

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-7-2 - 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. 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

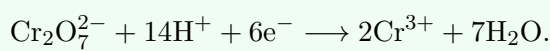
Solution:

Concept:

- One Faraday, F , is the charge carried by one mole of electrons.
- Reduction lowers oxidation number; the charge required is $Q = n_e F$, where n_e is the number of moles of electrons accepted.

Step 1: Find the change for each chromium atom If the oxidation number of chromium in $\text{Cr}_2\text{O}_7^{2-}$ is x , then $2x + 7(-2) = -2$, giving $x = +6$. Each chromium atom changes from +6 to +3 and accepts three electrons.

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



The value $3F$ counts only one chromium atom; $4F$ and $5F$ do not match the oxidation-number change.

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

Quick Tip to Solve: Multiply the oxidation-number decrease per chromium by the two chromium atoms in each dichromate ion.

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

[1 mark]

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

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

Solution:

Concept:

- The decrease in Gibbs energy equals the maximum electrical work obtainable from a reversible galvanic cell at constant temperature and pressure.
- The charge transferred per mole of cell reaction is nF , where n is the number of electrons in the balanced cell reaction and F is the Faraday constant.

Step 1: Relate electrical work to cell potential Electrical work delivered by the cell is charge multiplied by potential difference. Under standard conditions its maximum value per mole of reaction is $nF E^\circ_{\text{cell}}$. The system loses this amount of available Gibbs energy.

Step 2: Check the sign and dimensions Thus $\Delta_r G^\circ = -nF E^\circ_{\text{cell}}$. A positive standard cell potential corresponds to a negative Gibbs energy change, as required for a spontaneous standard cell reaction. Option (B) has the wrong sign, while (A) and (C) omit the Faraday constant needed to convert potential into energy per mole.

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

Quick Tip to Solve: Check that a positive galvanic cell potential gives a negative Gibbs energy change; this fixes the minus sign.

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

[1 mark]

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

Correct Answer: (C) Manganese

Solution:

Concept:

- Transition elements have variable oxidation states because the energies of their outer ns and inner $(n-1)d$ orbitals are relatively close.
- Manganese has configuration $[\text{Ar}]3d^5 4s^2$, allowing participation of several valence electrons in bonding.

Step 1: Examine the oxidation states of manganese Manganese displays the broad range

Quick Tip to Solve: For the first transition series, associate the widest oxidation-state range with manganese and its seven valence electrons.

+2, +3, +4, +5, +6, +7. Familiar examples include Mn^{2+} , MnO_2 , MnO_4^{2-} and MnO_4^- , in which manganese has oxidation states +2, +4, +6 and +7, respectively.

Step 2: Compare the other listed elements Scandium predominantly forms +3, and zinc predominantly forms +2, with a stable filled 3d subshell in Zn^{2+} . Cobalt commonly exhibits +2 and +3, and has fewer accessible oxidation states than manganese. Thus none of the other three listed elements matches manganese's range.

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 the first transition series, associate the widest oxidation-state range with manganese and its seven valence electrons.

4. 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

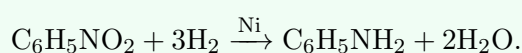
Correct Answer: (B) Reaction of Nitrobenzene with Hydrogen gas in presence of finely divided Nickel

Solution:

Concept:

- Reduction of an aromatic nitro group converts $-\text{NO}_2$ into $-\text{NH}_2$ without changing the carbon skeleton.
- Reduction of an amide or nitrile with LiAlH_4 retains its carbon atom, producing a $-\text{CH}_2\text{NH}_2$ group in these examples.

Step 1: Identify the direct synthesis of aniline Hydrogen in the presence of finely divided nickel reduces nitrobenzene to aniline:



The amino group in the product is bonded directly to the benzene ring.

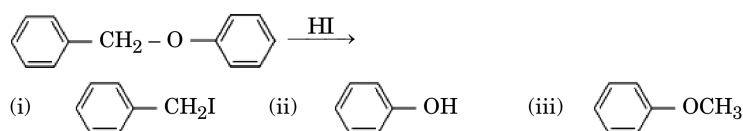
Step 2: Test the remaining reactions Chlorobenzene does not undergo ordinary ammonolysis with ethanolic ammonia because its aryl carbon-chlorine bond has partial double-bond character. Both benzamide, $\text{C}_6\text{H}_5\text{CONH}_2$, and benzonitrile, $\text{C}_6\text{H}_5\text{CN}$, give benzylamine, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$, on reduction with LiAlH_4 . Benzylamine has an intervening methylene group and is different from aniline.

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

Quick Tip to Solve: Distinguish aniline from benzylamine by checking whether nitrogen is attached directly to the ring or through a methylene group.

5. 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)

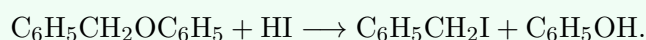
Solution:

Concept:

- Hydrogen iodide cleaves an ether after protonation of its oxygen atom, making the carbon–oxygen bond easier to break.
- In an aryl–alkyl ether, cleavage occurs on the alkyl side; the aryl carbon–oxygen bond has partial double-bond character and resists cleavage.

Step 1: Identify which bond is cleaved The given ether is benzyl phenyl ether, $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$. After oxygen is protonated, iodide replaces the phenoxy group at the benzylic carbon. The bond between oxygen and the aromatic ring remains intact, so that ring emerges as phenol.

Step 2: Match the products with the printed structures The overall reaction is



Benzyl iodide is structure (i), and phenol is structure (ii). Structure (iii) is anisole, which is not produced by this cleavage. Every alternative containing (iii) is therefore excluded.

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

Quick Tip to Solve: For an aryl–alkyl ether with HI, keep oxygen attached to the aryl ring and put iodine on the alkyl fragment.

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

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

[1 mark]

(A) Oxidation occurs at copper electrode

(B) Reduction occurs at H₂ electrode

(C) H₂ is cathode and Cu is anode

(D) H₂ is anode and Cu is cathode

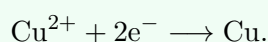
Correct Answer: (D) H₂ is anode and Cu is cathode

Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction occurs at the cathode.
- The electrode with the higher standard reduction potential acts as the cathode under standard conditions; $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

Step 1: Compare the given reduction potentials The copper electrode has $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, higher than the hydrogen electrode's 0.00 V. Copper ions therefore accept electrons at the cathode:



Step 2: Identify oxidation and check spontaneity Hydrogen is oxidised at the platinum-supported hydrogen anode:



The standard cell potential is $0.34 - 0.00 = +0.34 \text{ V}$, consistent with galvanic operation. Hence oxidation at copper, reduction at hydrogen and the reversed anode/cathode assignment in (A), (B) and (C) are incorrect.

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

Quick Tip to Solve: Compare reduction potentials first: the more positive copper value identifies the cathode immediately.

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

[1 mark]

- (A) $3^\circ > 1^\circ > 2^\circ$
- (B) $2^\circ > 1^\circ > 3^\circ$
- (C) $1^\circ > 2^\circ > 3^\circ$
- (D) $3^\circ > 2^\circ > 1^\circ$

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

Solution:

Concept:

- Lucas reagent is concentrated hydrochloric acid with anhydrous ZnCl_2 ; it converts alcohols into alkyl chlorides.
- For ordinary aliphatic alcohols, the rate follows carbocation stability: tertiary > secondary > primary.

Step 1: Relate substitution to alcohol structure Zinc chloride helps activate the hydroxyl group for substitution. Tertiary alcohols form the most stable carbocations, stabilised by the electron-releasing effect and hyperconjugation of alkyl groups. Secondary carbocations are less stable, and primary carbocation formation is strongly disfavoured.

Step 2: Compare the observed rates Tertiary alcohols give turbidity immediately at room temperature, secondary alcohols give turbidity after a short delay, and ordinary primary alcohols do not show turbidity at room temperature. Thus (A) incorrectly puts primary ahead of secondary, (B) puts tertiary last, and (C) reverses the required order.

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

Quick Tip to Solve: Match the fastest Lucas-test turbidity with the most stable carbocation: tertiary first, primary last.

8. 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:

- Colligative properties depend on the number of solute particles in a dilute solution. For a non-electrolyte, osmotic pressure is $\pi = CRT$, where C is molarity, R is the gas constant and T is absolute temperature.
- Temperature changes obey $\Delta T_b = K_b m$ and $\Delta T_f = K_f m$, where m is molality and K_b, K_f are solvent constants.

Step 1: Match pressure and temperature properties Osmotic pressure corresponds to formula ii, so a-ii. Elevation of boiling point uses the ebullioscopic constant K_b , giving b-iv. Depression of freezing point uses the cryoscopic constant K_f , giving c-i.

Step 2: Match relative vapour-pressure lowering and check the choices For a dilute solution containing a non-volatile solute, relative lowering of vapour pressure is approximately the ratio of solute moles to solvent moles:

$$\frac{P_1^\circ - P_1}{P_1^\circ} \simeq \frac{W_2/M_2}{W_1/M_1} = \frac{W_2 M_1}{M_2 W_1}.$$

Here W and M denote masses and molar masses, respectively; subscripts 1 and 2 denote solvent and solute. Thus d-iii. Options (A) and (C) mismatch osmotic pressure, while (B) assigns the freezing-point formula to boiling-point elevation.

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

Quick Tip to Solve: First pair π with CRT ; then use the subscripts b and f to match boiling and freezing.

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

[1 mark]

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

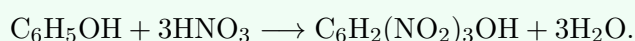
Correct Answer: (C) Picric acid

Solution:

Concept:

- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution towards the ortho and para positions.
- Concentrated nitric acid nitrates phenol at both ortho positions and the para position, producing 2,4,6-trinitrophenol.

Step 1: Apply the stated nitrating conditions Heating phenol with concentrated HNO_3 gives extensive nitration. The three ring hydrogen atoms at positions 2, 4 and 6 are replaced by nitro groups:



The product 2,4,6-trinitrophenol is commonly called picric acid.

Step 2: Check the other products Ortho-nitrophenol and para-nitrophenol are the mononitration products obtained with dilute nitric acid; neither describes the final product under the concentrated-acid conditions stated here. Sodium phenoxide requires a sodium-containing base or sodium metal, which is absent from this reaction.

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

Quick Tip to Solve: Check the nitric acid concentration: dilute acid gives mononitrophenols; concentrated acid gives picric acid.

10. 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:

- Amino acids contain an amino group, $-\text{NH}_2$, and a carboxyl group, $-\text{COOH}$.
- The usual general formula of an α -amino acid is $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, where R is the side chain.

Quick Tip to Solve: Read the name as amino plus carboxylic acid; do not count the OH inside COOH as a separate alcohol group.

Step 1: Identify the two characteristic groups The amino part of the name refers to the nitrogen-containing amino group, while the acid part refers to the carboxylic acid group. In the general structure $\text{H}_2\text{N} - \text{CH}(\text{R}) - \text{COOH}$, both are attached to the same α -carbon. The carboxyl group is treated as a single functional group, rather than as an independent alcohol group.

Step 2: Eliminate the other pairs Option (A) lacks a carboxyl group, and option (B) lacks an amino group. Option (D) contains a sulphonic acid group, $-\text{SO}_3\text{H}$, in place of the required carboxyl group. Some amino-acid side chains contain additional groups, but the characteristic pair asked for is the amino and carboxyl pair.

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

Quick Tip to Solve: Read the name as amino plus carboxylic acid; do not count the OH inside COOH as a separate alcohol group.

11. According to Alfred Werner, the secondary valence(s) of the central metal atom/ion in a complex: Identify the incorrect statement from the 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 non-ionisable.
- Secondary valences are satisfied by ligands, which may be neutral molecules or negative ions, directly coordinated to the central metal.

Step 1: Apply the distinction between the two valences Species satisfying secondary valence are within the coordination sphere. They remain directly coordinated to the central metal when the complex dissociates in solution. Thus secondary valences are non-ionisable, making statement (A) correct and statement (B) incorrect.

Step 2: Verify the remaining statements Neutral molecules such as NH_3 and negative ions such as Cl^- can satisfy secondary valence, so (C) agrees with Werner's theory. Secondary valence equals the coordination number and is normally fixed for a metal in this theory, as stated in (D). The question asks for the incorrect statement, so the true statements must be rejected as answers.

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

Quick Tip to Solve: Underline incorrect, then recall the pairing: primary valence is ionisable; secondary valence is non-ionisable.

12. 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 produces current through a spontaneous redox reaction, with cell emf E_{cell} .
- An external voltage E_{ext} applied in opposition to the cell can stop or reverse the spontaneous current.

Step 1: Compare the opposing voltages If $E_{\text{ext}} < E_{\text{cell}}$, the cell drives the spontaneous reaction and continues to act as a galvanic cell. When the opposing voltage equals the cell emf, the net driving voltage is zero and the current stops. Equality therefore does not make the cell electrolytic.

Step 2: Identify the condition for electrolysis When the opposing external voltage exceeds the cell emf, the external source drives current in the reverse direction and forces the non-spontaneous reverse reaction. Electrical energy is then converted to chemical energy, characteristic of an electrolytic cell. Thus (C) satisfies the requirement; (A) stops current, (B) permits galvanic action, and (D) alone supplies no reverse-driving voltage.

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

Quick Tip to Solve: Compare the opposing emf with the cell emf: smaller means galvanic, equal means no current, larger means electrolytic.

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

Reason (R): Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to carboxyl group. [1 mark]

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

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

Solution:

Concept:

- Friedel-Crafts alkylation and acylation are electrophilic aromatic substitution reactions that usually employ a Lewis acid catalyst such as AlCl_3 .
- The $-\text{COOH}$ group withdraws electron density from an aromatic ring and can bind to the Lewis acid catalyst through oxygen.

Step 1: Judge the assertion Aromatic carboxylic acids, such as benzoic acid, do not undergo the usual Friedel-Crafts reaction. Their benzene ring is strongly deactivated towards electrophilic substitution by the attached carboxyl group. Hence Assertion (A) is true.

Step 2: Judge the reason The carboxyl group is electron withdrawing and reduces the ring's reactivity. Its oxygen atoms also coordinate to the electron-deficient aluminium of AlCl_3 , binding the catalyst. Both statements in Reason (R) are chemically correct, so R is true.

Step 3: Check whether the reason explains the assertion Deactivation of the ring and binding of the Lewis acid catalyst are precisely why aromatic carboxylic acids fail to undergo normal Friedel-Crafts alkylation or acylation. Thus the reason directly explains the assertion, rather than merely stating a separate true fact.

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

Quick Tip to Solve: For Friedel-Crafts reactions, check both ring electron density and whether the functional group binds the Lewis acid catalyst.

14. 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:

- An ideal solution obeys Raoult's law throughout the composition range and has $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$.
- In an ideal mixture of A and B, A–B intermolecular attractions are approximately as strong as A–A and B–B attractions.

Step 1: Judge the assertion The volume change on mixing is $\Delta_{\text{mix}}V = V_{\text{solution}} - (V_A + V_B)$. For an ideal solution this change is zero, so $V_{\text{solution}} = V_A + V_B$. Assertion (A) is therefore true.

Step 2: Judge the reason The reason says that unlike solute–solvent attractions are weaker than the like attractions. This is not the condition for ideal behaviour: the strengths should be approximately equal. Weaker unlike interactions instead characterise solutions showing positive deviation from Raoult's law. Therefore Reason (R) is false.

Step 3: Select the assertion-reason code Since the assertion is true and the reason is false, the reason cannot explain volume additivity. Codes (A) and (B) require both statements to be true, while code (D) requires a false assertion. Only code (C) matches these truth values.

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

Quick Tip to Solve: For ideal solutions, remember equal attraction strengths, zero heat of mixing and zero volume change; weaker unlike forces mean non-ideal behaviour.

15. 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:

- A chelating ligand binds a metal ion through two or more donor atoms and forms rings containing the metal. Ethane-1,2-diamine, abbreviated en, is a neutral bidentate ligand.
- Complex stability depends on the metal and the nature of its ligands as well as chelation. The chelate effect does not imply that every chelated complex is more stable than every complex with monodentate ligands.

Step 1: Evaluate the assertion The printed comparison is with cyanide, CN^- , not ammonia. Cyanide forms an exceptionally stable cobalt(III) complex: the overall formation constant of $[\text{Co(CN)}_6]^{3-}$ is larger than that of $[\text{Co(en)}_3]^{3+}$. Thus the stated greater stability of the en complex is false; counting chelate rings alone cannot establish this comparison between different ligands.

Step 2: Evaluate the reason Ethane-1,2-diamine has the structure $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$. Its two nitrogen atoms donate lone pairs to the same metal centre, forming a five-membered ring. It is therefore a chelating ligand, so the reason is true.

Step 3: Check whether the reason establishes the assertion Chelation helps explain enhanced stability when otherwise comparable ligands are considered, but it cannot override the different bonding properties of cyanide in this question. A true statement about en therefore does not make the printed assertion true. Options (A), (B) and (C) all require a true assertion and are unsuitable.

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

Quick Tip to Solve: Check the comparison ligand before applying the chelate effect: cyanide is not interchangeable with ammonia in a stability comparison.

16. 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:

- Alcohols react with chlorinating agents by replacing their hydroxyl group with chlorine to form alkyl chlorides.
- Thionyl chloride, SOCl_2 , is preferred because its other products are gases and escape, leaving an alkyl chloride that is readily obtained pure.

Step 1: Evaluate the assertion For converting an alcohol to an alkyl chloride, thionyl chloride is preferred over phosphorus chlorides. Thus the assertion reverses the preferred reagent and is false.

Step 2: Evaluate the reason The reaction is



Sulphur dioxide and hydrogen chloride escape as gases. Their removal simplifies isolation of pure alkyl chloride, so the stated reason is true.

Step 3: Select the matching truth combination The reason supports using thionyl chloride, whereas the assertion prefers phosphorus halides. It therefore cannot make the assertion true. Options (A), (B) and (C) all require a true assertion and must be rejected.

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 conversion, recall that both by-products of thionyl chloride are gases; this explains its preference.

Section B (10 marks)

17. 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 solution containing a non-volatile solute, Raoult's law gives $(p^0 - p)/p^0 = x_2$, where p^0 is the pure solvent's vapour pressure, p is the solution's vapour pressure and x_2 is the solute mole fraction.
- In a dilute solution, $x_2 \simeq n_2/n_1 = (w_2/M_2)/(w_1/M_1)$. Here w , M and n denote mass, molar mass and moles; subscripts 1 and 2 refer to water and solute.

Step 1: Calculate the relative lowering The pressure lowering is $32 - 31.84 = 0.16$ mm Hg, so

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

The pressure units cancel, as required for a mole fraction. Its small value justifies the usual dilute-solution approximation.

Step 2: Substitute the masses and solve Taking the molar mass of water as 18 g mol^{-1} , the standard dilute-solution relation gives

$$0.005 = \frac{10/M_2}{200/18}.$$

Rearranging before substitution,

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

If the exact mole-fraction denominator is retained, $n_2/n_1 = x_2/(1 - x_2)$, giving $M_2 = 179.1 \text{ g mol}^{-1}$; this differs by only 0.5% from the dilute result.

Step 3: Conclusion The solute molar mass is approximately 180 g mol^{-1} using the standard dilute-solution approximation (exact Raoult-law value: 179.1 g mol^{-1}).

Quick Tip to Solve: Use the pressure lowering, 0.16 mm Hg, in the numerator; using the solution pressure itself would not give the solute mole fraction.

18. A reaction is of first order with respect to A and of second order with respect to B. How is the rate of reaction affected, when the concentration of (i) both A and B are doubled, and (ii) A is doubled and B is reduced to half? [2 marks]

Solution:

Concept:

- The order with respect to a reactant is its concentration exponent in the rate law. First order in A and second order in B therefore give $r = k[A][B]^2$.
- At constant temperature, the rate constant k is unchanged. If the concentrations of A and B change by factors f_A and f_B , the rate changes by the factor $f_A f_B^2$.

Step 1: Double both concentrations Let the initial rate be $r = k[A][B]^2$. For part (i), substitute $[A]' = 2[A]$ and $[B]' = 2[B]$:

$$r' = k(2[A])(2[B])^2 = 8k[A][B]^2.$$

The factor from A is 2, while that from B is $2^2 = 4$. Multiplying them gives $r'/r = 8$.

Step 2: Double A and halve B For part (ii), substitute $[A]'' = 2[A]$ and $[B]'' = [B]/2$:

$$r'' = k(2[A])\left(\frac{[B]}{2}\right)^2 = \frac{1}{2}k[A][B]^2.$$

Halving B contributes a factor of $1/4$, which more than offsets the factor of 2 from A. Thus $r''/r = 1/2$; these factors are compared with the original rate in both parts.

Step 3: Conclusion (i) The rate becomes $\boxed{8r}$, eight times its initial value. (ii) The rate becomes $\boxed{r/2}$, half its initial value.

Quick Tip to Solve: Square every concentration-change factor for B before multiplying by the factor for A; the second-order dependence makes halving B especially significant.

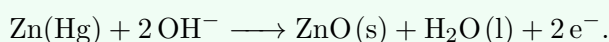
19. Write the reactions taking place at anode and cathode in a Mercury cell. [2 marks]

Solution:

Concept:

- In a mercury cell, zinc amalgam acts as the anode, mercuric oxide mixed with carbon acts as the cathode, and an alkaline paste provides the electrolyte.
- Oxidation releases electrons at the anode; reduction consumes electrons at the cathode. Half-reactions in the alkaline medium are balanced using water and hydroxide ions.

Step 1: Write the anode oxidation Zinc in the amalgam is oxidised from oxidation state 0 to +2, releasing two electrons:

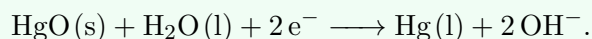


Here Zn(Hg) denotes zinc in the amalgam; mercury serves as the amalgam medium. The two hydroxide ions supply the oxygen and hydrogen needed for the oxide and water. Both sides have net

Quick Tip to Solve: Put electrons on the product side for zinc oxidation and on the reactant side for mercury(II) reduction; hydroxide ions must cancel on adding the equations.

charge -2 .

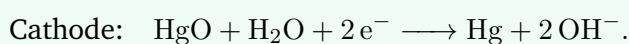
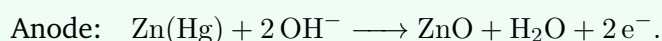
Step 2: Write the cathode reduction Mercury(II) in mercuric oxide gains the two electrons and is reduced to metallic mercury:



This half-reaction also has net charge -2 on each side. Adding the two half-reactions cancels electrons, water and hydroxide ions, giving the overall change



Step 3: Conclusion The required electrode reactions are:



Quick Tip to Solve: Put electrons on the product side for zinc oxidation and on the reactant side for mercury(II) reduction; hydroxide ions must cancel on adding the equations.

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

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

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

[2 marks]

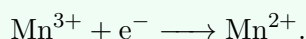
Solution:

Concept:

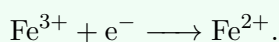
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series, due to the poor shielding by $4f$ electrons.
- A more positive standard reduction potential indicates a greater tendency for reduction. The half-filled $3d^5$ configuration has extra stability.

Step 1: (i) Compare the sizes of Zr and Hf Hf follows the lanthanoids in the periodic table. During filling of the $4f$ subshell, poor shielding increases the effective nuclear charge and contracts the atoms. Consequently, the atomic and ionic radii of Hf are nearly equal to those of Zr despite the additional shell. Their similar sizes and identical valence-shell pattern, $(n-1)d^2ns^2$, account for their closely similar chemical properties.

Step 2: (ii) Compare the electronic changes during reduction For manganese, Mn³⁺ is $3d^4$, whereas Mn²⁺ is $3d^5$:



This reduction produces the particularly stable half-filled subshell. For iron, Fe³⁺ already has $3d^5$, while Fe²⁺ has $3d^6$:



Quick Tip to Solve: Write the d-electron counts on both sides of each reduction; check whether gaining an electron creates or destroys a half-filled subshell.

Thus reduction of iron(III) removes the half-filled configuration, whereas reduction of manganese(III) produces it. Manganese(III) therefore has a greater tendency to accept an electron.

Step 3: Conclusion (i) Zr and Hf exhibit similar properties because lanthanoid contraction makes their sizes nearly equal. (ii) Formation of stable $3d^5$ Mn^{2+} makes $E^\circ(\text{Mn}^{3+}/\text{Mn}^{2+})$ more positive than $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$.

Quick Tip to Solve: Write the d-electron counts on both sides of each reduction; check whether gaining an electron creates or destroys a half-filled subshell.

OR

20(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 arise when different numbers of the outer ns and $(n - 1)d$ electrons participate in bonding.
- Colour in hydrated transition-metal ions commonly arises from absorption of visible light in transitions between crystal-field-split d orbitals; a completely filled d subshell cannot undergo such d–d transitions.

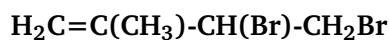
Step 1: (i) Identify the element with a single common oxidation state Scandium, Sc, has the ground-state configuration $[\text{Ar}] 3d^1 4s^2$. Loss of its two 4s electrons and one 3d electron gives Sc^{3+} , with the stable noble-gas configuration $[\text{Ar}]$. Removing another electron would disrupt this inner closed shell and require very high energy. Thus scandium exhibits the +3 oxidation state in its usual compounds and does not show variable oxidation states.

Step 2: (ii) Compare the d subshells of the copper ions Neutral copper has configuration $[\text{Ar}] 3d^{10} 4s^1$. Thus Cu^+ is $[\text{Ar}] 3d^{10}$, with all d orbitals filled, so d–d absorption is not possible and it is colourless. In contrast, Cu^{2+} is $[\text{Ar}] 3d^9$. In an aqueous complex its d orbitals split into different energy levels. Absorption of visible light promotes an electron between these levels, so the hydrated ion appears coloured.

Step 3: Conclusion (i) Scandium shows the stable +3 state, forming $[\text{Ar}]$. (ii) Cu^+ is colourless because it is $3d^{10}$, whereas $3d^9$ Cu^{2+} permits d–d transitions and is coloured.

Quick Tip to Solve: Remove the 4s electron before counting copper's d electrons: Cu^+ is d^{10} , but Cu^{2+} is d^9 .

21. (a) Write the IUPAC name of the given compound:



(b) Arrange the following compounds in decreasing order of their boiling points: 1-Chlorobutane, Isopropyl chloride, 1-Chloropropane [2 marks]

Solution:

Concept:

- Name a substituted alkene using the longest chain containing the double bond, numbered to give that double bond the lowest locant. List substituents alphabetically, ignoring multiplicative prefixes.
- For comparable haloalkanes, boiling point rises with molecular size and polarizability. Branching reduces molecular surface contact and weakens London dispersion forces.

Step 1: (a) Choose and number the parent chain The longest chain containing the double bond has four carbon atoms. Number from the terminal CH_2 end so that the double bond starts at carbon 1, giving the parent but-1-ene. The methyl group is on carbon 2, and the bromine atoms are on carbons 3 and 4. Alphabetically, bromo comes before methyl; the prefix di does not affect this order. Combining these locants gives 3,4-dibromo-2-methylbut-1-ene.

Step 2: (b) Compare molecular size and branching 1-Chlorobutane has four carbon atoms and is larger than either three-carbon chloride, so its greater polarizability gives stronger dispersion forces and the highest boiling point. 1-Chloropropane and isopropyl chloride have the same molecular formula, $\text{C}_3\text{H}_7\text{Cl}$. The straight-chain arrangement of 1-chloropropane provides greater effective intermolecular contact than the more compact isopropyl chloride, giving it the higher boiling point of the pair.

Step 3: Conclusion (a) The IUPAC name is **3,4-dibromo-2-methylbut-1-ene**. (b) The decreasing boiling-point order is



Quick Tip to Solve: Give the double bond priority over halogens when numbering the chain; for boiling points, compare carbon count first, then molecular compactness.

Section C (21 marks)

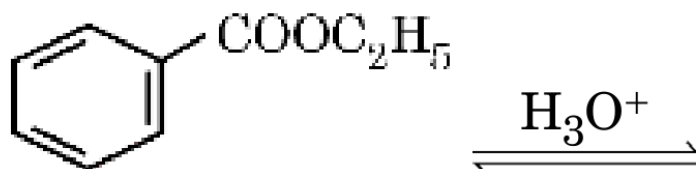
22(a). (i) Give a chemical test to distinguish between benzaldehyde and ethanal.

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

$\text{CH}_2\text{FCH}_2\text{CH}_2\text{COOH}$ or $\text{CH}_2\text{CHFCH}_2\text{COOH}$

(iii) Complete the given equation:

[3 marks]

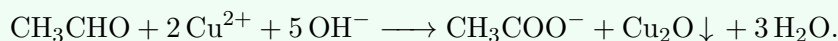


Solution:

Concept:

- Fehling's solution distinguishes an aliphatic aldehyde from benzaldehyde: the former reduces alkaline copper(II) ions to brick-red copper(I) oxide on warming.
- An electron-withdrawing group increases carboxylic-acid strength by stabilising the carboxylate ion through its negative inductive effect; this effect weakens rapidly with distance.
- Acid-catalysed ester hydrolysis produces the parent carboxylic acid and alcohol and is reversible.

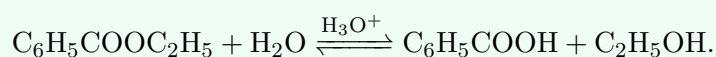
Step 1: (i) Apply Fehling's test Warm separate samples with freshly prepared Fehling's solution. Ethanal gives a brick-red precipitate of Cu_2O , while benzaldehyde gives no such precipitate. The reaction of ethanal in alkaline medium is



Ethanal is oxidised to ethanoate as copper(II) is reduced to copper(I). Tollens' reagent would not distinguish this pair, because both aldehydes give a positive silver-mirror test.

Step 2: (ii) Compare the positions of fluorine The second acid in the given pair, $\text{CH}_2\text{CHFCH}_2\text{COOH}$, is stronger. Its fluorine atom is closer to the COOH group than in $\text{CH}_2\text{FCH}_2\text{CH}_2\text{COOH}$. Fluorine withdraws electron density through sigma bonds by its strong negative inductive effect. This stabilises the negative charge of the conjugate carboxylate ion and favours loss of H^+ . Since the inductive effect decreases with distance, fluorine at the nearer position produces the greater increase in acidity.

Step 3: (iii) Hydrolyse ethyl benzoate The ester contains a benzoyl part and an ethoxy part. On hydrolysis with water in the presence of H_3O^+ , these give benzoic acid and ethanol respectively:



The acid acts as a catalyst, and the equilibrium arrow expresses the reversibility of esterification and hydrolysis. There is no change to the benzene ring.

Step 4: Conclusion (i) Ethanal gives brick-red Cu_2O with Fehling's solution; benzaldehyde does not. (ii) The second acid is stronger because fluorine is nearer to COOH . (iii) The products are benzoic

Quick Tip to Solve: Choose Fehling's test for ethanal versus benzaldehyde; compare the fluorine-to-carboxyl distance for acidity, and split an ester into its acid and alcohol parts for hydrolysis.

acid, $\text{C}_6\text{H}_5\text{COOH}$, and ethanol, $\text{C}_2\text{H}_5\text{OH}$.

Quick Tip to Solve: Choose Fehling's test for ethanal versus benzaldehyde; compare the fluorine-to-carboxyl distance for acidity, and split an ester into its acid and alcohol parts for hydrolysis.

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]

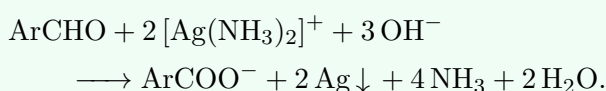
Solution:

Concept:

- A 2,4-DNP derivative indicates a carbonyl group; reduction of Tollens' reagent identifies an aldehyde in this problem.
- Aldehydes without alpha-hydrogen undergo Cannizzaro disproportionation in concentrated alkali, forming an alcohol and a carboxylate salt.
- Vigorous oxidation converts oxidisable benzene side chains into carboxyl groups. Phthalic acid has two adjacent carboxyl groups.

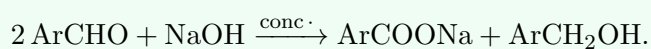
Step 1: Identify the compound The carbonyl and Tollens' tests establish an aldehyde group, $-\text{CHO}$. Cannizzaro reaction is consistent with this group attached directly to a benzene ring, whose attached carbon has no alpha-hydrogen. The formula $\text{C}_9\text{H}_{10}\text{O}$ then requires an ethyl substituent: $\text{C}_6\text{H}_4(\text{C}_2\text{H}_5)(\text{CHO})$. Vigorous oxidation converts the ethyl and aldehyde side chains to carboxyl groups. Phthalic acid places them ortho to each other. The compound is therefore **2-ethylbenzaldehyde**, $o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4\text{CHO}$.

Step 2: Write the Tollens' reaction Let Ar denote the 2-ethylphenyl group, $o\text{-C}_2\text{H}_5\text{C}_6\text{H}_4^-$. In alkaline Tollens' reagent the aldehyde is oxidised to 2-ethylbenzoate, while silver ions are reduced to a silver mirror:



The ethyl substituent is unchanged in this test.

Step 3: Write the Cannizzaro reaction Concentrated aqueous sodium hydroxide causes two aldehyde molecules to disproportionate:



One aldehyde molecule is oxidised to sodium 2-ethylbenzoate and the other is reduced to 2-ethylbenzyl alcohol, giving equimolar products.

Step 4: Conclusion The compound is **2-ethylbenzaldehyde**. It gives a silver mirror with Tollens' reagent and sodium 2-ethylbenzoate plus 2-ethylbenzyl alcohol with concentrated sodium hydroxide.

Quick Tip to Solve: Phthalic acid fixes the two side chains in an ortho arrangement; the molecular formula then fixes the extra side chain as ethyl.

23. 2 g of Na_2SO_4 is dissolved in 50 g of water to form a solution. Calculate the freezing point of this solution, assuming Na_2SO_4 undergoes complete dissociation.

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

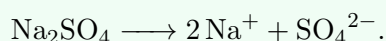
[3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the molal freezing-point depression constant and m is the molality of the dissolved solute.
- Molality is moles of solute per kilogram of solvent. Complete dissociation into three ions makes the effective particle concentration three times the formula-unit molality.

Step 1: Find the van't Hoff factor Sodium sulphate dissociates completely according to



One formula unit produces two sodium ions and one sulphate ion, giving three solute particles. Hence $i = 3$. The charge on an ion does not itself count as additional particles.

Step 2: Convert the solvent mass and calculate molality The number of moles of sodium sulphate is calculated using its given molar mass:

$$n = \frac{2 \text{ g}}{142 \text{ g mol}^{-1}} = 0.0140845 \text{ mol}.$$

Water is the solvent, so use its mass, not the total mass of the solution:

$$m_{\text{water}} = \frac{50}{1000} \text{ kg} = 0.050 \text{ kg}, \quad m = \frac{0.0140845}{0.050} = 0.281690 \text{ mol kg}^{-1}.$$

Step 3: Calculate the depression and the new freezing point Substituting the van't Hoff factor, molality and the given constant,

$$\begin{aligned}\Delta T_f &= 3 \times 1.86 \times 0.281690 \text{ K} \\ &= 1.57183 \text{ K}.\end{aligned}$$

A temperature interval of 1 K equals an interval of 1°C . Pure water freezes at 0°C , and the solute lowers this temperature:

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

Step 4: Conclusion The solution freezes at approximately -1.57°C , or 271.58 K, assuming complete dissociation of Na_2SO_4 .

Quick Tip to Solve: Count three ions for completely dissociated sodium sulphate, convert the water mass to kilograms, and subtract the positive depression from water's freezing point.

24. (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?

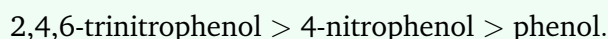
(c) Name the reagent used in the oxidation of a primary unsaturated alcohol to an aldehyde. [3 marks]

Solution:

Concept:

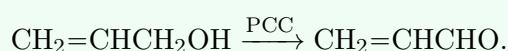
- Greater stability of the conjugate base increases acid strength. Nitro groups withdraw electron density by inductive and resonance effects and stabilise phenoxide ions when placed ortho or para to the oxygen group.
- Hydrogen bonding with water promotes the dissolution of alcohols. Selective oxidation of a primary alcohol gives an aldehyde while preserving a carbon-carbon double bond.

Step 1: Compare the stability of the phenoxide ions (a) Phenol loses a proton to form the phenoxide ion. A para nitro group withdraws electron density and allows greater stabilisation of the negative charge in the conjugate base, so 4-nitrophenol is more acidic than phenol. In 2,4,6-trinitrophenol, three nitro groups exert electron-withdrawing effects; the ortho and para groups also help stabilise the conjugate base by resonance. Its conjugate base is therefore more stable than that of 4-nitrophenol. The decreasing order of acidic strength is



Step 2: Explain the greater water solubility of alcohols (b) The polar hydroxyl group of an alcohol can form intermolecular hydrogen bonds with water. Its oxygen can accept a hydrogen bond from water, and its hydroxyl hydrogen can donate a hydrogen bond to water. These favourable alcohol-water interactions support dissolution. Hydrocarbons of comparable molecular mass are nonpolar and cannot form such hydrogen bonds with water, so their water solubility is lower. The hydrocarbon portion of an alcohol still opposes dissolution, which is why solubility decreases as the alkyl chain becomes longer.

Step 3: Choose a selective oxidising reagent (c) Use **pyridinium chlorochromate (PCC)** in an anhydrous medium, commonly dichloromethane. This mild reagent oxidises a primary unsaturated alcohol to the corresponding aldehyde without attacking its carbon-carbon double bond. For example,



Anhydrous conditions also help prevent further oxidation of the aldehyde to a carboxylic acid.

Step 4: Conclusion (a) The acidic-strength order is 2,4,6-trinitrophenol > 4-nitrophenol > phenol. (b) Alcohols form hydrogen bonds with water. (c) The required reagent is PCC.

Quick Tip to Solve: For acidity, compare conjugate-base stabilisation by nitro groups; for selective oxidation of an unsaturated primary alcohol to an aldehyde, recall PCC.

25. (a) Mention any two bases present in DNA.

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

(c) Write the name of the linkage present between amino acids. How is it represented? [3 marks]

Solution:

Concept:

- DNA contains nitrogenous bases of two classes: purines and pyrimidines. These bases carry the information in the nucleic acid.
- Starch contains amylose and amylopectin; their glucose chains differ in the presence of branching and the types of glycosidic linkages.
- A peptide bond is an amide linkage formed by condensation of the carboxyl group of one amino acid with the amino group of another.

Step 1: (a) Identify two DNA bases Two bases present in DNA are **adenine and guanine**. Both are purines. The other two DNA bases are cytosine and thymine, which are pyrimidines; any two of these four satisfy the question. Uracil is characteristic of RNA and is not one of the usual bases of DNA.

Step 2: (b) Identify the unbranched starch component The component is **amylose**. It consists of an unbranched chain of α -D-(+) glucose units connected through α -(1→4) glycosidic linkages. One characteristic feature is that **amylose is water-soluble**. In contrast, amylopectin is the branched component of starch, with additional (1→6) linkages at its branch points.

Step 3: (c) Name and represent the amino-acid linkage Amino acids are joined by a **peptide linkage**, represented as $-\text{CO}-\text{NH}-$. The carboxyl group contributes the carbonyl part and the amino group contributes the nitrogen, with elimination of one water molecule:



Thus the bond links the carbonyl carbon of one amino-acid residue to the nitrogen of the next residue.

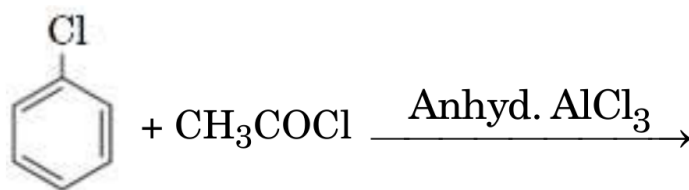
Step 4: Conclusion (a) Adenine and guanine; (b) amylose, which is water-soluble; (c) peptide linkage, $-\text{CO}-\text{NH}-$.

Quick Tip to Solve: Associate amylose with an unbranched starch chain, and locate the carbonyl carbon directly bonded to nitrogen to recognise a peptide linkage.

26. (a) When alkyl chlorides are treated with aqueous KOH, alcohol is formed, whereas when alkyl chlorides are treated with alcoholic KOH, alkenes are formed. Explain.

(b) Complete the given equation:

[3 marks]

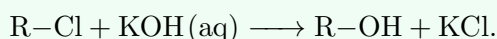


Solution:

Concept:

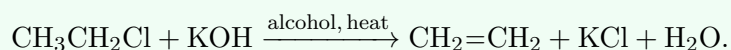
- Hydroxide ions can attack carbon as nucleophiles or remove a hydrogen as bases. Aqueous alkali favours substitution; alcoholic alkali favours elimination.
- Chlorine deactivates a benzene ring but directs electrophilic substitution to the ortho and para positions through resonance donation of a lone pair.

Step 1: (a) Explain substitution in aqueous alkali In aqueous KOH, hydroxide ions act mainly as nucleophiles. They attack the electron-deficient carbon bonded to chlorine and displace Cl^- . Replacement of chlorine by a hydroxyl group gives an alcohol:



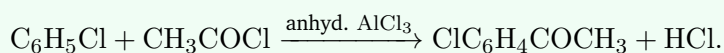
This is nucleophilic substitution, retaining the carbon skeleton.

Step 2: Explain elimination in alcoholic alkali Alcoholic KOH provides strongly basic conditions, including alkoxide ions. The base removes a β -hydrogen from a carbon adjacent to the carbon bearing chlorine. Chloride is lost and a double bond forms between these carbons. This dehydrohalogenation gives an alkene, for example:



A β -hydrogen is necessary. Thus the distinction is nucleophilic attack at carbon versus basic removal of hydrogen.

Step 3: (b) Complete the acylation reaction Acetyl chloride with anhydrous AlCl_3 supplies the acyl electrophile CH_3CO^+ . Chlorobenzene undergoes Friedel-Crafts acylation:



The ortho product is **2-chloroacetophenone**. The para product is **4-chloroacetophenone**. The less crowded para isomer is the major product. Chlorine stays on the ring; an aromatic hydrogen is replaced by an acetyl group.

Step 4: Conclusion Aqueous alkali gives alcohol by substitution; alcoholic alkali gives alkene by elimination. Acylation gives ortho- and para-chloroacetophenone, predominantly the para isomer.

Quick Tip to Solve: Check the solvent to choose substitution or elimination; in the aromatic reaction, retain chlorine and place the acetyl group ortho or para to it.

27. The electrical resistance of a column of 0.05 M KOH solution of area 0.5 cm^2 and length 50 cm is $2.5 \times 10^4 \text{ ohm}$. Calculate its molar conductivity. [3 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$, where G is measured in siemens (S) and R in ohms.
- Conductivity is $\kappa = G(l/A) = l/(RA)$, where l is the length of the solution column and A is its cross-sectional area. The ratio l/A is the cell constant.
- Molar conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1} and concentration C is in mol L^{-1} .

Step 1: Calculate the cell constant The solution column has length $l = 50 \text{ cm}$ and area $A = 0.5 \text{ cm}^2$. Hence,

$$\frac{l}{A} = \frac{50}{0.5} = 100 \text{ cm}^{-1}.$$

Using centimetres throughout gives the conductivity in S cm^{-1} , suitable for the molar-conductivity formula with concentration in molarity.

Step 2: Convert resistance into conductivity The given resistance is $R = 2.5 \times 10^4 \Omega$, so the conductance is

$$G = \frac{1}{2.5 \times 10^4} = 4.0 \times 10^{-5} \text{ S}.$$

Multiplying by the cell constant removes the effect of the column geometry:

$$\kappa = G \frac{l}{A} = (4.0 \times 10^{-5})(100) = 4.0 \times 10^{-3} \text{ S cm}^{-1}.$$

Step 3: Use the molar concentration For $C = 0.05 \text{ mol L}^{-1}$,

$$\Lambda_m = \frac{1000\kappa}{C} = \frac{1000(4.0 \times 10^{-3})}{0.05} = 80 \text{ S cm}^2 \text{ mol}^{-1}.$$

The factor 1000 converts the concentration from moles per litre to moles per cubic centimetre. No additional dissociation factor is required: the measured resistance already reflects all ions carrying current in the solution.

Step 4: Conclusion The molar conductivity of the KOH solution is $80 \text{ S cm}^2 \text{ mol}^{-1}$, equivalent to $8.0 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: With length in cm, area in square cm and concentration in molarity, combine the steps as $\Lambda_m = 1000l/(RAC)$; do not confuse conductivity with conductance.

28. (a) What are anomers? Explain.

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

(c) Name the disease caused by the deficiency of Vitamin B₁₂.

[3 marks]

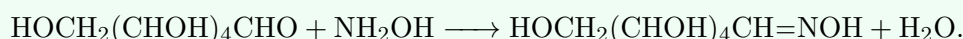
Solution:

Concept:

- Anomers are cyclic stereoisomers of a sugar which differ in configuration only at the anomeric carbon, the former carbonyl carbon.
- An aldehyde reacts with hydroxylamine, NH₂OH, to form an oxime by condensation with elimination of water.
- Vitamin B₁₂ is needed for normal red-blood-cell formation; its deficiency is associated with pernicious anaemia.

Step 1: (a) Identify the anomeric carbon When open-chain glucose cyclises, its aldehyde carbon, C-1, becomes a new stereogenic centre. The two configurations at this carbon give α -D-glucose and β -D-glucose. They are anomers because their configurations at all the other stereogenic centres are unchanged. In the usual Haworth representation of D-glucopyranose, the C-1 hydroxyl group is opposite to the CH₂OH group in the α form and on the same side in the β form.

Step 2: (b) Form the oxime of glucose Glucose reacts through the aldehyde group of its open-chain form. Hydroxylamine converts the carbonyl group into CH=NOH, producing glucose oxime and water. The reaction is



The rest of the carbon chain remains unchanged. This reaction gives evidence for a carbonyl group in the open-chain structure of glucose.

Step 3: (c) State the deficiency disease The expected deficiency disease for vitamin B₁₂ is pernicious anaemia. Thus the answer concerns impaired formation of normal red blood cells, rather than scurvy or rickets, which involve other vitamins.

Step 4: Conclusion (a) Anomers differ only at the anomeric carbon; α - and β -D-glucose are examples. (b) Glucose forms glucose oxime with hydroxylamine. (c) Vitamin B₁₂ deficiency causes pernicious anaemia.

Quick Tip to Solve: For glucose, locate C-1 when identifying anomers; replace its aldehyde C=O group by C=NOH when writing the oxime reaction.

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 gradual decrease in size across the lanthanoids because 4f electrons shield nuclear charge poorly.
- The ns and $(n-1)d$ orbitals of transition metals have comparable energies, allowing different numbers of electrons to participate in bonding.

Step 1: (i) Explain the resemblance of the second and third series Before the 5d series is reached, the 4f subshell is filled across the lanthanoids. Its poor shielding allows the increasing nuclear charge to contract the electron cloud. This lanthanoid contraction largely offsets the increase in radius expected from adding another shell. Corresponding 4d and 5d elements therefore have nearly equal atomic and ionic sizes, for example zirconium and hafnium, and show closely similar chemical properties. The increase from 3d to 4d is much larger, so the first series is less similar.

Step 2: (ii) Explain the variable oxidation states The energy difference between the outer ns and inner $(n-1)d$ electrons is small. Both can participate in bond formation, so the number of electrons involved can vary with the compound and its bonding environment. For example, iron commonly forms Fe^{2+} and Fe^{3+} . In forming these ions, the outer 4s electrons are removed before a 3d electron.

Step 3: Conclusion (i) Lanthanoid contraction makes corresponding 4d and 5d metals nearly equal in size. (ii) Comparable energies of ns and $(n-1)d$ electrons permit variable oxidation states.

Quick Tip to Solve: Connect series resemblance to lanthanoid contraction, but connect variable oxidation states to the small energy gap between s and d electrons.

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 cations.
- A d^{10} subshell is completely filled and does not satisfy this criterion.

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

Step 2: Check its usual cation Zinc loses the two outer $4s$ electrons to form Zn^{2+} , whose configuration is $[\text{Ar}] 3d^{10}$. The d subshell remains full. Being located in the d block is insufficient: both the atom and its usual ion fail the incomplete- d -subshell criterion.

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

Quick Tip to Solve: For zinc, remove the two $4s$ electrons first; the remaining $3d^{10}$ configuration immediately explains the classification.

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 required to form one mole of gaseous atoms from an element in its standard state.
- Strong metallic bonding requires a large energy input to separate the metal into individual gaseous atoms.

Step 1: Identify the electrons available for metallic bonding Transition metals generally have several unpaired d electrons as well as outer s electrons available for bonding. Participation of these electrons gives strong interatomic attraction in the metallic lattice.

Step 2: Relate bond strength to atomisation Atomisation separates the lattice into isolated gaseous atoms, so the cohesive metallic interactions must be overcome. Since those interactions are strong in most transition metals, a large amount of energy is absorbed. This accounts for their generally high standard enthalpies of atomisation.

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

Quick Tip to Solve: In an atomisation question, connect unpaired d electrons to strong metallic bonds, then to the energy needed to separate gaseous atoms.

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:

- Increasing nuclear charge tends to pull the electron cloud inward and reduce atomic radius.
- Electrons added to the inner $(n - 1)d$ subshell increase shielding and electron-electron repulsion, opposing this contraction.

Step 1: Track the changes across a transition series With increasing atomic number across a transition series, nuclear charge increases while the additional electrons mainly enter the same inner $(n - 1)d$ subshell. There is no successive addition of a new principal shell across the series.

Step 2: Combine the opposing effects The increasing attraction of the nucleus tends to decrease atomic size. Added d electrons partly shield the outer electrons and increase repulsion, counteracting this effect. The compensation is approximate: a small initial decrease occurs, followed by nearly constant radii through much of the series, rather than exactly equal radii for every element.

Step 3: Conclusion Atomic radii change only slightly because increased nuclear attraction is largely counterbalanced by the shielding and repulsion associated with added d electrons.

Quick Tip to Solve: For radius trends within a transition series, state both opposing changes: greater nuclear charge and increasing shielding by added d electrons.

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 α -carbon is directly adjacent to the carbonyl carbon.
- Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation in concentrated alkali, producing an alcohol and a carboxylate salt.

Quick Tip to Solve: Locate the carbon next to the carbonyl before counting hydrogens; the aldehydic hydrogen itself is never an alpha-hydrogen.

Step 1: Identify compounds with alpha-hydrogen Cyclohexanone has CH_2 groups on both sides of the ring carbonyl carbon, so it possesses α -hydrogens. In 2-methylpentanal, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$, the α -carbon is the $\text{CH}(\text{CH}_3)$ carbon and still carries one hydrogen. Both can form an enolate in dilute alkali and therefore undergo aldol condensation. A methyl substituent on the α -carbon does not remove its remaining hydrogen.

Step 2: Identify aldehydes without alpha-hydrogen In benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, the ring carbon bonded directly to the aldehyde group carries no hydrogen. Methanal, HCHO , has no α -carbon at all; its hydrogens are attached to the carbonyl carbon. Thus neither aldehyde has an α -hydrogen. In concentrated alkali, one molecule is oxidised while another is reduced, which is the Cannizzaro reaction.

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

Quick Tip to Solve: Locate the carbon next to the carbonyl before counting hydrogens; the aldehydic hydrogen itself is never an alpha-hydrogen.

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

Solution:

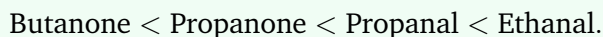
Concept:

- Nucleophilic addition is favoured by greater positive character at the carbonyl carbon and less steric hindrance around it.
- Alkyl groups donate electron density by the $+I$ effect and obstruct attack, so aldehydes are generally more reactive than ketones.

Step 1: Compare the ketones Butanone has an ethyl group and a methyl group, whereas propanone has two methyl groups. The larger ethyl group increases steric hindrance and electron donation. Butanone is therefore less reactive than propanone.

Step 2: Compare the aldehydes Propanal has an ethyl group, whereas ethanal has a smaller methyl group. Ethanal therefore offers less steric hindrance and has a more electrophilic carbonyl carbon than propanal. Each aldehyde has only one alkyl group, making both more reactive than the two ketones.

Step 3: Conclusion The increasing order is



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

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

[1 mark]

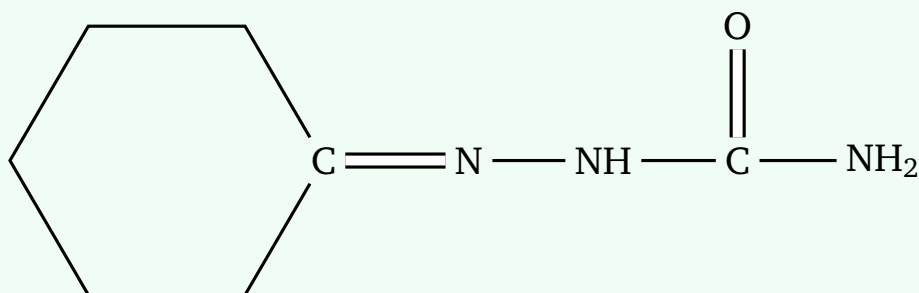
Solution:

Concept:

- Semicarbazide, $\text{H}_2\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$, condenses with a ketone through its terminal hydrazino NH_2 group.
- In a semicarbazone, the original carbonyl $\text{C}=\text{O}$ group becomes $\text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$, with elimination of water.

Step 1: Locate the reacting groups Cyclohexanone has its carbonyl carbon within the six-membered ring. Semicarbazide reacts through the terminal NH_2 group attached to nitrogen; the NH_2 group directly attached to its own carbonyl is resonance-deactivated.

Step 2: Draw the condensation product Replace the ketone oxygen by $\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$, retaining a double bond from the ring carbon to the first nitrogen. Keep all six ring carbons and the carbonyl group of semicarbazide unchanged. The five unlabelled ring vertices in the structure each represent a CH_2 group.



Structure of cyclohexanone semicarbazone

Step 3: Conclusion The required product is cyclohexanone semicarbazone, with an exocyclic $\text{C}=\text{N}-\text{NH}-\text{C}(=\text{O})-\text{NH}_2$ group at the original ketone carbon.

Quick Tip to Solve: Replace only the cyclohexanone oxygen by the semicarbazone chain; retain the second carbonyl in the reagent-derived portion.

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

[1 mark]

Solution:

Concept:

- An α -hydrogen is bonded to the carbon directly adjacent to a carbonyl group.
- Acidity increases when the conjugate base formed by removal of a proton is stabilised by electron withdrawal and resonance.

Step 1: Consider the carbonyl group's effect The carbonyl group withdraws electron density by its negative inductive effect. This facilitates removal of an α -hydrogen as a proton by a base, leaving an

Quick Tip to Solve: To explain alpha-hydrogen acidity, remove that proton and show the resulting negative charge delocalising onto oxygen.

electron pair on the adjacent carbon.

Step 2: Stabilise the resulting enolate The negative charge of the conjugate base is delocalised between the α -carbon and electronegative oxygen. For example, the enolate of ethanal has the resonance contributors



This resonance lowers the energy of the conjugate base and makes proton loss more favourable than from an ordinary alkane.

Step 3: Conclusion The α -hydrogen is acidic because the electron-withdrawing carbonyl group facilitates its removal and the resulting enolate ion is stabilised by resonance.

Quick Tip to Solve: To explain alpha-hydrogen acidity, remove that proton and show the resulting negative charge delocalising onto oxygen.

Section E (15 marks)

31(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's d -electron count. Electrons are removed from the $4s$ orbital before the $3d$ orbitals when the free transition-metal atom forms a cation.
- Strong-field ligands can cause pairing of $3d$ electrons. An octahedral inner orbital complex uses d^2sp^3 hybridisation, whereas an outer orbital complex uses sp^3d^2 hybridisation.
- Ligand-field splitting determines the energy of a $d-d$ transition: $\Delta E = h\nu$, where h is Planck's constant and ν is the absorbed frequency. Visible-light absorption produces colour; pairing by itself does not establish whether a complex is coloured.

Step 1: (i)(I) Find the iron ion configuration Each of the six CN^- or F^- ligands has charge -1 . If the oxidation state of iron is x , charge balance gives

$$x + 6(-1) = -3 \Rightarrow x = +3.$$

The electronic configuration of Fe is $[\text{Ar}] 3d^6 4s^2$. Removing two $4s$ electrons and one $3d$ electron gives Fe^{3+} with configuration $[\text{Ar}] 3d^5$. Both complexes therefore start with the same metal ion and differ because of their ligands.

Step 2: (i)(I) Compare the orbitals used in bonding In $[\text{Fe}(\text{CN})_6]^{3-}$, CN^- is a strong-field ligand. It causes pairing of the $3d$ electrons, leaving two $3d$ orbitals vacant. These two inner $3d$ orbitals, one $4s$ orbital and three $4p$ orbitals form six d^2sp^3 hybrid orbitals. Thus the octahedral complex is an inner

Quick Tip to Solve: First calculate the oxidation state and the d -electron count. Then compare ligand strength and geometry; use the energy of absorption, rather than unpaired-electron count alone, to explain colour.

orbital complex; it has one unpaired electron.

In $[\text{FeF}_6]^{3-}$, F^- is a weak-field ligand and does not cause pairing of the five $3d$ electrons. All five $3d$ orbitals remain singly occupied. The metal therefore uses one $4s$, three $4p$ and two outer $4d$ orbitals to form six sp^3d^2 hybrid orbitals. This octahedral complex is an outer orbital complex and has five unpaired electrons.

Step 3: (i)(II) Write the coordination ion and balance its charge Hexaammine specifies six neutral NH_3 ligands, and nickel(II) specifies Ni^{2+} . The coordination entity is consequently $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Two chloride counterions are needed outside the coordination brackets to give the neutral salt $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. The chloride ions balance the charge and are not included among the six coordinated ligands.

Step 4: (ii) Explain the green colour of the aqua complex Nickel has configuration $[\text{Ar}] 3d^8 4s^2$, so Ni^{2+} is $[\text{Ar}] 3d^8$. In octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, the relatively weak-field water ligands split the d orbitals into lower t_{2g} and higher e_g levels. The configuration is $t_{2g}^6 e_g^2$, with two unpaired electrons. Electronic transitions between ligand-field levels absorb selected wavelengths of visible light, and the transmitted light gives the solution its green colour.

Step 5: (ii) Explain the absence of visible colour in the cyanide complex In $[\text{Ni}(\text{CN})_4]^{2-}$, charge balance again gives nickel in the +2 state, so it is also $3d^8$. The strong-field CN^- ligands cause pairing and produce a square-planar dsp^2 complex, with all electrons paired. The orbital-energy separation for the relevant excitation is large: absorption occurs at higher energy, in the ultraviolet region, rather than in the visible region. Hence its solution is colourless. The difference in colour is explained by the ligand-dependent energy separation, not merely by whether the electrons are paired.

Step 6: Conclusion (i)(I) $[\text{Fe}(\text{CN})_6]^{3-}$ uses inner $3d$ orbitals and is $d^2 sp^3$; $[\text{FeF}_6]^{3-}$ uses outer $4d$ orbitals and is $sp^3 d^2$. (i)(II) Hexaamminenickel(II) chloride is $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$. (ii) The aqua complex absorbs visible light and appears green, whereas the strong-field, square-planar cyanide complex absorbs outside the visible region and is colourless.

Quick Tip to Solve: First calculate the oxidation state and the d -electron count. Then compare ligand strength and geometry; use the energy of absorption, rather than unpaired-electron count alone, to explain colour.

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

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

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

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

[5 marks]

Solution:

Concept:

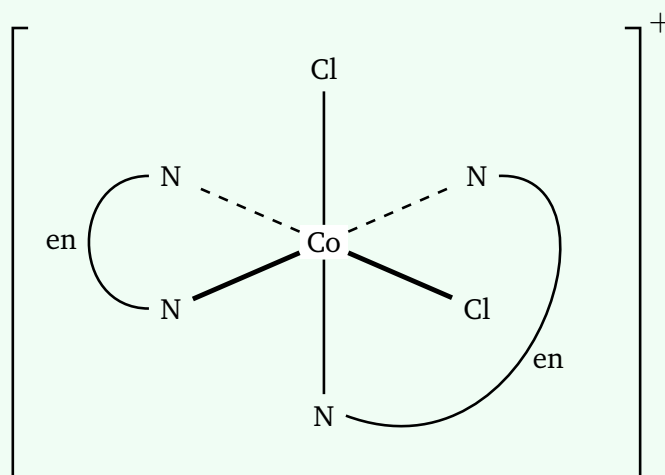
- Name the complex cation before the complex anion, irrespective of their order in the formula. Ligand names precede the metal name, and the metal oxidation state is written in Roman numerals.
- Coordination number counts donor atoms directly bonded to the metal: oxalato and ethane-1,2-diamine (en) are bidentate, while ammine and chlorido are monodentate ligands.
- The cis form of octahedral $[\text{CoCl}_2(\text{en})_2]^+$ has non-superimposable mirror images. In valence bond theory, four equivalent sp^3 orbitals give tetrahedral geometry; absence of unpaired electrons gives diamagnetism.

Step 1: (i) (I) Name the cation and anion In $[\text{Ag}(\text{NH}_3)_2]^+$, each ammine ligand is neutral, so silver has oxidation state +1. The cation is therefore diamminesilver(I). In $[\text{Ag}(\text{CN})_2]^-$, the two cyanido ligands contribute -2 , giving $x - 2 = -1$, hence $x = +1$ for silver. An anionic silver complex uses the metal name argentate, so this ion is dicyanidoargentate(I). Combining the cation and anion names gives **diamminesilver(I) dicyanidoargentate(I)**. Although the printed formula places the anionic complex first, the naming order remains cation followed by anion.

Step 2: (i) (II) Count the donor atoms In $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, each of the three oxalato ligands binds 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 each donate through one nitrogen atom and the three chlorido ligands each donate through one chlorine atom. Thus the coordination number of chromium is $3 + 3 = 6$. Count donor atoms rather than simply counting the number of ligand molecules.

Step 3: (i) (III) Draw the optically active cis isomer Put the two chlorido ligands at adjacent octahedral positions, so the Cl–Co–Cl angle is 90° . Join the remaining four nitrogen donor sites in pairs, each pair belonging to one en ligand. The diagram shows one member of the optically active cis pair. Each curved connection labelled en represents the $-\text{CH}_2-\text{CH}_2-$ bridge joining the two nitrogen donors of that ligand. Its mirror image cannot be superimposed on it by rotation. The trans isomer, with opposite chlorido ligands, is optically inactive and is not the required drawing.

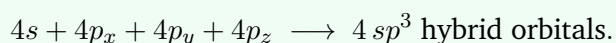
Quick Tip to Solve: Count both donor atoms of every oxalato or en ligand. For the optical-isomer drawing, first place the two chlorido ligands cis; for nickel carbonyl, use neutral nickel with the paired $3d^{10}$ bonding configuration.



cis: adjacent chlorido ligands

One optically active cis isomer; each en arc joins two nitrogen donors of one ligand.

Step 4: (ii) Apply valence bond theory to nickel tetracarbonyl Carbonyl is a neutral ligand, so nickel in $[\text{Ni}(\text{CO})_4]$ has oxidation state zero. A free nickel atom has configuration $[\text{Ar}] 3d^8 4s^2$. In the presence of the strong-field carbonyl ligands, the two $4s$ electrons enter the $3d$ subshell and all the $3d$ electrons pair, giving the bonding configuration $[\text{Ar}] 3d^{10}$, with vacant $4s$ and $4p$ orbitals.



Each vacant hybrid orbital accepts an electron pair donated by a carbon atom of a carbonyl ligand. The four equivalent metal-ligand bonds point towards the corners of a tetrahedron. Hence the complex is tetrahedral and sp^3 -hybridised. All ten metal d electrons are paired, and the donated bonding electrons are also paired. The number of unpaired electrons is therefore $n = 0$, so $\mu = \sqrt{n(n+2)} = 0$ BM and the complex is diamagnetic.

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

Quick Tip to Solve: Count both donor atoms of every oxalato or en ligand. For the optical-isomer drawing, first place the two chlorido ligands cis; for nickel carbonyl, use neutral nickel with the paired $3d^{10}$ bonding configuration.

- 32(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 availability of the nitrogen lone pair for protonation. Since $pK_b = -\log K_b$, a weaker base has a higher pK_b .
- Resonance delocalisation reduces aniline's basicity, whereas the positive inductive effect of alkyl groups increases the basicity of aliphatic amines.
- Diazotisation converts a primary aromatic amine into a diazonium salt at 273–278 K. Reduction of a nitrile converts its carbon into the terminal $-\text{CH}_2\text{NH}_2$ group.

Step 1: (i)(I) Compare the availability of the lone pair In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, the nitrogen lone pair participates in resonance with the benzene ring. It is consequently less available to accept a proton. The phenyl group also exerts a negative inductive effect. In methylamine, CH_3NH_2 , there is no such resonance delocalisation, and the methyl group's positive inductive effect increases the electron density on nitrogen. Thus methylamine is the stronger base: aniline has the smaller K_b , and therefore the higher pK_b .

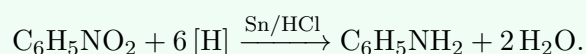
Step 2: (i)(II) Apply the gaseous-phase basicity order In the gaseous phase, differential hydration of the protonated amines does not operate. Increasing the number of electron-releasing ethyl groups increases the ability of nitrogen to accept a proton and stabilises the protonated species. Hence the decreasing order is



The order for aqueous solutions should not be substituted here because solvation can change the relative basicities.

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. With a primary amine it forms a sulphonamide containing an acidic N–H bond, which dissolves in alkali. The secondary-amine sulphonamide has no N–H bond and is insoluble in alkali. A tertiary amine does not form a sulphonamide under these test conditions.

Step 4: (ii)(I) Reduce nitrobenzene, then diazotise aniline First reduce nitrobenzene using tin and hydrochloric acid, followed by alkaline work-up to obtain free aniline:



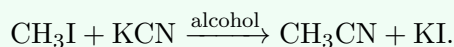
Then treat aniline with sodium nitrite and hydrochloric acid, maintaining 273–278 K:



Quick Tip to Solve: Check the phase before ordering amine basicity. To turn a one-carbon halide into a two-carbon amine, introduce CN with KCN before reduction.

Nitrous acid is generated in situ. The low temperature preserves the benzenediazonium chloride formed.

Step 5: (ii)(II) Extend the carbon chain, then reduce Treat iodomethane with alcoholic potassium cyanide. Carbon attack by cyanide produces ethanenitrile and adds one carbon atom:



Reduce ethanenitrile using lithium aluminium hydride in dry ether, followed by hydrolysis:



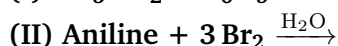
The product is ethanamine. Direct ammonolysis of iodomethane would give methylamine and would not lengthen the carbon chain.

Step 6: Conclusion Aniline is weaker and has higher pK_b ; gaseous basicity follows tertiary > secondary > primary ethylamine > ammonia. Hinsberg's reagent is $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$. The required conversion routes are nitrobenzene $\rightarrow$ aniline $\rightarrow$ benzenediazonium chloride, and iodomethane $\rightarrow$ ethanenitrile $\rightarrow$ ethanamine.

Quick Tip to Solve: Check the phase before ordering amine basicity. To turn a one-carbon halide into a two-carbon amine, introduce CN with KCN before reduction.

OR

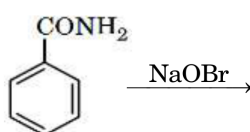
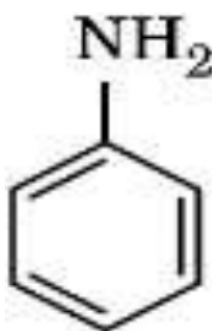
32(b). (i) Complete the following equations:



(ii) (I) Explain the carbylamine reaction.

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

[5 marks]

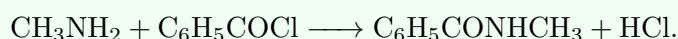


Solution:

Concept:

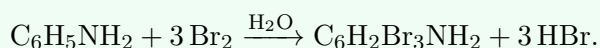
- Primary and secondary amines undergo acylation with acid chlorides. The amino group in aniline strongly activates the benzene ring at its ortho and para positions.
- Hofmann bromamide degradation changes RCONH_2 into RNH_2 , removing the carbonyl carbon. The amine therefore contains one carbon atom fewer than the amide.
- The carbylamine test is given by primary amines. Gabriel synthesis relies on nucleophilic substitution of a halide by the phthalimide anion.

Step 1: (i)(I) Complete the benzoilation reaction Methylamine attacks the carbonyl carbon of benzoyl chloride, and chloride is displaced. Replacement of one nitrogen-bound hydrogen by the benzoyl group gives the secondary amide N-methylbenzamide:



A base such as pyridine or aqueous alkali can remove the liberated hydrogen chloride and prevent protonation of unreacted amine.

Step 2: (i)(II) Brominate the activated ring In bromine water, the $-\text{NH}_2$ group directs electrophilic substitution to both ortho positions and the para position. The highly activated ring undergoes substitution at all three positions without a Lewis-acid catalyst:



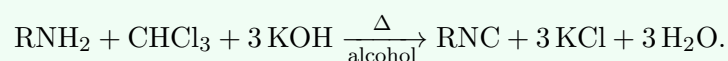
The product is **2,4,6-tribromoaniline**, obtained as a white precipitate. Each substituted ring hydrogen forms one molecule of HBr, which accounts for the coefficient three.

Step 3: (i)(III) Apply Hofmann degradation to benzamide Sodium hypobromite converts benzamide into aniline. The carbonyl carbon is removed, while the phenyl group becomes bonded directly to nitrogen. The balanced equation in alkaline medium is



Thus the organic product of the printed reaction is aniline, $\text{C}_6\text{H}_5\text{NH}_2$, rather than benzylamine. The starting amide contains seven carbons and the product contains six.

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



Here R denotes an alkyl or aryl group. For example, aniline gives phenyl isocyanide, $\text{C}_6\text{H}_5\text{NC}$. The nitrogen is bonded to R in the isocyanide $\text{R}-\text{NC}$; this differs from a nitrile $\text{R}-\text{CN}$. Secondary and tertiary amines do not give this test, so it identifies primary amines.

Step 5: (ii)(II) Explain the limitation of Gabriel synthesis Potassium phthalimide normally reacts

Quick Tip to Solve: Track the carbonyl carbon: benzoilation retains it, whereas Hofmann degradation removes it. In the carbylamine test, write RNC, not RCN.

with an alkyl halide by nucleophilic substitution to form an N-alkylphthalimide, which gives a primary amine on hydrolysis. Preparation of an aromatic primary amine by this route would require substitution on an aryl halide. Ordinary aryl halides do not undergo the required substitution with the phthalimide anion: their carbon-halogen bond has partial double-bond character through resonance, and the halogen-bearing carbon is sp^2 -hybridised, preventing the usual S_N2 displacement. Hence the necessary N-aryl intermediate is not obtained in the Gabriel method.

Step 6: Conclusion The products are N-methylbenzamide, 2,4,6-tribromoaniline and aniline. The carbylamine test identifies primary amines; Gabriel synthesis is unsuitable for aromatic primary amines.

Quick Tip to Solve: Track the carbonyl carbon: benzoylation retains it, whereas Hofmann degradation removes it. In the carbylamine test, write RNC, not RCN.

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

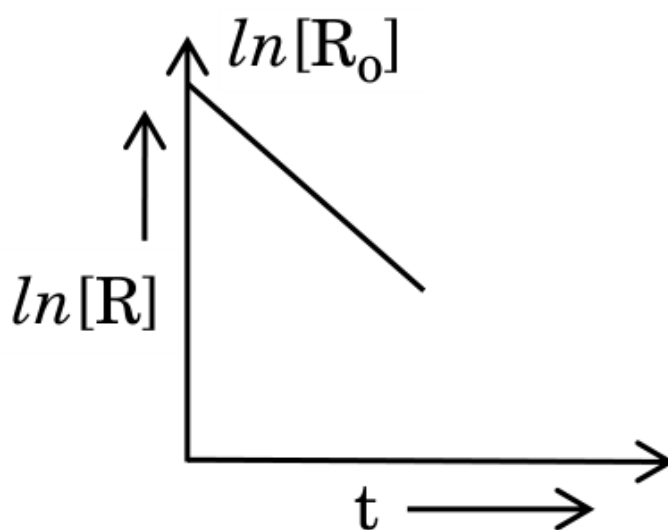
[Given: $\log 5 = 0.7$, $\log 4 = 0.6$]

(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, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$, where k is the rate constant, $[R]_0$ is the initial concentration and $[R]_t$ is the concentration remaining after time t .
- The natural-logarithm form is $\ln[R]_t = \ln[R]_0 - kt$. Comparing it with $y = c + mx$ identifies the intercept and slope of the concentration plot.

Quick Tip to Solve: Use the percentage remaining in the logarithm. Here the times are in the ratio $\log 5 : \log(5/4) = 0.7 : 0.1 = 7 : 1$, so the required time is seven times 10 minutes.

Step 1: (i) Convert completion into concentration remaining Take the initial amount as 100 units. After 10 minutes, 20 units have reacted, leaving 80 units. Thus the concentration ratio needed in the integrated rate law is $100/80 = 5/4$. The fraction reacted must not be substituted in place of the fraction remaining.

$$\log \frac{5}{4} = \log 5 - \log 4 = 0.7 - 0.6 = 0.1.$$

Step 2: Evaluate the rate constant using the supplied logarithms Substitution of the given time and the concentration ratio gives

$$k = \frac{2.303}{10} \log \frac{100}{80} = \frac{2.303}{10} (0.1) = 0.02303 \text{ min}^{-1}.$$

The unit is inverse minutes because a first order rate constant has dimensions of inverse time.

Step 3: Calculate the time for 80 percent completion At 80% completion, only 20% of the initial reactant remains. The required ratio is now $100/20 = 5$. At the same temperature the rate constant is unchanged, so

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

This is the total time measured from the start of the reaction. The result uses the approximate logarithms provided in the question; it is not obtained by scaling time in direct proportion to percentage completion.

Step 4: (ii) Identify the order and slope from the plotted variables The vertical coordinate is $\ln[R]$ and the horizontal coordinate is time. A straight line decreasing from the intercept $\ln[R]_0$ therefore follows

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

(I) This is the integrated equation of a first order reaction. (II) The coefficient of time is the slope, hence

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

The negative sign expresses the decrease of reactant concentration with time. Since the graph uses natural logarithms, its slope is $-k$; the factor 2.303 would enter a plot using common logarithms.

Step 5: Conclusion (i) Using the given logarithms, 80% completion requires 70 min from the start. (ii) (I) The reaction is first order. (II) The slope of the $\ln[R]$ versus t line is $-k$.

Quick Tip to Solve: Use the percentage remaining in the logarithm. Here the times are in the ratio $\log 5 : \log(5/4) = 0.7 : 0.1 = 7 : 1$, so the required time is seven times 10 minutes.

33(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, the time to reach concentration $[R]_t$ is $t = \frac{1}{k} \ln \frac{[R]_0}{[R]_t}$. Here k is the rate constant and $[R]_0$ is the initial reactant concentration.
- A complex reaction proceeds through two or more elementary steps. Its overall equation represents the net chemical change and does not by itself describe the mechanism.
- A pseudo first order reaction has an observed first order rate law when the concentration of another participating reactant remains effectively constant, commonly because that reactant is present in large excess.

Step 1: (i) Write the time for three-fourths completion When three-fourths of the reactant has reacted, one-fourth remains. Substitute $[R]_t = [R]_0/4$ into the integrated first order equation:

$$t_{3/4} = \frac{1}{k} \ln \frac{[R]_0}{[R]_0/4} = \frac{\ln 4}{k}.$$

The subscript 3/4 denotes the fraction consumed, not the fraction remaining.

Step 2: Obtain the half-life and divide the two times At half completion, $[R]_t = [R]_0/2$, so

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

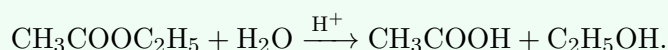
For the same reaction under the same conditions, k cancels in the ratio:

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

This also follows from successive halvings: after one half-life half remains, and after two half-lives a quarter remains. The initial concentration does not affect this ratio.

Step 3: (ii)(I) Define a complex reaction A complex reaction is one that occurs through a sequence of two or more elementary reactions instead of a single elementary step. The steps together constitute the reaction mechanism and may form intermediates that are consumed in later steps. Adding the elementary equations cancels these intermediates and gives the overall reaction. The rate law must be obtained from the mechanism or experiment; it cannot in general be inferred from the overall stoichiometric coefficients.

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



Quick Tip to Solve: Three-fourths completion means one-fourth remains: count two successive half-lives. For a pseudo first order example, always state which reactant is in excess and absorbed into k' .

At fixed acid concentration, the rate may be written as

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

Water is the solvent and is present in such a large excess that its concentration changes negligibly during the reaction. Absorb this effectively constant concentration into the observed rate constant:

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

The measured rate therefore depends only on the first power of the ester concentration, giving pseudo first order behaviour under these 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) Acid-catalysed hydrolysis of ethyl ethanoate in excess water is pseudo first order because the water concentration remains effectively constant.

Quick Tip to Solve: Three-fourths completion means one-fourth remains: count two successive half-lives. For a pseudo first order example, always state which reactant is in excess and absorbed into k' .