CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-7-2

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. Among the following outermost electronic configurations of transition metals, which one shows the highest oxidation state? [1 mark]

(A) $3d^6 4s^2$

(B) $3d^5 4s^1$

(C) $3d^5 4s^2$

(D) $3d^3 4s^2$

Correct Answer: (C) $3d^5 4s^2$

Solution:

Concept:

- Transition metals can use their outer ns and inner $(n-1)d$ electrons in bonding.
- The highest oxidation states in the first transition series rise to $+7$ for manganese, then generally decrease.

Step 1: Identify the elements The configurations $3d^6 4s^2$, $3d^5 4s^1$, $3d^5 4s^2$ and $3d^3 4s^2$ correspond to Fe, Cr, Mn and V respectively. The number of outer electrons alone must not be used blindly: iron does not show a higher oxidation state than manganese.

Step 2: Compare their highest states In the standard first-row transition-metal comparison, Fe reaches $+6$, Cr $+6$, Mn $+7$, and V $+5$. Manganese uses its two $4s$ and five $3d$ electrons in its highest state, as in MnO_4^-. Thus options (A), (B) and (D) have lower maxima.

Step 3: Conclusion $3d^5 4s^2$ shows the highest oxidation state, $+7$. Hence, the correct option is (C).

Quick Tip to Solve: Identify Mn first: its seven outer electrons allow the familiar $+7$ state in permanganate.

2. Which of the following solution in water will have the lowest freezing point? [1 mark]

(A) 1% KCl

(B) 1% glucose

(C) 1% urea

(D) 1% $CaCl_2$

Correct Answer: (D) 1% $CaCl_2$

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor and m the molality.
- For equal mass percentages with the same solvent, compare i/M, where M is solute molar mass.

Step 1: Count solute particles For dilute aqueous solutions, KCl gives two ions, calcium chloride gives three ions, while glucose and urea remain molecular: their ideal i values are 2, 3, 1 and 1 respectively.

Quick Tip to Solve: For equal mass percentages, compare i divided by molar mass; KCl and calcium chloride are very close.

Equal percentage by mass gives the same solute mass and solvent mass, but does not give equal numbers of moles.

Step 2: Compare depression quantitatively Using molar masses in $\mathrm{g\,mol^{-1}}$, the values of i/M are $2/74.5 = 0.02685$ for KCl, $1/180 = 0.00556$ for glucose, $1/60 = 0.01667$ for urea and $3/111 = 0.02703$ for calcium chloride. Calcium chloride has the largest value, slightly exceeding KCl; merely comparing the number of ions without molar masses would be insufficient.

Step 3: Conclusion 1% calcium chloride gives the greatest freezing-point depression and therefore the lowest freezing point. The correct option is (D).

Quick Tip to Solve: For equal mass percentages, compare i divided by molar mass; KCl and calcium chloride are very close.

3. Kohlrausch gave the following relation for strong electrolytes:

$\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$

Which of the following equality holds true? [1 mark]

(A) $\Lambda_m = \Lambda_m^\circ$ as $C \to 1$

(B) $\Lambda_m = \Lambda_m^\circ$ as $C \to 0$

(C) $\Lambda_m = \Lambda_m^\circ$ as $C \to \infty$

(D) $\Lambda_m = \Lambda_m^\circ$ as $C \to \sqrt{A}$

Correct Answer: (B) $\Lambda_m = \Lambda_m^\circ$ as $C \to 0$

Solution:

Concept:

- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$.
- Λ_m° is limiting molar conductivity, attained as concentration approaches zero.

Step 1: Take the dilution limit As $C \to 0$, $\sqrt{C} \to 0$, so the correction $A\sqrt{C}$ vanishes. Substitution in the given relation gives $\lim_{C\to 0} \Lambda_m = \Lambda_m^\circ$. This is the limit of infinite dilution, where interionic interactions become negligible.

Step 2: Check the other limits At $C \to 1$, the correction tends to A, not zero. At $C \to \sqrt{A}$, it also does not generally vanish. The limit $C \to \infty$ is outside the dilute-solution validity of this relation and certainly does not produce the zero-concentration intercept. Thus (A), (C) and (D) do not express limiting conductivity.

Step 3: Conclusion $\Lambda_m = \Lambda_m^\circ$ in the limit $C \to 0$. Hence, the correct option is (B).

Quick Tip to Solve: Set the concentration-dependent correction to zero to locate the limiting molar conductivity.

4. Unit of rate constant 'k' for a second order reaction is: [1 mark]

(A) s^{-1}

(B) $mol\ L^{-1}\ s^{-1}$

(C) $mol^{-1}\ L\ s^{-1}$

(D) $mol^{-2}\ L^{2}\ s^{-1}$

Correct Answer: (C) $mol^{-1}\ L\ s^{-1}$

Solution:

Concept:

- For a second-order reaction, $r = k[A]^2$, or a rate law of total concentration power two.
- Rate has units $\mathrm{mol\,L^{-1}\,s^{-1}}$, and concentration has units $\mathrm{mol\,L^{-1}}$.

Step 1: Isolate the constant From $k = r/[A]^2$, the unit of the rate constant is obtained by dividing the rate unit by the square of the concentration unit. The same dimensional result applies to $r = k[A][B]$, because its total order is also two.

Step 2: Simplify the dimensions

$$[k] = \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{\mathrm{mol^2\,L^{-2}}} = \mathrm{L\,mol^{-1}\,s^{-1}}.$$

Option (A) is the first-order unit, (B) is the zero-order unit (the rate unit), and (D) is the third-order unit. Each corresponds to a different total concentration power.

Step 3: Conclusion The second-order rate constant has unit $\mathrm{mol^{-1}\,L\,s^{-1}}$. Hence, the correct option is (C).

Quick Tip to Solve: Divide the rate unit by concentration squared; do not confuse the rate unit with the unit of k.

5. Which of the following represents the fraction of molecules with energies equal to or greater than E_a? [1 mark]

(A) $-E_a/RT$

(B) $e^{-E_a/RT}$

(C) $e^{+E_a/RT}$

(D) $+E_a/RT$

Correct Answer: (B) $e^{-E_a/RT}$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, with activation energy E_a, gas constant R, and absolute temperature T.
- The activation factor $e^{-E_a/(RT)}$ represents the fraction of molecules with sufficient energy in the textbook kinetic model.

Quick Tip to Solve: An activation fraction must lie between zero and one and increase when temperature increases.

Step 1: Identify the activation factor A molecule must have energy at least equal to the activation energy to overcome the reaction barrier. In the Arrhenius treatment, the relevant fraction is the exponential factor $e^{-E_a/(RT)}$; the prefactor A accounts for the frequency and orientation of collisions.

Step 2: Check the sign and range For positive E_a, R and T, the negative exponential lies between zero and one and increases with temperature. Option (A) is negative and cannot be a fraction. Option (C) exceeds one. Option (D) is the positive exponent magnitude, which is not a probability and need not lie below one.

Step 3: Conclusion The required fraction is $e^{-E_a/(RT)}$. Hence, the correct option is (B).

Quick Tip to Solve: An activation fraction must lie between zero and one and increase when temperature increases.

6. The number of moles of AgCl precipitated when excess $AgNO_3$ solution is mixed with one mole of $[Co(NH_3)_4Cl_2]Cl$ is: [1 mark]

(A) 1

(B) 0

(C) 2

(D) 3

Correct Answer: (A) 1

Solution:

Concept:

- Only counter-ions outside the coordination sphere ionise freely in aqueous solution.
- Free chloride reacts as $Ag^+ + Cl^- \longrightarrow AgCl(s)$, in a 1:1 mole ratio.

Step 1: Separate the coordination sphere The compound dissociates as

$$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-.$$

The two chloride ligands inside the square brackets are coordinated to cobalt; they are not released as free chloride in the standard precipitation test.

Step 2: Count the precipitated chloride One mole of the complex salt supplies one mole of free chloride, so excess silver nitrate precipitates one mole of silver chloride. Zero ignores the external chloride, two incorrectly counts the coordinated ligands, and three incorrectly treats all chlorides as ionisable counter-ions.

Step 3: Conclusion One mole of $AgCl$ is precipitated. Hence, the correct option is (A).

Quick Tip to Solve: Count chloride ions outside the square brackets, not the total chlorine atoms in the formula.

7. The synthesis of alkyl fluoride is best carried out by: [1 mark]

(A) Finkelstein reaction

(B) Swarts reaction

(C) Sandmeyer reaction

(D) Wurtz reaction

Correct Answer: (B) Swarts reaction

Solution:

Concept:

- The Swarts reaction exchanges chlorine or bromine of an alkyl halide for fluorine using a metallic fluoride.
- Reagents include AgF, SbF_3, Hg_2F_2 or CoF_2.

Step 1: Select the fluorination method Heating an alkyl chloride or bromide with a suitable metallic fluoride produces an alkyl fluoride. For example,

$$RCl + AgF \longrightarrow RF + AgCl.$$

This halogen-exchange preparation is called the Swarts reaction.

Step 2: Distinguish the alternatives The Finkelstein reaction typically prepares alkyl iodides using sodium iodide in acetone. Sandmeyer reactions replace the diazonium group of aromatic diazonium salts, rather than serving as this standard alkyl-fluoride preparation. The Wurtz reaction couples alkyl halides with sodium to make a higher alkane. Thus (A), (C) and (D) do not match the required conversion.

Step 3: Conclusion Alkyl fluoride is best prepared by the Swarts reaction. Hence, the correct option is (B).

Quick Tip to Solve: Associate Swarts with fluoride and Finkelstein with iodide when identifying halogen-exchange reactions.

8. In the reaction $R - OH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, what is the correct order of reactivity of alcohols? [1 mark]

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

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

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

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

Correct Answer: (A) $1^\circ < 2^\circ < 3^\circ$

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous $ZnCl_2$; it converts alcohols into alkyl chlorides.

Quick Tip to Solve: For Lucas reagent, rank tertiary fastest and primary slowest; then match the complete increasing order.

- For ordinary alkyl alcohols, ease of carbocation formation increases with substitution: $3^\circ > 2^\circ > 1^\circ$.

Step 1: Compare the alcohol classes $ZnCl_2$ helps activate the hydroxyl group for replacement. Tertiary alcohols form the most stable carbocations and react rapidly; secondary alcohols react more slowly. Primary alcohols react very slowly at room temperature because primary carbocations are unstable.

Step 2: Test the printed orders The complete increasing order is $1^\circ < 2^\circ < 3^\circ$. Option B incorrectly puts secondary below primary, while D reverses the order. Option C gives two inequalities but does not state the complete ordering of all three classes, unlike A.

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

Quick Tip to Solve: For Lucas reagent, rank tertiary fastest and primary slowest; then match the complete increasing order.

9. Phenol reacts with Bromine (Br_2) water to form: [1 mark]

(A) 2,4-dibromophenol

(B) 2-bromophenol

(C) 2,4,6-tribromophenol

(D) 4-bromophenol

Correct Answer: (C) 2,4,6-tribromophenol

Solution:

Concept:

- The $-OH$ group activates the benzene ring by resonance and directs electrophilic substitution to the ortho and para positions.
- Bromine water gives extensive substitution at positions 2, 4 and 6 of phenol.

Step 1: Locate the substituted positions Number the carbon bearing $-OH$ as 1. Both ortho positions, 2 and 6, and the para position, 4, are activated. In bromine water, bromination occurs at all three of these positions and a white precipitate is formed.

Step 2: Identify the product The balanced equation is

$$C_6H_5OH + 3Br_2 \longrightarrow C_6H_2Br_3OH + 3HBr.$$

The mono-brominated products in B and D and the dibrominated product in A do not describe the product with bromine water; controlled bromination in a nonpolar medium has different conditions.

Step 3: Conclusion Phenol forms 2,4,6-tribromophenol with bromine water. Hence, the correct option is (C).

Quick Tip to Solve: Bromine water with phenol means substitution at both ortho sites and the para site: remember 2,4,6.

10. When excess of alkyl iodide is treated with ammonia, the product obtained is: [1 mark]

(A) Primary amine

(B) Secondary amine

(C) Tertiary amine

(D) A mixture of amines

Correct Answer: (D) A mixture of amines

Solution:

Concept:

- Ammonolysis replaces the halogen of an alkyl halide by an amino group.
- The initially formed amine remains nucleophilic and can undergo further alkylation.

Step 1: Follow successive alkylations Ammonia first gives a primary amine, RNH_2. This primary amine can react again with alkyl iodide to form R_2NH, and the secondary amine can form R_3N. Thus reaction does not stop automatically after introducing one alkyl group.

Step 2: Account for excess alkyl iodide Excess alkyl iodide permits repeated alkylation, so the products include a mixture of primary, secondary and tertiary amines; a quaternary ammonium iodide can also arise by further alkylation. Options A, B and C each name only one amine class and omit the other products. Excess ammonia, instead, favours the primary amine.

Step 3: Conclusion A mixture of amines is obtained. Hence, the correct option is (D).

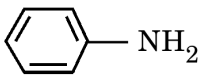
Quick Tip to Solve: Distinguish excess ammonia from excess alkyl halide: excess ammonia favours primary amine; alkyl halide allows repeated alkylation.

11. An amine 'X' reacts with Hinsberg reagent and the product obtained is insoluble in alkali. The amine 'X' is: [1 mark]

(A) $(CH_3)_2-NH$

(B) $(CH_3)_3N$

(C) $CH_3 - CH_2 - NH_2$

(D) 

Correct Answer: (A) $(CH_3)_2-NH$

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$.
- A secondary amine forms a sulphonamide with no N–H bond, so it cannot form a soluble salt with alkali.

Step 1: Use insolubility to identify the class A primary amine gives a sulphonamide retaining an N–H bond. This hydrogen is acidic due to the electron-withdrawing sulphonyl group, so the product dissolves in alkali. A secondary amine gives $C_6H_5SO_2NR_2$, which has no N–H hydrogen and remains insoluble.

Quick Tip to Solve: For Hinsberg tests, ask whether a reaction product forms first, then whether that product retains an acidic N–H bond.

Step 2: Check every candidate Dimethylamine, $(CH_3)_2NH$, is secondary and gives the stated product. Trimethylamine in B is tertiary and does not form this sulphonamide, so failure to react is distinct from an insoluble reaction product. Ethylamine in C and aniline in D are primary amines and give alkali-soluble sulphonamides.

Step 3: Conclusion The amine is dimethylamine, $(CH_3)_2NH$. Hence, the correct option is (A).

Quick Tip to Solve: For Hinsberg tests, ask whether a reaction product forms first, then whether that product retains an acidic N–H bond.

12. 'Scurvy' is caused due to the deficiency of: [1 mark]

(A) Vitamin A

(B) Vitamin B_2

(C) Vitamin C

(D) Vitamin D

Correct Answer: (C) Vitamin C

Solution:

Concept:

- Vitamin C is ascorbic acid, a water-soluble vitamin needed for healthy connective tissue.
- Deficiency diseases help distinguish vitamins: vitamin C deficiency causes scurvy.

Step 1: Connect scurvy with the missing vitamin Vitamin C supports normal collagen formation. Its deficiency causes scurvy, which may produce bleeding gums and poor wound healing because connective tissues are weakened. Therefore the disease in the question identifies ascorbic acid deficiency.

Step 2: Eliminate the other vitamins Vitamin A deficiency is associated with night blindness, vitamin B_2 deficiency with cheilosis, and vitamin D deficiency with rickets in children. These are different deficiency disorders and do not identify the cause of scurvy. Only vitamin C matches the named disease.

Step 3: Conclusion Scurvy is caused by deficiency of vitamin C. Hence, the correct option is (C).

Quick Tip to Solve: Pair scurvy with ascorbic acid (vitamin C); use night blindness and rickets to eliminate vitamins A and D.

13. Assertion (A): A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation.
Reason (R): o-nitrophenol is steam volatile due to intramolecular hydrogen bonding. [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:

- Steam distillation separates a steam-volatile substance from a substance that is much less steam volatile.
- Intramolecular hydrogen bonding reduces intermolecular association, whereas intermolecular hydrogen bonding increases association.

Step 1: Judge the assertion The assertion is true. o-Nitrophenol is steam volatile and distils with steam, whereas p-nitrophenol is much less volatile because its molecules associate through intermolecular hydrogen bonds. The two isomers can consequently be separated by steam distillation.

Step 2: Judge the reason The reason is true. In o-nitrophenol the hydroxyl and nitro groups are adjacent, allowing a hydrogen bond within the same molecule. This intramolecular bond reduces association between molecules and makes the compound sufficiently volatile to pass over with steam.

Step 3: Check the explanatory link The steam volatility explained by the reason is the property that enables o-nitrophenol to distil away from the associated p-isomer. Thus the reason directly explains the separation asserted. B wrongly denies this link, while C and D wrongly reject a true statement.

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

Quick Tip to Solve: Ortho nitrophenol hydrogen-bonds within itself; para nitrophenol associates between molecules, so ortho distils with steam.

14. Assertion (A): Cooking time is reduced in pressure cooker.

Reason (R): Boiling point of water inside the pressure cooker is lowered down. [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:

- A liquid boils when its vapour pressure equals the external pressure.
- Increasing the external pressure raises the boiling temperature of water.

Step 1: Judge the assertion The assertion is true. A pressure cooker traps steam and raises the pressure inside. Water and steam can therefore reach temperatures above the normal boiling temperature, and the higher cooking temperature reduces the time required to cook food.

Step 2: Judge the reason The reason is false. Under the increased pressure, water must be heated more strongly before its vapour pressure equals the surrounding pressure. Hence its boiling point is raised, not lowered as the printed reason states.

Step 3: Select the matching code The statements have the truth pattern: Assertion true, Reason false. The codes claiming both statements are true cannot apply, and the code making Assertion false also fails. The pressure cooker works through an increased boiling point and higher temperature.

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

Quick Tip to Solve: Use the boiling condition: higher outside pressure requires higher vapour pressure and therefore a higher boiling temperature.

15. Assertion (A): Actinoids show irregularities in their electronic configurations.

Reason (R): This is due to varying stability of f^0, f^7 and f^{14} configurations. [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:

- Actinoids involve filling of the $5f$ subshell; the $5f$, $6d$ and $7s$ orbitals have comparable energies.
- Empty, half-filled and completely filled subshells, denoted by f^0, f^7 and f^{14}, have distinctive relative stabilities.

Step 1: Judge the assertion The assertion is true. Actinoid electronic configurations do not always follow a simple, uniform addition of one electron to the $5f$ subshell. Because neighbouring subshells are close in energy, small changes in relative stability can change their electron distribution.

Step 2: Judge the reason The reason is true. The relative stability associated with f^0, f^7 and f^{14} arrangements influences which electron distribution is energetically favoured.

Step 3: Connect the reason to the assertion This stability consideration accounts for irregular electron arrangements in the actinoid series. Thus the reason explains the assertion; option (B) incorrectly denies the connection, while (C) and (D) incorrectly reject one of the true statements.

Step 4: Conclusion Both A and R are true, and R correctly explains A. Hence, the correct option is $\boxed{\text{(A)}}$.

Quick Tip to Solve: For this assertion, link configuration irregularity to the relative stability of empty, half-filled and filled f subshells.

16. Assertion (A): Maltose is a reducing sugar.

Reason (R): One of the two glucose units can open to expose free aldehydic group in solution.

[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:

- A reducing sugar possesses a free anomeric hemiacetal group that can open to a carbonyl form in solution.
- Maltose contains two glucose units joined by an $\alpha(1 \rightarrow 4)$ glycosidic linkage; only one anomeric carbon participates in the linkage.

Step 1: Judge the assertion The assertion is true: maltose is a reducing sugar. Its free reducing end can reduce reagents such as Tollens' reagent or Fehling' solution.

Step 2: Judge the reason The reason is true. The anomeric carbon of the second glucose unit retains a free hemiacetal group. That ring can open in solution to yield the corresponding open-chain form with a free aldehydic group.

Step 3: Check the explanatory relationship The available aldehydic form is precisely why maltose can act as a reducing sugar. The glycosidic bond does not lock both anomeric carbons. Option (B) therefore wrongly denies the explanation, and (C) and (D) wrongly call a true statement false.

Step 4: Conclusion Both A and R are true, and R is the correct explanation of A. Hence, the correct option is $\boxed{\text{(A)}}$.

Quick Tip to Solve: Check whether both anomeric carbons are locked: maltose retains one free anomeric carbon and is reducing.

Section B (10 marks)

17. What is meant by negative deviation from Raoult's law? Give an example. What type of azeotrope is formed by negative deviation? [2 marks]

Solution:

Concept:

- Raoult' s law for an ideal binary solution is $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$, where x is liquid mole fraction and p° is pure-component vapour pressure.

Quick Tip to Solve: Remember the inverse link: lower vapour pressure needs a higher temperature to boil, so negative deviation gives a boiling maximum.

- Stronger unlike-molecule attractions reduce escaping tendency and hence lower vapour pressure; an azeotrope boils at constant composition.

Step 1: Define negative deviation A solution shows negative deviation when its observed partial vapour pressures are lower than the values predicted by Raoult' s law at the same temperature:

$$p_A < x_A p_A^\circ, \qquad p_B < x_B p_B^\circ.$$

Consequently its total vapour pressure is lower than the ideal total. Interactions between unlike molecules are stronger than those between like molecules, so fewer molecules escape into the vapour.

Step 2: Give an example A mixture of acetone and chloroform shows negative deviation. The hydrogen of chloroform forms an attractive interaction with the oxygen of the acetone carbonyl group, strengthening the intermolecular attraction in the mixture.

Step 3: Identify the azeotrope A solution showing sufficiently large negative deviation forms a maximum-boiling azeotrope. The vapour-pressure minimum corresponds to a boiling-temperature maximum; at the azeotropic composition the vapour and liquid have the same composition.

Step 4: Conclusion Negative deviation means vapour pressure below the Raoult' s-law prediction. An example is acetone–chloroform; sufficiently large negative deviation gives a maximum-boiling azeotrope.

Quick Tip to Solve: Remember the inverse link: lower vapour pressure needs a higher temperature to boil, so negative deviation gives a boiling maximum.

18(a). Write the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. Draw the structure of geometrical isomer of this complex which is optically inactive. [2 marks]

Solution:

Concept:

- In $[Pt(en)_2Cl_2]^{2+}$, en is neutral bidentate ethane-1,2-diamine and each chlorido ligand carries charge -1.
- Two bidentate en ligands and two chlorido ligands give coordination number six and an octahedral arrangement; the trans isomer has the two chlorido ligands opposite each other.

Step 1: Determine the oxidation state and name Let the oxidation state of platinum be x. Charge balance gives

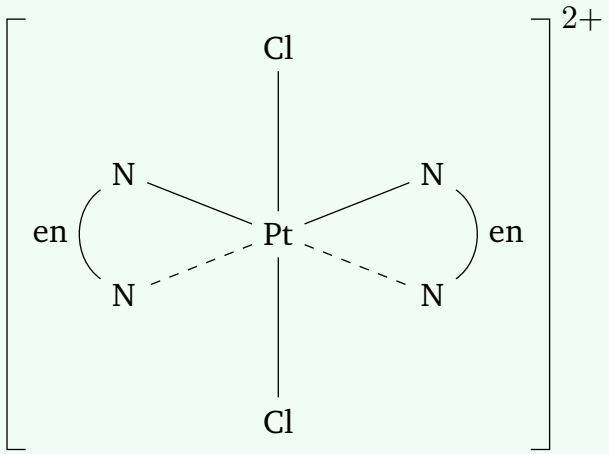
$$x + 2(0) + 2(-1) = +2 \quad \Rightarrow \quad x = +4.$$

In the name, chlorido precedes ethane-1,2-diamine alphabetically. The complex is therefore named dichloridobis(ethane-1,2-diamine)platinum(IV) ion. The prefix bis is used for the two named bidentate en ligands.

Step 2: Choose and draw the optically inactive isomer The optically inactive geometrical isomer is trans-$[Pt(en)_2Cl_2]^{2+}$. Place the two chlorido ligands at opposite axial positions. The four nitrogen donor atoms of the two en ligands occupy the equatorial positions, with each en joining two adjacent

Quick Tip to Solve: For this octahedral bis(en) complex, opposite chlorido ligands identify the achiral trans geometrical isomer.

positions. In the drawing each curved N–N connection denotes one $-CH_2CH_2-$ bridge of an en ligand.



Optically inactive trans isomer; each curved connection represents one en chelate.

Step 3: Explain optical inactivity The trans arrangement has a plane of symmetry through the equatorial donor positions, interchanging the two opposite chlorido ligands. It is therefore achiral and does not occur as a pair of non-superimposable mirror images.

Step 4: Conclusion Dichloridobis(ethane-1,2-diamine)platinum(IV) ion; the optically inactive isomer is trans.

Quick Tip to Solve: For this octahedral bis(en) complex, opposite chlorido ligands identify the achiral trans geometrical isomer.

OR

18(b). (i) Write the formula of the following coordination compound:
Pentaamminecarbonatocobalt(III)chloride
(ii) Write the IUPAC name of the linkage isomer of the complex $[Co(NH_3)_5(NO_2)]Cl_2$. [2 marks]

Solution:

Concept:

- In a coordination formula, ligands are placed inside square brackets with the metal; counter-ions are outside. Ammine is neutral and carbonato, CO_3^{2-}, has charge -2.
- Linkage isomers arise when an ambidentate ligand bonds through different donor atoms. NO_2^- can coordinate through nitrogen (nitro) or oxygen (nitrito).

Step 1: (i) Balance the charge of the coordination entity Cobalt(III) contributes $+3$, five ammine ligands contribute zero and one carbonato ligand contributes -2. Thus the complex ion has charge $+1$:

$$+3 + 5(0) - 2 = +1.$$

One chloride ion balances this charge. The required formula is therefore $[Co(NH_3)_5(CO_3)]Cl$. Chloride

Quick Tip to Solve: Determine the complex charge before adding chloride; for linkage isomerism change N-bound nitro to O-bound nitrito without changing the oxidation state.

is the counter-ion, so it must remain outside the square brackets.

Step 2: (ii) Change the donor atom of the ambidentate ligand The given nitro complex has nitrogen-bound NO_2^-. Its linkage isomer contains oxygen-bound ONO^-, giving $[Co(NH_3)_5(ONO)]Cl_2$. The two external chloride ions show that the complex ion has charge $+2$; with neutral ammines and a singly negative nitrito ligand, cobalt is in oxidation state $+3$. Its IUPAC name is pentaamminenitrito-O-cobalt(III) chloride.

Step 3: Conclusion (i) $\boxed{[Co(NH_3)_5(CO_3)]Cl}$. (ii) The linkage isomer is named pentaamminenitrito-O-cobalt(III) chloride.

Quick Tip to Solve: Determine the complex charge before adding chloride; for linkage isomerism change N-bound nitro to O-bound nitrito without changing the oxidation state.

19. State a condition under which a bimolecular reaction is kinetically first order reaction. Give an example. For which type of reactions, do order and molecularity have the same value? [2 marks]

Solution:

Concept:

- Reaction order is the sum of the concentration exponents in the experimentally determined rate law. Molecularity counts the reacting species in an elementary step.
- A reactant in large excess has an effectively constant concentration, which can be included in an observed rate constant.

Step 1: Establish the condition for pseudo-first-order kinetics For a bimolecular reaction with rate $r = k[A][B]$, take B in very large excess. Its concentration changes negligibly during the reaction, so

$$r = k[B]_0[A] = k_{obs}[A], \qquad k_{obs} = k[B]_0.$$

The measured rate is then first order in A. This is a pseudo-first-order reaction: the apparent order is one although two reactant species participate in the underlying reaction.

Step 2: Give an example and identify when order equals molecularity Acid-catalysed hydrolysis of ethyl acetate in excess water is an example, with the acid concentration held constant:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH.$$

Water acts as the solvent and is present in such large excess that its concentration is effectively constant; the observed rate is first order in the ester. Order and molecularity have the same value for an elementary, single-step reaction whose rate follows the law of mass action. This equality cannot in general be assigned to the overall equation of a complex multistep reaction.

Step 3: Conclusion A bimolecular reaction becomes kinetically first order when one reactant is in large excess, as in ester hydrolysis in excess water. Order equals molecularity for elementary reactions.

Quick Tip to Solve: Replace the nearly constant excess-reactant concentration by part of the observed rate constant to read off the apparent order.

20. Write two differences between Amylose and Amylopectin components of starch. [2 marks]

Solution:

Concept:

- Starch contains amylose and amylopectin, both polymers of α-D-glucose. Their differences arise from the arrangement of glycosidic bonds.
- An $\alpha(1 \rightarrow 4)$ bond joins carbon 1 of one glucose unit to carbon 4 of the next; an $\alpha(1 \rightarrow 6)$ bond creates a branch point.

Step 1: Difference 1: chain structure and glycosidic linkage Amylose is an unbranched polymer. Its glucose units are linked by $\alpha(1 \rightarrow 4)$ glycosidic bonds, and the chain adopts a helical shape. Amylopectin is a branched polymer: its main chains contain $\alpha(1 \rightarrow 4)$ bonds, while its branch points contain $\alpha(1 \rightarrow 6)$ bonds. Thus amylopectin has an additional type of linkage responsible for branching; amylose does not have these branch points.

Step 2: Difference 2: solubility in water Amylose is the water-soluble component of starch, whereas amylopectin is the water-insoluble component. These are the standard distinctions between the two starch fractions. Both are made from α-D-glucose, so the identity of their monomer is a similarity and must not be given as a difference.

Step 3: Conclusion Amylose is unbranched, has only $\alpha(1 \rightarrow 4)$ linkages and is water-soluble. Amylopectin is branched, has $\alpha(1 \rightarrow 4)$ chains with $\alpha(1 \rightarrow 6)$ branch linkages and is water-insoluble.

Quick Tip to Solve: Associate the extra 1-to-6 linkage in amylopectin with its branch points; both starch components have the same glucose monomer.

21. Why are haloarenes less reactive towards nucleophilic substitution reaction? How does the presence of nitro (-NO_2) group at ortho- and para-positions in haloarenes increase the reactivity towards nucleophilic substitution reaction? [2 marks]

Solution:

Concept:

- Resonance between a halogen lone pair and the aromatic ring gives the aryl carbon-halogen bond partial double-bond character.
- Electron-withdrawing groups at ortho or para positions stabilise the negatively charged intermediate formed during nucleophilic aromatic substitution.

Step 1: Explain the low reactivity of haloarenes A halogen lone pair overlaps with the aromatic π-system, producing resonance and partial double-bond character in the carbon-halogen bond. This makes the bond shorter and stronger than in a haloalkane, so its cleavage is difficult. Also, the halogen is attached to an sp^2-hybridised carbon, which holds the bonding electrons more strongly than an sp^3 carbon. An ordinary S_N1 pathway is unfavourable because a phenyl carbocation is unstable; backside attack required for an ordinary S_N2 pathway is hindered by the aromatic ring and its electron cloud.

Step 2: Explain activation by ortho and para nitro groups The $-NO_2$ group withdraws electrons through both inductive and resonance effects, making the carbon bearing halogen more susceptible

Quick Tip to Solve: For nitro-group activation, track the negative charge of the addition intermediate to the ortho and para positions, where it can enter the nitro group.

to attack by a nucleophile. Nucleophilic addition produces an anionic intermediate whose negative charge is delocalised to the ortho and para positions. A nitro group at either of these positions can accept and delocalise this charge further onto its oxygen atoms. This extra resonance stabilisation lowers the activation barrier for substitution; subsequent loss of halide restores aromaticity. A meta nitro group cannot provide the same direct resonance stabilisation of this intermediate.

Step 3: Conclusion Haloarenes resist nucleophilic substitution because their carbon-halogen bond is strengthened by resonance and attachment to an sp^2 carbon. Ortho and para nitro groups increase reactivity by stabilising the anionic substitution intermediate through resonance.

Quick Tip to Solve: For nitro-group activation, track the negative charge of the addition intermediate to the ortho and para positions, where it can enter the nitro group.

Section C (21 marks)

22. Differentiate between:

(a) Essential amino acids and Non-essential amino acids

(b) Peptide linkage and Glycosidic linkage

(c) Fibrous protein and Globular protein [3 marks]

Solution:

Concept:

- Amino acids are classified by whether the human body can synthesise them in adequate amounts; dietary necessity is the distinguishing criterion.
- A condensation linkage joins monomer units with elimination of water. Proteins contain peptide bonds, whereas many carbohydrates contain glycosidic bonds.
- Protein shape depends on the folding and arrangement of polypeptide chains and determines solubility and biological function.

Step 1: (a) Essential and non-essential amino acids Essential amino acids cannot be synthesised by the human body in sufficient amounts and must be supplied through the diet; valine and lysine are examples. Non-essential amino acids can be synthesised by the body and therefore need not necessarily be obtained through the diet; glycine and alanine are examples. Both classes are needed for normal protein synthesis: non-essential does not mean biologically unnecessary.

Step 2: (b) Peptide and glycosidic linkages A peptide linkage, $-\mathrm{CO}-\mathrm{NH}-$, forms between the carboxyl group of one amino acid and the amino group of another by loss of $\mathrm{H_2O}$; it joins amino acids in proteins. A glycosidic linkage, $\mathrm{C}-\mathrm{O}-\mathrm{C}$, joins monosaccharide units through oxygen by condensation involving an anomeric hydroxyl group. It occurs in disaccharides and polysaccharides, for example sucrose and starch.

Step 3: (c) Fibrous and globular proteins Fibrous proteins have polypeptide chains arranged in extended, thread-like structures and are generally insoluble in water. They usually perform structural functions; keratin and myosin are examples. Globular proteins have chains folded into compact, approximately spherical structures and are generally soluble in water. They commonly perform

Quick Tip to Solve: For each pair state the defining difference, then attach one familiar example to each member.

metabolic or regulatory functions; insulin and albumin are examples.

Step 4: Conclusion Essential/non-essential distinguishes dietary requirement; peptide/glycosidic distinguishes the bond and monomers joined; fibrous/globular distinguishes shape, solubility and usual function.

Quick Tip to Solve: For each pair state the defining difference, then attach one familiar example to each member.

23. Give reasons for the following:

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

(b) HCHO is more reactive than CH_3CHO towards addition of HCN.

(c) Vinyl group directly attached with carboxylic acid should decrease the acidity of corresponding carboxylic acid due to resonance, but on the contrary it increases the acidity. [3 marks]

Solution:

Concept:

- Friedel-Crafts reactions are electrophilic aromatic substitution reactions and require an aromatic ring sufficiently reactive towards an electrophile.
- Nucleophilic addition at a carbonyl group is favoured by greater positive character at the carbonyl carbon and less steric hindrance.
- Electron-withdrawing groups stabilise a carboxylate conjugate base and increase acidity; electron donation has the opposite effect.

Step 1: (a) Benzoic acid and Friedel-Crafts reaction The $-COOH$ group withdraws electron density from the benzene ring through both its negative inductive and resonance effects. The ring is consequently strongly deactivated towards electrophilic substitution and does not undergo Friedel-Crafts alkylation or acylation. In addition, the carboxyl group can coordinate with the Lewis-acid catalyst $AlCl_3$, further inhibiting the reaction.

Step 2: (b) Relative reactivity towards HCN In the addition of HCN, CN^- attacks the electrophilic carbonyl carbon. Formaldehyde, $HCHO$, has no electron-releasing alkyl group, whereas the methyl group in CH_3CHO supplies electron density through its positive inductive effect and decreases the positive character of the carbonyl carbon. Formaldehyde also has only two small hydrogen atoms attached to this carbon, so attack encounters less steric hindrance than in ethanal. Both electronic and steric factors favour HCHO.

Step 3: (c) Effect of a vinyl group on acidity A vinyl group, $CH_2{=}CH-$, conjugated with $-COOH$ can donate electron density by resonance, which by itself would decrease acidity. However, the carbon attached to the carboxyl group is sp^2-hybridised and has greater s-character and electronegativity than an sp^3-hybridised alkyl carbon. Thus the vinyl group has an electron-withdrawing negative inductive effect. This effect dominates its resonance donation, stabilising the carboxylate ion and increasing acidity relative to the corresponding saturated alkyl carboxylic acid.

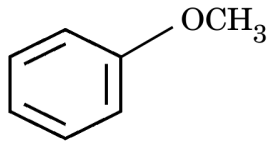
Step 4: Conclusion Benzoic acid is too deactivated for Friedel-Crafts reaction; HCHO is more electrophilic and less hindered than ethanal; the dominant negative inductive effect of vinyl accounts

Quick Tip to Solve: For vinyl substitution compare the competing resonance and inductive effects, and explicitly identify which effect dominates.

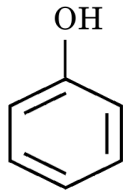
for its acidity-increasing effect.

Quick Tip to Solve: For vinyl substitution compare the competing resonance and inductive effects, and explicitly identify which effect dominates.

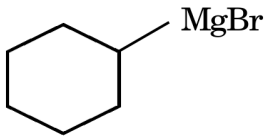
24. Write structure of the products of the following reactions: [3 marks]

(a) 

$+ HI \longrightarrow$

(b) 

$+$ conc. $HNO_3 \longrightarrow$

(c) 

$+ HCHO \xrightarrow{H^+/H_2O}$

Solution:

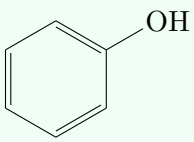
Concept:

- Hydrogen iodide cleaves an aryl alkyl ether at the alkyl–oxygen bond because iodide can attack the alkyl carbon by substitution.
- The phenolic hydroxyl group strongly activates the aromatic ring and directs nitration to the ortho and para positions.
- A Grignard reagent $RMgBr$ adds R to formaldehyde; acid hydrolysis gives the primary alcohol RCH_2OH.

Step 1: (a) Cleavage of anisole by HI Protonation of the ether oxygen is followed by attack of I^- at the methyl carbon. The methyl–oxygen bond breaks; the aryl–oxygen bond is retained because substitution at the aromatic sp^2 carbon is not an ordinary S_N2 process.

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I$$

The products are phenol and iodomethane. The phenol structure is

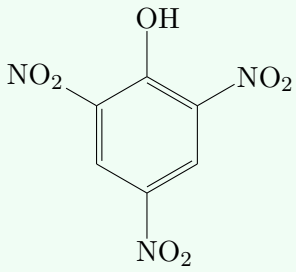


$CH_3 - I$.

Step 2: (b) Nitration of phenol with concentrated nitric acid Concentrated HNO_3 causes substitution

Quick Tip to Solve: With formaldehyde, insert one CH2 between the Grignard carbon group and OH; do not place OH directly on the ring.

at both ortho positions and the para position relative to $-OH$, yielding 2,4,6-trinitrophenol (picric acid). Its structure has the hydroxyl group at carbon 1 and nitro groups at carbons 2, 4 and 6:

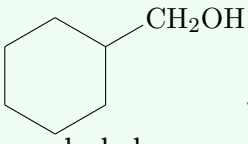


$$C_6H_5OH + 3HNO_3 \longrightarrow C_6H_2(NO_2)_3OH + 3H_2O.$$

Step 3: (c) Addition to formaldehyde followed by hydrolysis The cyclohexyl group bonds to the carbonyl carbon of formaldehyde, giving the magnesium alkoxide $C_6H_{11}CH_2OMgBr$. Acidic hydrolysis protonates its oxygen to form cyclohexylmethanol:

$$C_6H_{11}MgBr + HCHO \longrightarrow C_6H_{11}CH_2OMgBr$$

$$C_6H_{11}CH_2OMgBr \xrightarrow{H^+/H_2O} C_6H_{11}CH_2OH.$$

The product structure is 

. The extra carbon supplied by HCHO lies outside the ring, so the product is a primary alcohol.

Step 4: Conclusion (a) Phenol and CH_3I; (b) 2,4,6-trinitrophenol (picric acid); (c) cyclohexylmethanol, $C_6H_{11}CH_2OH$.

Quick Tip to Solve: With formaldehyde, insert one CH2 between the Grignard carbon group and OH; do not place OH directly on the ring.

25. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume:

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

Calculate rate constant.

[Given: log 2 = 0.3010, log 10 = 1] [3 marks]

S.No.	Time/s	Total Pressure/atm
1	0	0·5
2	100	0·625

Solution:

Concept:

- At constant temperature and volume, the partial pressure of a gas is proportional to its amount. The first-order law therefore uses the partial pressure of the reactant, not the total pressure of the mixture.
- For $2N_2O_5 \rightarrow 2N_2O_4 + O_2$, decomposition of reactant corresponding to pressure x produces N_2O_4 at pressure x and oxygen at pressure $x/2$.
- The integrated first-order equation is $k = (2.303/t)\log_{10}(p_0/p_A)$, where p_0 and p_A are the initial and remaining reactant pressures.

Step 1: Obtain the remaining reactant pressure Initially only N_2O_5 is present, so $p_0 = 0.500$ atm. Let x atm of this reactant decompose in 100 s. The total pressure is the sum of all three partial pressures:

$$P_t = (p_0 - x) + x + \frac{x}{2} = p_0 + \frac{x}{2}.$$

Thus $x = 2(0.625 - 0.500) = 0.250$ atm, and the reactant partial pressure is $p_A = 0.500 - 0.250 = 0.250$ atm. The rise in total pressure arises from the additional oxygen; it does not mean that reactant concentration has increased.

Step 2: Apply the first-order integrated law Substituting the reactant pressures and elapsed time gives

$$\begin{aligned} k &= \frac{2.303}{100}\log_{10}\left(\frac{0.500}{0.250}\right) \\ &= \frac{2.303}{100}\log_{10} 2 \\ &= \frac{2.303 \times 0.3010}{100} = 0.00693203\ \text{s}^{-1}. \end{aligned}$$

The reactant pressure has halved in 100 s, consistent with $t_{1/2} = 0.693/k$. Pressure units cancel in the ratio, leaving inverse time as the unit of the rate constant.

Step 3: Conclusion The rate constant is $\boxed{k = 6.93 \times 10^{-3}\ \text{s}^{-1}}$.

Quick Tip to Solve: First convert total pressure into reactant partial pressure using stoichiometry; here $p_A = 3p_0 - 2P_t$.

26. A compound (A) with molecular formula C_4H_9I which is a primary alkyl halide, reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HI to give (C) which is an isomer of (A). When (A) reacts with Na metal in the presence of dry ether, it gives a compound (D), C_8H_{18}, which is different from the compound formed when n-butyl iodide reacts with sodium. Write the structures of (A), (B), (C) and (D). Write the chemical equation when compound (A) is reacted with alcoholic KOH. [3 marks]

Solution:

Concept:

- A primary alkyl iodide has iodine on a carbon attached to only one other carbon. The two primary iodides of formula C_4H_9I are n-butyl iodide and isobutyl iodide.
- Alcoholic KOH causes elimination of HI from adjacent carbon atoms. HI then adds to the resulting unsymmetrical alkene by Markovnikov's rule, with iodine on the more substituted carbon.
- In the Wurtz reaction, $2R - I + 2Na \rightarrow R - R + 2NaI$ in dry ether; coupling preserves the carbon skeleton of each alkyl group.

Step 1: Identify the starting primary iodide n-Butyl iodide would give n-octane by Wurtz coupling. Since the question explicitly says that (D) differs from this product, (A) must be the other primary isomer, isobutyl iodide (1-iodo-2-methylpropane):

$$(A): \quad CH_3 - CH(CH_3) - CH_2I.$$

The iodine-bearing CH_2 carbon is attached to one carbon, confirming that (A) is primary.

Step 2: Eliminate HI and identify the addition product Alcoholic KOH removes iodine from the terminal carbon and a hydrogen from the adjacent carbon:

$$(CH_3)_2CHCH_2I + KOH \xrightarrow[\Delta]{\text{alcoholic}} CH_2 = C(CH_3)_2 + KI + H_2O.$$

Hence (B) is 2-methylpropene. Addition of HI follows Markovnikov's rule: hydrogen adds to the terminal CH_2 carbon, giving the more stable tertiary carbocation, and iodide attaches to the central carbon:

$$CH_2 = C(CH_3)_2 + HI \longrightarrow (CH_3)_3CI.$$

Thus (C) is 2-iodo-2-methylpropane, an isomer of (A) with the same formula C_4H_9I.

Step 3: Couple two isobutyl groups Sodium in dry ether joins the two carbons that originally bore iodine:

$$2(CH_3)_2CHCH_2I + 2Na \xrightarrow{\text{dry ether}} (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2NaI.$$

The product (D) is 2,5-dimethylhexane, C_8H_{18}. Its branched skeleton explains why it differs from n-octane formed from n-butyl iodide.

Step 4: Conclusion (A) is isobutyl iodide, $(CH_3)_2CHCH_2I$; (B) is 2-methylpropene, $CH_2 = C(CH_3)_2$; (C) is tert-butyl iodide, $(CH_3)_3CI$; and (D) is 2,5-dimethylhexane, $(CH_3)_2CHCH_2CH_2CH(CH_3)_2$. The alcoholic-KOH equation is given in the elimination step.

Quick Tip to Solve: Use the Wurtz product first: a product different from n-octane rules out n-butyl iodide and fixes the branched primary isomer.

27(a). Write the name of the cell which is generally used in inverters. Write the reactions taking place at anode and cathode of this cell, when it is in use. [3 marks]

Solution:

Concept:

- A lead storage battery (lead-acid accumulator) is a rechargeable secondary battery commonly used in inverters. Its electrodes are lead and lead dioxide, and its electrolyte is aqueous sulphuric acid.
- When the battery supplies electrical energy, it discharges as a galvanic cell: oxidation occurs at the negative anode and reduction at the positive cathode.
- During discharge both electrodes form lead sulphate, while sulphuric acid is consumed and water is produced. Recharging reverses the discharge reactions.

Step 1: Name the cell and identify its electrodes The cell is the lead storage cell, also called the lead-acid cell. In use, the lead plate is the anode and the lead-dioxide-coated plate is the cathode. The sulphuric acid electrolyte supplies H^+ and SO_4^{2-} ions required for the electrode reactions. The reactions requested are those during discharge, because the inverter is drawing energy from the battery.

Step 2: Write the anode oxidation reaction Lead is oxidised from oxidation state zero to $+2$, releasing two electrons. It combines with sulphate ions to form lead sulphate:

$$Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-.$$

The two negative charges on the left balance the two electrons on the right. These electrons pass through the external circuit and provide current to the inverter.

Step 3: Write the cathode reduction reaction Lead in PbO_2 is reduced from $+4$ to $+2$, accepting the two electrons supplied by the anode:

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

Hydrogen ions convert the oxide oxygen into water. Adding the two half-reactions cancels the electrons and gives

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

Step 4: Conclusion The inverter uses a $\boxed{\text{lead storage (lead-acid) cell}}$. During discharge, Pb is oxidised at the anode and PbO_2 is reduced at the cathode, with $PbSO_4$ forming at both electrodes as shown above.

Quick Tip to Solve: Remember that both lead-acid electrodes become $PbSO_4$ on discharge; put electrons on the right at the anode and on the left at the cathode.

OR

27(b). Explain why electrolysis of an aqueous solution of NaCl gives H_2 gas at cathode and Cl_2 gas at anode? Write overall reaction.

(Given: $E^\circ_{Na^+/Na}$ = -2.71 V, $E^\circ_{H_2O/H_2}$ = -0.83 V, $E^\circ_{Cl_2/2Cl^-}$ = +1.36 V, $E^\circ_{H^+/O_2/H_2O}$ = +1.23 V) [3 marks]

Solution:

Concept:

- At the cathode reduction occurs. The species with the more positive reduction potential is preferentially reduced.
- At the anode oxidation occurs. Actual product selection depends on electrode potentials as well as the overpotential required for gas evolution.

Step 1: Identify the cathode product The competing reductions in aqueous sodium chloride are

$$\begin{aligned} \mathrm{Na^+} + e^- &\longrightarrow \mathrm{Na}, & E^\circ &= -2.71\,\mathrm{V}, \\ 2\mathrm{H_2O} + 2e^- &\longrightarrow \mathrm{H_2} + 2\mathrm{OH^-}, & E^\circ &= -0.83\,\mathrm{V}. \end{aligned}$$

Since $-0.83\,\mathrm{V}$ is more positive than $-2.71\,\mathrm{V}$, reduction of water is easier than reduction of sodium ions. Thus hydrogen gas is liberated at the cathode, while sodium ions remain in solution.

Step 2: Explain the anode product The competing oxidation processes are

$$\begin{aligned} 2\mathrm{Cl^-} &\longrightarrow \mathrm{Cl_2} + 2e^-, \\ 2\mathrm{H_2O} &\longrightarrow \mathrm{O_2} + 4\mathrm{H^+} + 4e^-. \end{aligned}$$

The given reduction potentials, $+1.36\,\mathrm{V}$ for chlorine and $+1.23\,\mathrm{V}$ for oxygen, suggest water oxidation would be thermodynamically easier. However, oxygen evolution requires a significant overpotential. Because of this kinetic barrier, chloride ions are oxidised preferentially in the aqueous NaCl electrolysis described, and chlorine gas is evolved at the anode.

Step 3: Combine the half-reactions Adding the cathode and chloride-oxidation half-reactions cancels two electrons:

$$2\mathrm{Cl^-} + 2\mathrm{H_2O} \longrightarrow \mathrm{Cl_2} + \mathrm{H_2} + 2\mathrm{OH^-}.$$

Including the spectator sodium ions gives the molecular equation. Sodium hydroxide is formed in the solution; both gases are released at their respective electrodes.

Step 4: Conclusion H_2 forms at the cathode and Cl_2 at the anode. Overall:

$$2\mathrm{NaCl(aq)} + 2\mathrm{H_2O(l)} \longrightarrow 2\mathrm{NaOH(aq)} + \mathrm{H_2(g)} + \mathrm{Cl_2(g)}.$$

Quick Tip to Solve: Compare reduction potentials at the cathode, but include oxygen overpotential when explaining the anode product.

28. 0.3 g of acetic acid (Molar mass = 60 g mol^{-1}) dissolved in 30 g of benzene shows a depression in freezing point equal to 0.45°C. Calculate the percentage association of acid if it forms a dimer in the solution.

(Given: K_f for benzene = 5.12 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f is the molal depression constant and m is the initial molality.
- For dimerisation $2A \rightleftharpoons A_2$, the degree of association α satisfies $i = 1 - \alpha/2$. Association reduces the number of solute particles.

Step 1: Calculate the initial molality The amount of acetic acid is

$$n = \frac{0.3\,\text{g}}{60\,\text{g mol}^{-1}} = 0.005\,\text{mol}.$$

The solvent mass is $30\,\text{g} = 0.030\,\text{kg}$, so the molality calculated before association is

$$m = \frac{0.005}{0.030} = \frac{1}{6}\,\text{mol kg}^{-1}.$$

The mass in the denominator is that of benzene, not the total solution. If no association occurred, the predicted depression would be $5.12/6 = 0.8533\,\text{K}$.

Step 2: Find the particle-number factor A temperature difference of 0.45°C is numerically $0.45\,\text{K}$. Therefore

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.45}{5.12 \times (1/6)} = \frac{2.70}{5.12} = 0.52734375.$$

This value is less than unity, as expected when two acid molecules join to form one dimer in benzene.

Step 3: Relate the factor to association Start with one mole of acid molecules. If the fraction associated is α, the unassociated amount is $1 - \alpha$ mole and the dimer amount is $\alpha/2$ mole. The total amount of solute particles is thus $1 - \alpha/2$ mole. Hence

$$i = 1 - \frac{\alpha}{2},$$
$$\alpha = 2(1 - 0.52734375) = 0.9453125.$$

Multiplying this fraction by 100 converts it into the percentage of acid molecules participating in dimer formation.

Step 4: Conclusion The percentage association of acetic acid is $0.9453125 \times 100 = \boxed{94.53\%}$ (approximately).

Quick Tip to Solve: For a dimer, use $\alpha = 2(1 - i)$; calculate molality with the solvent mass expressed in kilograms.

Section D (8 marks)

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

29(a). Amines are usually formed from amides, imides, halides, nitro compounds, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. Amines being basic in nature, react with acids to form salts. Aryldiazonium salts, undergo replacement of the diazonium group with a variety of nucleophiles to produce aryl halides, cyanides, phenols and arenes.

Answer the following questions:

How can you convert the following?

(i) Ethanoic acid to methanamine

(ii) Propanenitrile to 1-aminopropane [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine with one carbon atom fewer, using Br_2 and aqueous $NaOH$.
- Reduction of a nitrile with $LiAlH_4$ followed by hydrolysis retains the nitrile carbon and converts $-C \equiv N$ into $-CH_2NH_2$.

Step 1: Convert ethanoic acid to methanamine First react ethanoic acid with ammonia to form ammonium ethanoate, then heat to obtain ethanamide:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Treat the ethanamide with bromine and aqueous sodium hydroxide:

$$CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is removed in the Hofmann reaction, giving the required one-carbon amine.

Step 2: Convert propanenitrile to 1-aminopropane Reduce propanenitrile with lithium aluminium hydride in dry ether and then carry out aqueous work-up:

$$CH_3CH_2C \equiv N \xrightarrow[2.\ H_2O]{1.\ LiAlH_4,\ \text{dry ether}} CH_3CH_2CH_2NH_2.$$

Here the nitrile carbon becomes the terminal CH_2 group, so all three carbon atoms are retained. The product is propan-1-amine, also called 1-aminopropane.

Step 3: Conclusion (i) CH_3COOH is converted through ethanamide to CH_3NH_2. (ii) Reduction of CH_3CH_2CN gives $CH_3CH_2CH_2NH_2$.

Quick Tip to Solve: Count carbons first: use Hofmann degradation to remove one carbon, and nitrile reduction to retain every carbon.

29(b). Why is pK_b value of aniline more than that of methylamine? [1 mark]

Solution:

Concept:

- $pK_b = -\log K_b$: a weaker base has a smaller K_b and therefore a larger pK_b.
- Basicity depends on the availability of the nitrogen lone pair for accepting a proton.

Step 1: Compare lone-pair availability In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available to accept H^+. In methylamine, the methyl group exerts a positive inductive effect, increasing electron density on nitrogen and making the lone pair more available for protonation.

Step 2: Translate basicity into pKb Aniline is consequently a weaker base than methylamine, so $K_b(\text{aniline}) < K_b(\text{methylamine})$. The negative logarithm reverses this order: a smaller base-dissociation constant corresponds to a larger pK_b.

Step 3: Conclusion Aniline has a larger pK_b because resonance lowers its basicity, whereas the methyl group increases the basicity of methylamine by its $+I$ effect.

Quick Tip to Solve: Remember the reversed order: stronger base means larger K_b but smaller pK_b.

29(c). Arrange the following in increasing order of their basic strength in aqueous solution: CH_3-NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- Basic strength measures the tendency of nitrogen to accept a proton through its lone pair.
- In aqueous solution, the electron-releasing effect of methyl groups and hydration of the conjugate acid both determine basicity.

Step 1: Compare the electronic effect Methyl groups show the positive inductive effect and increase electron density on nitrogen. This favours proton acceptance. However, ranking the amines using only this effect would give the gas-phase trend and ignores the aqueous medium specified here.

Step 2: Include hydration in water The protonated primary and secondary amines are effectively stabilised by hydrogen bonding with water. The bulky tertiary ammonium ion is less effectively hydrated. For these methylamines, dimethylamine has the best balance of electron donation and hydration; trimethylamine is weaker than methylamine in water.

Step 3: Conclusion The increasing order of basic strength in aqueous solution is

$$\boxed{(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH.}$$

Quick Tip to Solve: For methylamines in water, remember the order tertiary < primary < secondary; account for hydration as well as the inductive effect.

OR

29(c). Give the structures of A and B in the following reaction:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{HNO_2} B$$

[1 mark]

Solution:

Concept:

- Iron and hydrochloric acid reduce an aromatic nitro group, $-NO_2$, to an amino group, $-NH_2$.
- A primary aromatic amine reacts with nitrous acid at 273–278 K to form an arenediazonium salt (diazotisation).

Step 1: Identify the reduction product A The benzene ring is retained while the nitro group is reduced. Hence A is aniline, whose condensed structure is $C_6H_5 - NH_2$.

$$C_6H_5NO_2 + 6[H] \longrightarrow C_6H_5NH_2 + 2H_2O.$$

Step 2: Identify the diazotisation product B At the specified low temperature, aniline undergoes diazotisation rather than conversion to phenol. The product has the diazonium group $-N \equiv N^+$ attached to the benzene ring. In the hydrochloric-acid medium, the counter-ion is chloride.

$$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow [C_6H_5N_2]^+Cl^- + 2H_2O.$$

Step 3: Conclusion $\boxed{A = C_6H_5 - NH_2}$ (aniline), and $\boxed{B = [C_6H_5 - N \equiv N]^+Cl^-}$ (benzenediazonium chloride).

Quick Tip to Solve: Read the temperature over the second arrow: cold nitrous acid converts aniline into a diazonium salt.

30(a). **The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. In tetrahedral coordination entity formation, the d-orbital splitting is smaller as compared to the octahedral entity.**

Answer the following questions:

On the basis of CFT, explain why $[Ti(H_2O)_6]Cl_3$ complex is coloured? What happens on heating the complex $[Ti(H_2O)_6]Cl_3$? Give reason.

[Atomic no.: Ti = 22] [2 marks]

Solution:

Concept:

- In an octahedral complex, the five metal d-orbitals split into lower-energy t_{2g} and higher-energy e_g sets, separated by Δ_o.
- A partially occupied d-shell can absorb visible light through a d–d transition when the photon energy equals the splitting.

Step 1: Determine the metal configuration Each water ligand is neutral and the three external chloride ions contribute total charge -3. Thus the complex cation is $[\mathrm{Ti(H_2O)_6}]^{3+}$, with titanium in oxidation state $+3$. Titanium has configuration $[\mathrm{Ar}]3d^2 4s^2$, so Ti^{3+} is $[\mathrm{Ar}]3d^1$. Its octahedral configuration is $t_{2g}^1 e_g^0$.

Step 2: Explain the colour The single electron absorbs a photon of suitable visible-light frequency and is promoted from a t_{2g} orbital to an e_g orbital:

$$h\nu = \Delta_o.$$

Absorption removes part of the incident white light; the remaining transmitted light gives the complex its violet colour.

Step 3: Explain heating On heating, water ligands are removed from the coordination sphere and the violet colour disappears. Loss of the coordinated water destroys the original octahedral crystal field responsible for its visible-light absorption. Thus the same t_{2g}-to-e_g transition of the hexaaqua complex no longer produces its characteristic colour.

Step 4: Conclusion The complex is violet because Ti^{3+} is d^1 and undergoes a visible-light d–d transition. On heating it loses coordinated water and becomes colourless as the original crystal field is lost.

Quick Tip to Solve: First find the titanium oxidation state using neutral water ligands; a single d electron is sufficient for a coloured complex.

30(b). What is crystal field splitting energy? [1 mark]

Solution:

Concept:

- Ligands remove the degeneracy (equal energy) of the metal d-orbitals by interacting differently with orbitals of different orientation.
- The separation between the resulting groups is denoted by Δ; its value depends on the ligands, metal ion and coordination geometry.

Step 1: Identify the two orbital groups In an octahedral field, the orbitals d_{xy}, d_{yz}, d_{xz} form the lower-energy t_{2g} set, while $d_{x^2-y^2}, d_{z^2}$ form the higher-energy e_g set. The ligands repel electrons in the second set more strongly because these orbitals point towards the ligand directions.

Step 2: Express the energy separation The energy difference between these sets is

$$\Delta_o = E(e_g) - E(t_{2g}).$$

This is the energy needed to promote an electron from the lower set to the upper set; it is an energy difference, rather than the absolute energy of either set.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the two sets of metal d-orbitals produced by the ligand field; in an octahedral complex it is $\boxed{\Delta_o = E(e_g) - E(t_{2g})}$.

Quick Tip to Solve: Define splitting as the energy gap between orbital sets, and use the geometry-specific symbol Delta-o for an octahedral field.

OR

30(b). On the basis of Δ_o and P (pairing energy), how can you differentiate between a strong field ligand and a weak field ligand? [1 mark]

Solution:

Concept:

- Δ_o is the octahedral crystal field splitting energy; P is the energy required to pair electrons in the same orbital.
- Electrons choose the lower-energy arrangement by comparing the cost of occupying the upper orbital set with the cost of pairing in the lower set.

Step 1: Strong field ligand A strong field ligand causes a large splitting such that $\Delta_o > P$. Pairing electrons in the lower t_{2g} orbitals is energetically preferable to promoting them into the upper e_g orbitals. Where a spin-state choice exists, this gives a low-spin complex.

Step 2: Weak field ligand A weak field ligand produces a small splitting such that $\Delta_o < P$. Electrons enter the upper e_g orbitals before pairing because excitation costs less energy than pairing. Where a spin-state choice exists, this produces a high-spin complex with more unpaired electrons.

Step 3: Conclusion $\boxed{\text{Strong field: } \Delta_o > P; \qquad \text{weak field: } \Delta_o < P.}$ Strong fields favour pairing (low

Quick Tip to Solve: Compare the two energy costs: pair when P is smaller; occupy the upper orbital set when Delta-o is smaller.

spin), while weak fields favour unpaired occupation (high spin).

Quick Tip to Solve: Compare the two energy costs: pair when P is smaller; occupy the upper orbital set when Delta-o is smaller.

30(c). Why are low spin tetrahedral complexes rarely observed? [1 mark]

Solution:

Concept:

- In a tetrahedral field, the lower e and upper t_2 sets are separated by the tetrahedral splitting energy Δ_t.
- For comparable metal ions and ligands, $\Delta_t \simeq \frac{4}{9}\Delta_o$, so tetrahedral splitting is relatively small.

Step 1: Compare splitting with pairing energy Tetrahedral ligands do not approach directly along the axes, and there are only four ligands. The resulting orbital energy separation is generally much smaller than the electron pairing energy P; hence $\Delta_t < P$ in most tetrahedral complexes.

Step 2: Determine the electron arrangement Because occupying the upper t_2 set costs less energy than pairing electrons in the lower e set, electrons prefer separate orbitals before pairing. This arrangement maximises the number of unpaired electrons and produces high spin. A low-spin arrangement would require an unusually large splitting sufficient to favour pairing.

Step 3: Conclusion Low-spin tetrahedral complexes are rarely observed because $\boxed{\Delta_t < P}$ in almost all cases, so electrons occupy higher orbitals instead of pairing; tetrahedral complexes are normally high spin.

Quick Tip to Solve: Use Delta-t, not Delta-o, for tetrahedral splitting, and compare that small gap directly with the pairing energy.

Section E (15 marks)

31(a)(i). Calculate the emf of the following cell at 25°C:

Zn(s) | Zn^{2+} (0.1 M) || H^+ (0.01 M) | H_2(g) (1 bar), Pt(s)

[Given: $E^\circ_{Zn^{2+}/Zn}$ = -0.76 V, $E^\circ_{2H^+/H_2}$ = 0.00 V, log 10 = 1] [3 marks]

Solution:

Concept:

- Cell potential is the cathode reduction potential minus the anode reduction potential: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrode reactions Zinc is the anode and undergoes oxidation; hydrogen ions

Quick Tip to Solve: Write the overall reaction before forming Q: the coefficient 2 on hydrogen ions means their concentration must be squared.

are reduced at the platinum cathode:

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2e^-,$$
$$\mathrm{2H^+(aq)} + 2e^- \longrightarrow \mathrm{H_2(g)}.$$

Thus the overall reaction is $\mathrm{Zn(s)} + \mathrm{2H^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{H_2(g)}$, with $n = 2$. Platinum is an inert conducting electrode.

Step 2: Calculate the standard potential and reaction quotient Using the supplied reduction potentials gives

$$E^\circ_{\text{cell}} = 0.00 - (-0.76) = 0.76\,\text{V}.$$

For the reaction written above, the hydrogen-ion concentration is squared because its stoichiometric coefficient is two. With the gas pressure relative to the standard pressure of $1\,\text{bar}$,

$$Q = \frac{[\mathrm{Zn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.1 \times 1}{(0.01)^2} = 10^3.$$

Concentrations here are numerical values relative to $1\,\text{mol}\,\text{L}^{-1}$; therefore Q is dimensionless and $\log Q = 3$.

Step 3: Apply the Nernst correction Substituting the temperature coefficient, electron number and reaction quotient,

$$E_{\text{cell}} = 0.76 - \frac{0.0591}{2} \times 3 = 0.76 - 0.08865 = 0.67135\,\text{V}.$$

The correction lowers the standard emf because the given product-to-reactant activity ratio is greater than unity.

Step 4: Conclusion The emf of the cell at 25°C is $\boxed{E_{\text{cell}} \approx 0.671\,\text{V}}$.

Quick Tip to Solve: Write the overall reaction before forming Q: the coefficient 2 on hydrogen ions means their concentration must be squared.

31(a)(ii). State Faraday's second law of electrolysis. How much electricity is required in terms of Faraday for the reduction of 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+}? [2 marks]

Solution:

Concept:

- Faraday's second law compares substances deposited or liberated by the same quantity of electricity: their masses are proportional to their chemical equivalent masses.
- One Faraday is the charge of one mole of electrons, $F \approx 96500\,\text{C}\,\text{mol}^{-1}$. Electron requirements are found from the change in oxidation number.

Step 1: State Faraday's second law When the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated at their electrodes are directly proportional

Quick Tip to Solve: Count both chromium atoms: each changes from +6 to +3, so dichromate requires twice the three-electron change.

to their equivalent masses:

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}, \qquad E = \frac{M}{z}.$$

Here m is the deposited mass, E the equivalent mass, M the molar mass and z the number of electrons required per atom or formula unit in the electrode reaction.

Step 2: Count electrons for dichromate reduction In $Cr_2O_7^{2-}$, each chromium has oxidation number $+6$. Reduction to Cr^{3+} requires three electrons per chromium atom. Since one dichromate ion contains two chromium atoms, it requires six electrons:

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

Hence one mole of dichromate consumes six moles of electrons. Multiplying the electron amount by Faraday's constant gives the required charge.

Step 3: Conclusion The charge required for reduction of $1\,\text{mol}$ of $Cr_2O_7^{2-}$ is $\boxed{6 \text{ Faradays}}$, equivalent to approximately $5.79 \times 10^5\,\text{C}$.

Quick Tip to Solve: Count both chromium atoms: each changes from $+6$ to $+3$, so dichromate requires twice the three-electron change.

OR

31(b)(i). The conductivity of 0.20 M solution of KCl is 2.48 $\times$ 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

[Given: $\lambda^\circ_{(K^+)}$ = 73.5 S cm^2 mol^{-1}, $\lambda^\circ_{(Cl^-)}$ = 76.5 S cm^2 mol^{-1}] [2 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in $\text{S}\,\text{cm}^{-1}$ and concentration c is in $\text{mol}\,\text{L}^{-1}$.
- Kohlrausch's law gives $\Lambda_m^\circ = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-}$. The conductivity-ratio estimate requested here is $\alpha = \Lambda_m/\Lambda_m^\circ$.

Step 1: Calculate molar conductivity The concentration is $0.20\,\text{mol}\,\text{L}^{-1}$, or $2.0 \times 10^{-4}\,\text{mol}\,\text{cm}^{-3}$. Dividing conductivity by concentration in these consistent units gives

$$\Lambda_m = \frac{1000(2.48 \times 10^{-2})}{0.20} = 124\,\text{S}\,\text{cm}^2\,\text{mol}^{-1}.$$

The factor 1000 converts the litre-based concentration into the cubic-centimetre basis of the supplied conductivity.

Step 2: Calculate the limiting value and requested ratio KCl produces one potassium ion and one chloride ion per formula unit. Therefore the supplied limiting ionic conductivities add directly:

$$\Lambda_m^\circ = 73.5 + 76.5 = 150\,\text{S}\,\text{cm}^2\,\text{mol}^{-1}.$$

Quick Tip to Solve: Add the two limiting ionic conductivities first, then divide the measured molar conductivity by that sum; the ratio has no units.

Using the ratio intended by the question,

$$\alpha = \frac{124}{150} = 0.8267 \approx 0.827.$$

This ratio is dimensionless because numerator and denominator have the same units. KCl is a strong electrolyte; at finite concentration its reduced molar conductivity reflects interionic effects. Thus the ratio is an apparent conductivity-based dissociation value rather than a literal undissociated molecular fraction.

Step 3: Conclusion $\boxed{\Lambda_m = 124\,\mathrm{S\,cm^2\,mol^{-1}}}$ and the requested conductivity-ratio value is $\boxed{\alpha \approx 0.827}$, or approximately 82.7%.

Quick Tip to Solve: Add the two limiting ionic conductivities first, then divide the measured molar conductivity by that sum; the ratio has no units.

31(b)(ii). Calculate $\Delta_r G^\circ$ of the following cell:

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

[Given: $E^\circ_{Mg^{2+}/Mg}$ = -2.37 V, $E^\circ_{Cu^{2+}/Cu}$ = +0.34 V, 1 F = 96500 C mol^{-1}] [2 marks]

Solution:

Concept:

- Standard cell emf is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using tabulated reduction potentials.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the electron number and F is Faraday's constant.

Step 1: Identify oxidation, reduction and electron number In the reaction as written, magnesium is oxidised and copper(II) ions are reduced:

$$\mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2e^-,$$
$$\mathrm{Cu^{2+}(aq)} + 2e^- \longrightarrow \mathrm{Cu(s)}.$$

Two electrons are exchanged per reaction as written, so $n = 2$. The magnesium electrode is the anode and the copper electrode is the cathode.

Step 2: Calculate standard emf Both supplied potentials are reduction potentials. Subtract the magnesium value from the copper value:

$$E^\circ_{\text{cell}} = 0.34 - (-2.37) = 2.71\,\mathrm{V}.$$

The positive result agrees with magnesium reducing copper(II) ions in the stated direction. Electrode potentials are not multiplied by the number of electrons.

Quick Tip to Solve: Subtract reduction potentials before applying -nFE; retain the minus sign on magnesium's potential and use n = 2.

Step 3: Convert emf to Gibbs energy Substituting the supplied Faraday constant,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(2.71)\\ &= -523030\,\mathrm{J\,mol^{-1}}\\ &= -523.03\,\mathrm{kJ\,mol^{-1}}.\end{aligned}$$

The units follow from $\mathrm{C} \times \mathrm{V} = \mathrm{J}$, and the molar value refers to the reaction as written. The negative sign shows that the forward reaction is thermodynamically favourable under standard conditions.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -523.03\,\mathrm{kJ\,mol^{-1}}}$ for the stated magnesium-copper cell reaction.

Quick Tip to Solve: Subtract reduction potentials before applying -nFE; retain the minus sign on magnesium's potential and use n = 2.

31(b)(iii). What type of cell is mercury cell? Why is it more advantageous than dry cell? [1 mark]

Solution:

Concept:

- A primary cell produces electricity through a reaction that is not reversed by ordinary recharging.
- A cell maintains a nearly constant potential when the activities of the species in its overall reaction remain essentially constant.

Step 1: Identify the cell A mercury cell is a primary cell. Its anode is zinc amalgam and its cathode contains mercury(II) oxide, with an alkaline electrolyte. It is used for a small, steady supply of electrical energy.

Step 2: Explain the advantage over a dry cell Its overall reaction is $\mathrm{Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)}$. No ion in solution appears in this net reaction, so the electrolyte concentration does not change appreciably during use. Consequently, its potential remains nearly constant at about $1.35\,\mathrm{V}$ throughout its useful life, whereas a dry cell's voltage falls during discharge.

Step 3: Conclusion A mercury cell is a primary cell. Its advantage over a dry cell is its nearly constant output voltage, about $1.35\,\mathrm{V}$, during its useful life.

Quick Tip to Solve: For the constant voltage, point to the absence of electrolyte ions from the overall cell reaction.

32(a). (i) Account for the following:

(I) The $E^{\circ}_{Mn^{2+}/Mn}$ value for manganese is highly negative, whereas $E^{\circ}_{Mn^{3+}/Mn^{2+}}$ is highly positive.

(II) Actinoids show wide range of oxidation states.

(III) Transition metals have high melting points.

(ii) Complete the following ionic equations:

(I) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow$

(II) $2MnO_4^- + H_2O + I^- \rightarrow$ [5 marks]

Solution:

Concept:

- The half-filled $3d^5$ configuration gives Mn^{2+} extra stability; reduction potentials reflect the relative stability of the oxidised and reduced forms.
- Actinoid $5f$, $6d$ and $7s$ orbitals have comparable energies, allowing different numbers of electrons to participate in bonding.
- Strong metallic bonding involves both ns and $(n-1)d$ electrons in transition metals. Greater bonding strength requires more energy to melt the solid.
- Permanganate gives Mn^{2+} in acidic solution and MnO_2 in neutral or mildly alkaline solution. Ionic equations must conserve atoms and charge.

Step 1: (i)(I) Explain the two manganese potentials Manganese has configuration $[Ar]3d^5 4s^2$, while Mn^{2+} is $[Ar]3d^5$. Formation of this stable half-filled ion by oxidation of the metal is favoured. The reverse reduction, $Mn^{2+} + 2e^- \rightarrow Mn$, is relatively unfavourable, accounting for the highly negative $E^{\circ}_{Mn^{2+}/Mn}$. In contrast, Mn^{3+} has $3d^4$ configuration. It readily accepts an electron to form stable $3d^5$ Mn^{2+}, so $E^{\circ}_{Mn^{3+}/Mn^{2+}}$ is highly positive.

Step 2: (i)(II) Explain actinoid oxidation states The energies of the $5f$, $6d$ and $7s$ subshells in actinoids are close. Therefore, electrons from all three subshells can participate in bond formation. Different numbers of these electrons can be used in different compounds, producing a wide range of oxidation states, especially among the earlier actinoids.

Step 3: (i)(III) Explain the high melting points Transition metals generally have strong interatomic metallic bonding because both their outer ns electrons and available $(n-1)d$ electrons contribute to bonding. Their high enthalpies of atomisation reflect this cohesion. Considerable thermal energy is consequently required to disrupt the metallic lattice during melting. This is a general trend; metals with filled d subshells have weaker bonding and can be exceptions.

Step 4: (ii)(I) Balance oxidation of sulphite in acid Sulphur changes from $+4$ in sulphite to $+6$ in sulphate, losing two electrons per sulphur atom. Manganese changes from $+7$ in permanganate to $+2$, gaining five electrons per manganese atom. Thus five sulphite ions balance two permanganate ions. The balanced equation is

$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O.$$

Both sides have five sulphur atoms, two manganese atoms, twenty-three oxygen atoms and six hydrogen atoms. Their total charge is -6 on each side.

Step 5: (ii)(II) Balance oxidation of iodide Under the stated neutral or alkaline conditions, manganese

Quick Tip to Solve: For permanganate equations, select the manganese product from the reaction medium first, then check both oxygen atoms and total ionic charge.

is reduced from $+7$ to $+4$ in MnO_2. Two permanganate ions accept six electrons. Iodide is oxidised from -1 to $+5$ in iodate and supplies those six electrons. Completing the given reactants gives

$$2MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + IO_3^- + 2OH^-.$$

Each side has two manganese atoms, one iodine atom, nine oxygen atoms and two hydrogen atoms. The charge is -3 on both sides, confirming the balance.

Step 6: Conclusion The manganese potentials arise from stable half-filled $3d^5$ Mn^{2+}; actinoids use electrons from closely spaced $5f$, $6d$ and $7s$ subshells; and transition metals generally melt at high temperatures because of strong metallic bonding. The products in (ii)(I) are $5SO_4^{2-} + 2Mn^{2+} + 3H_2O$, and those in (ii)(II) are $2MnO_2 + IO_3^- + 2OH^-$.

Quick Tip to Solve: For permanganate equations, select the manganese product from the reaction medium first, then check both oxygen atoms and total ionic charge.

OR

32(b). Answer the following questions:

(i) Name two elements of 3d series for which the third ionisation enthalpies are quite high.

(ii) Out of $KMnO_4$ and K_2MnO_4, which one is paramagnetic and why?

(iii) Write any one consequence of lanthanoid contraction.

(iv) How do you prepare potassium manganate from pyrolusite ore?

(v) Why is the ability of oxygen more than fluorine to stabilise higher oxidation states of transition metals? [5 marks]

Solution:

Concept:

- Third ionisation enthalpy is the energy needed for $M^{2+}(g) \rightarrow M^{3+}(g) + e^-$. Removing an electron from a stable half-filled or completely filled d subshell requires especially high energy.
- Paramagnetism arises from unpaired electrons. The oxidation state fixes the d-electron count of a transition-metal ion.
- Lanthanoid contraction is the gradual decrease in lanthanoid ionic radii caused by ineffective shielding of nuclear charge by $4f$ electrons.
- Oxidative alkaline fusion converts manganese dioxide to manganate; oxygen can also stabilise high metal oxidation states through multiple bonding.

Step 1: (i) Identify the two elements The elements are **manganese (Mn) and zinc (Zn)**. Their divalent ions have the configurations

$$Mn^{2+} : [Ar]\,3d^5, \qquad Zn^{2+} : [Ar]\,3d^{10}.$$

The third ionisation removes a $3d$ electron from these particularly stable half-filled and fully filled subshells, respectively. Hence their third ionisation enthalpies are quite high.

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state first: $+7$ gives d^0, while $+6$ gives d^1, so only manganate is paramagnetic.

Step 2: (ii) Compare permanganate and manganate In $KMnO_4$, manganese has oxidation state $+7$, since $1 + x - 8 = 0$. Thus it has a $3d^0$ configuration and no unpaired d electrons, making permanganate diamagnetic. In K_2MnO_4, $2 + x - 8 = 0$, so manganese is in oxidation state $+6$ and has a $3d^1$ configuration. Its one unpaired electron makes **potassium manganate,** K_2MnO_4**, paramagnetic**.

Step 3: (iii) State one consequence of lanthanoid contraction The radii of zirconium (Zr) and hafnium (Hf) are almost the same, although hafnium belongs to the next transition series. The intervening lanthanoid contraction offsets the normal increase in size expected on moving down the group. Consequently, Zr and Hf have very similar chemical properties and are difficult to separate.

Step 4: (iv) Prepare potassium manganate from pyrolusite Pyrolusite, MnO_2, is fused with potassium hydroxide in the presence of air or oxygen. Oxidation of manganese from $+4$ to $+6$ produces green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{fusion}} 2K_2MnO_4 + 2H_2O.$$

The alkaline medium supplies potassium ions and enables formation of the manganate ion. The equation conserves Mn, K, O and H.

Step 5: (v) Explain oxygen's greater ability Oxygen can form **multiple bonds** with transition metals, whereas fluorine forms only single bonds. Strong metal–oxygen multiple bonding therefore provides additional stabilisation of high oxidation states. For example, manganese reaches $+7$ in Mn_2O_7, whereas its highest fluoride, MnF_4, contains manganese in $+4$. Thus oxygen's ability here follows from bonding, even though fluorine is more electronegative.

Step 6: Conclusion (i) Mn and Zn; (ii) K_2MnO_4, owing to one unpaired electron; (iii) almost equal radii and similar properties of Zr and Hf; (iv) oxidative fusion of MnO_2 with KOH; (v) oxygen forms stabilising multiple bonds with metals.

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state first: $+7$ gives d^0, while $+6$ gives d^1, so only manganate is paramagnetic.

33(a). **(i) An organic compound (X) having molecular formula $C_5H_{10}O$ can show various properties depending on its structures. Draw each of the structures if it:**

(I) shows Cannizzaro reaction.

(II) reduces Tollens' reagent and has a chiral carbon.

(III) gives positive iodoform test.

(ii) Write the reaction involved in the following:

(I) Clemmensen reduction

(II) Etard reaction [5 marks]

Solution:

Concept:

- An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali; one molecule is oxidised and the other is reduced.
- Aldehydes reduce Tollens' reagent to metallic silver. A chiral carbon is bonded to four different groups.
- The iodoform test identifies the methyl ketone group, CH_3CO-. Clemmensen reduction converts a carbonyl group to methylene; Etard oxidation converts the methyl group of toluene to an aldehyde.

Step 1: (i)(I) Choose an aldehyde without alpha-hydrogen The required isomer is 2,2-dimethylpropanal, $(CH_3)_3C-CHO$. Its carbon next to the aldehyde group is bonded to three methyl groups and to the aldehyde carbon, so it has no hydrogen. It therefore cannot undergo the usual aldol reaction and shows Cannizzaro reaction with concentrated alkali:

$$2(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCOONa + (CH_3)_3CCH_2OH.$$

Its five carbons and ten hydrogens agree with the stated molecular formula.

Step 2: (i)(II) Choose a chiral aldehyde The required structure is 2-methylbutanal:

$$CH_3CH_2CH(CH_3)CHO.$$

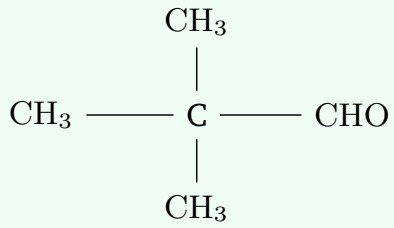
The carbon indicated by an asterisk in the drawing has four different substituents: H, CH_3, CH_2CH_3, and CHO, so it is chiral. Its aldehyde group is oxidised to carboxylate by Tollens' reagent, while silver ions are reduced to a silver mirror. Thus both stated conditions are satisfied.

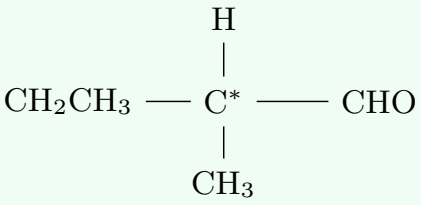
Step 3: (i)(III) Identify the methyl ketone isomers Pentan-2-one, $CH_3COCH_2CH_2CH_3$, gives the positive iodoform test. Another valid structure is 3-methylbutan-2-one, $CH_3COCH(CH_3)_2$. Both have molecular formula $C_5H_{10}O$ and the methyl ketone group. With iodine and alkali they form yellow iodoform, CHI_3:

$$RCOCH_3 + 3I_2 + 4NaOH \longrightarrow RCOONa + CHI_3 + 3NaI + 3H_2O.$$

Here R is propyl or isopropyl. A ketone with the carbonyl group between two ethyl groups would lack CH_3CO- and would fail this test.

Quick Tip to Solve: Check the alpha-carbon for Cannizzaro, four different groups for chirality, and the exact CH3CO group for iodoform before selecting an isomer.

(I)


(II)


(III) $\mathrm{CH_3{-}C(=O){-}CH_2{-}CH_2{-}CH_3}$

$\mathrm{CH_3{-}C(=O){-}CH(CH_3)_2}$

Structures satisfying the three tests; the asterisk denotes the chiral carbon.

Step 4: (ii)(I) Write Clemmensen reduction An aldehyde or ketone is reduced with zinc amalgam, $\mathrm{Zn(Hg)}$, and concentrated hydrochloric acid. The carbonyl oxygen is removed and the carbonyl carbon becomes a methylene carbon:

$$\mathrm{RCOR' + 4[H] \xrightarrow{Zn(Hg),\ conc.\ HCl} RCH_2R' + H_2O.}$$

For example, acetone gives propane. For an aldehyde, take $\mathrm{R' = H}$, so RCHO gives $\mathrm{RCH_3}$. The carbon skeleton is retained.

Step 5: (ii)(II) Write the Etard reaction Toluene is treated with chromyl chloride in a non-aqueous solvent such as carbon disulphide. The resulting Etard complex is hydrolysed to give benzaldehyde:

$$\mathrm{C_6H_5CH_3 \xrightarrow{CrO_2Cl_2/CS_2} \text{Etard complex} \xrightarrow{H_2O} C_6H_5CHO.}$$

Controlled oxidation of the side-chain methyl group stops at the aldehyde stage, unlike vigorous oxidation to benzoic acid.

Step 6: Conclusion The required structures are (I) 2,2-dimethylpropanal, (II) 2-methylbutanal, and (III) pentan-2-one or 3-methylbutan-2-one. Clemmensen reduction uses $\mathrm{Zn(Hg)/HCl}$ to convert carbonyl to methylene, while Etard oxidation uses $\mathrm{CrO_2Cl_2}$ followed by hydrolysis to convert toluene to benzaldehyde.

Quick Tip to Solve: Check the alpha-carbon for Cannizzaro, four different groups for chirality, and the exact CH3CO group for iodoform before selecting an isomer.

OR

33(b). Answer the following questions:

(i) Draw structure of the methyl hemiacetal of methanal.

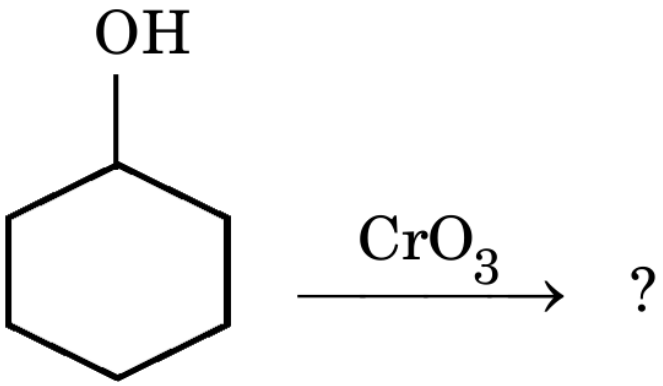
(ii) There are two –NH_2 groups in semicarbazide. However only one is involved in the formation of semicarbazones. Give reason.

(iii) How will you convert ethanol to 3-hydroxybutanal?

(iv) Complete the following equation:

(v) Write the final product formed when phthalic acid is treated with NH_3 followed by strong heating.

[5 marks]



Solution:

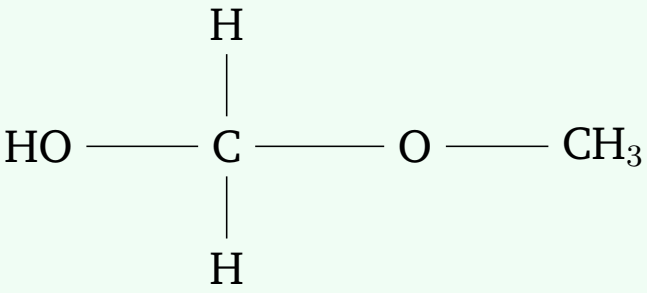
Concept:

- A hemiacetal has an –OH group and an –OR group on the same carbon atom; addition of methanol to methanal gives its methyl hemiacetal.
- The terminal amino group of semicarbazide is nucleophilic, whereas the lone pair on the amino nitrogen directly bonded to the carbonyl carbon is delocalised by resonance.
- Ethanal contains alpha-hydrogen atoms and undergoes aldol addition with dilute alkali. Secondary alcohols undergo oxidation to ketones, while heating an ammonium salt of a dicarboxylic acid can form a cyclic imide.

Step 1: (i) Structure of the methyl hemiacetal Methanal is HCHO. Methanol adds across its carbonyl group: the carbonyl oxygen becomes –OH, and the methoxy group attaches to the same carbon. The product is $HO-CH_2-O-CH_3$, shown below. The former carbonyl carbon retains its two hydrogen atoms and is bonded to both –OH and $–OCH_3$, which identifies it as a hemiacetal.

$$HCHO + CH_3OH \rightleftharpoons HOCH_2OCH_3.$$

Quick Tip to Solve: For the aldol conversion, first make ethanal from ethanol and use dilute alkali without heating; keep both –OH and –OR on the same carbon when drawing a hemiacetal.



Structure of the methyl hemiacetal of methanal

Step 2: (ii) Identify the reactive amino group Semicarbazide has the structure $H_2N{-}NH{-}C(=O){-}NH_2$. The lone pair on the nitrogen of the –$CONH_2$ group is delocalised into the carbonyl group by resonance, so it is much less available for nucleophilic attack. The terminal –NH_2 group, away from the carbonyl carbon, has an available lone pair and attacks the carbonyl carbon of an aldehyde or ketone. Subsequent loss of water forms a semicarbazone:

$$R_2C=O + H_2N{-}NH{-}CONH_2 \longrightarrow R_2C=N{-}NH{-}CONH_2 + H_2O.$$

Thus only the terminal amino group participates in this condensation.

Step 3: (iii) Convert ethanol to 3-hydroxybutanal First dehydrogenate ethanol over heated copper at 573 K to obtain ethanal. Then treat ethanal with dilute aqueous NaOH at low temperature to obtain its aldol addition product:

$$CH_3CH_2OH \xrightarrow{\text{Cu, } 573\,\text{K}} CH_3CHO + H_2,$$
$$2CH_3CHO \xrightarrow{\text{dilute NaOH}} CH_3CH(OH)CH_2CHO.$$

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Avoid heating the aldol product, because dehydration would give but-2-enal instead of the required 3-hydroxybutanal.

Step 4: (iv) Oxidise cyclohexanol Cyclohexanol is a secondary alcohol. Chromium trioxide oxidises its –CHOH group to a carbonyl group without changing the ring skeleton. The missing product is cyclohexanone:

$$C_6H_{11}OH + [O] \xrightarrow{CrO_3} C_6H_{10}O + H_2O.$$

Step 5: (v) Heat phthalic acid with ammonia Ammonia initially forms an ammonium salt with phthalic acid. Strong heating causes dehydration and ring closure, giving the five-membered cyclic imide, phthalimide. Its two carbonyl groups are joined through –NH. The overall balanced reaction is

$$C_6H_4(COOH)_2 + NH_3 \xrightarrow{\text{strong heating}} C_6H_4(CO)_2NH + 2H_2O.$$

Step 6: Conclusion (i) Methyl hemiacetal: $HOCH_2OCH_3$. (ii) Only the terminal –NH_2 group reacts because the carbonyl-adjacent amino lone pair is resonance-delocalised. (iii) Ethanol gives ethanal, which undergoes aldol addition to give $CH_3CH(OH)CH_2CHO$. (iv) Cyclohexanone. (v) Phthalimide.

Quick Tip to Solve: For the aldol conversion, first make ethanal from ethanol and use dilute alkali without heating; keep both –OH and –OR on the same carbon when drawing a hemiacetal.