, then connect each en pair at adjacent sites.

One $4s$ orbital and three $4p$ orbitals hybridise to produce four empty equivalent sp^3 hybrid orbitals. Each accepts a lone pair from the carbon donor atom of one CO ligand, producing four coordinate bonds directed towards the corners of a tetrahedron. No $3d$ orbital is used in this hybridisation. Since all ten $3d$ electrons are paired and each ligand donates an electron pair, the complex has no unpaired electrons and is diamagnetic.

Step 5: Conclusion (i) The name is **diamminesilver(I) dicyanidoargentate(I)**; both metal coordination numbers are 6; the optically active geometrical 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 donor atoms rather than ligands: three oxalato ligands give six donors. For this cobalt complex draw adjacent Cl groups, then connect each en pair at adjacent sites.

- 33(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 smaller $pK_b = -\log K_b$.
- Alkyl groups increase electron density on nitrogen by their electron-releasing inductive effect. In the gas phase, aqueous solvation effects are absent.
- Reduction changes a nitro group to an amino group; diazotisation of a primary aromatic amine requires nitrous acid at 273–278 K. Nitrile formation followed by reduction increases the carbon 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 and is therefore less available for bonding with a proton. The phenyl group also exerts an electron-withdrawing inductive effect. In methylamine, the methyl group donates electron density through its $+I$ effect and the nitrogen lone pair is localised and more readily available. Thus aniline is the weaker base: it has a smaller K_b , and hence a higher pK_b , than methylamine.

Step 2: (i)(II) Order the gas-phase basic strengths Each ethyl group releases electron density towards nitrogen and helps stabilise the protonated amine. Since there is no solvent to introduce differences in hydration, the electron-releasing effect determines the usual gas-phase order:

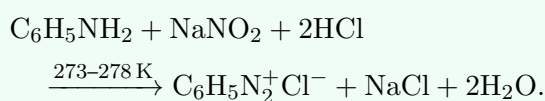
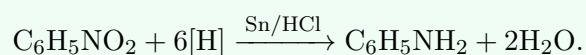


Quick Tip to Solve: For gas-phase amine basicity count electron-releasing alkyl groups; for $\text{CH}_3\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$, insert carbon with KCN before reducing.

The tertiary amine is therefore the strongest base of this set, followed by the secondary and primary amines and then ammonia.

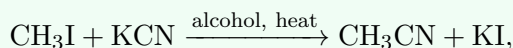
Step 3: (i)(III) Identify Hinsberg's reagent and its use Hinsberg's reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. It is used to distinguish primary, secondary and tertiary amines. A primary amine gives a sulphonamide containing an acidic N-H bond, soluble in aqueous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

Step 4: (ii)(I) Convert nitrobenzene into benzenediazonium chloride First reduce nitrobenzene with tin and hydrochloric acid, then liberate aniline from its salt with alkali. Diazotise the aniline with sodium nitrite and hydrochloric acid at 273–278 K:



Nitrous acid is generated in situ. The cold conditions prevent decomposition of the diazonium salt.

Step 5: (ii)(II) Convert iodomethane into ethanamine Heat iodomethane with alcoholic potassium cyanide to obtain ethanenitrile. Reduce this nitrile with lithium aluminium hydride in dry ether, followed by hydrolysis:

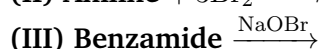
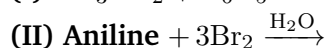
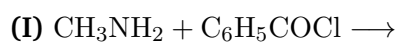


Cyanide introduces the additional carbon atom. Use KCN rather than AgCN, which predominantly gives an isocyanide.

Step 6: Conclusion Aniline has the higher pK_b because its lone pair is resonance-delocalised. Gas-phase basicity is $\text{Et}_3\text{N} > \text{Et}_2\text{NH} > \text{EtNH}_2 > \text{NH}_3$. Hinsberg's 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 gas-phase amine basicity count electron-releasing alkyl groups; for $\text{CH}_3\text{I} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$, insert carbon with KCN before reducing.

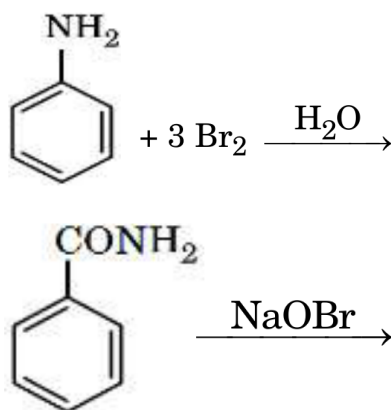
33(b). (i) Complete the following equations:



(ii) (I) Explain the carbylamine reaction.

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

[5 marks]

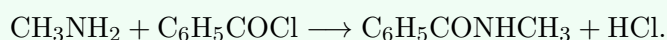


Solution:

Concept:

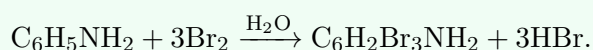
- A primary amine reacts with an acyl chloride to form an N-substituted amide. The strongly activating $-\text{NH}_2$ group directs electrophilic substitution to the ortho and para positions of aniline.
- Hofmann bromamide degradation converts a primary amide, RCONH_2 , into a primary amine, RNH_2 , with one fewer carbon atom.
- Carbylamine formation is a test for primary amines. Gabriel synthesis requires nucleophilic substitution of a halide by the phthalimide anion.

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



An N-H hydrogen is replaced by the benzoyl group, $\text{C}_6\text{H}_5\text{CO}-$. A base or excess amine removes the HCl formed, allowing acylation to proceed efficiently. The product is an amide, rather than a salt of benzoic acid.

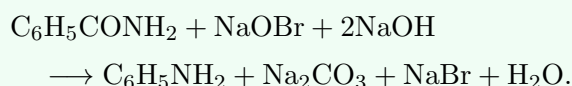
Step 2: (i)(II) Bromination of aniline Aniline reacts readily with bromine water without a Lewis acid catalyst:



The product is 2,4,6-tribromoaniline, obtained as a white precipitate. The amino group activates the ring through resonance donation, so substitution occurs at both ortho positions and the para position. Three ring hydrogen atoms are replaced by bromine atoms; the amino group is retained.

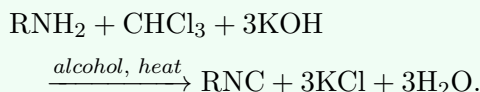
Quick Tip to Solve: Keep the carbonyl carbon during benzoylation, but remove it in Hofmann degradation; bromine water replaces all three available ortho/para hydrogens of aniline.

Step 3: (i)(III) Hofmann degradation of benzamide Sodium hypobromite converts benzamide into aniline. An overall equation in alkaline medium is



Thus the required organic product is $\text{C}_6\text{H}_5\text{NH}_2$, aniline. The carbonyl carbon is lost as carbonate in the alkaline medium; the six-carbon aromatic ring remains intact.

Step 4: (ii)(I) Explain the carbylamine reaction On heating a primary aliphatic or aromatic amine with chloroform and alcoholic potassium hydroxide, an offensive-smelling isocyanide (carbylamine) is produced:



For example, aniline produces phenyl isocyanide, $\text{C}_6\text{H}_5\text{NC}$. Secondary and tertiary amines do not give this reaction, so it distinguishes a primary amine from them.

Step 5: (ii)(II) Explain the limitation of Gabriel synthesis Gabriel synthesis begins with nucleophilic substitution of an alkyl halide by the phthalimide anion. To obtain an aromatic primary amine by the analogous route, an aryl halide would have to undergo this substitution. Ordinary aryl halides do not undergo nucleophilic substitution with the phthalimide anion under Gabriel conditions: resonance gives the aryl carbon-halogen bond partial double-bond character, and the halogen is attached to an sp^2 -hybridised carbon. Hence N-arylphthalimide is not formed by this method, and aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

Step 6: Conclusion The three organic products are N-methylbenzamide, 2,4,6-tribromoaniline and aniline, respectively. The carbylamine test gives RNC from primary amines, whereas Gabriel synthesis fails for aromatic primary amines because aryl halides do not undergo its required substitution.

Quick Tip to Solve: Keep the carbonyl carbon during benzylation, but remove it in Hofmann degradation; bromine water replaces all three available ortho/para hydrogens of aniline.