

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-4-3

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 **35** questions. All questions are **compulsory**.
- (ii) This question paper is divided into **five** Sections – **A, B, C, D** and **E**.
- (iii) In **Section A** – Questions no. **1 to 18** are multiple choice (MCQ) type questions, carrying **1** mark each.
- (iv) In **Section B** – Questions no. **19 to 25** very short answer (VSA) type questions, carrying **2** marks each.
- (v) In **Section C** – Questions no. **26 to 30** are short answer (SA) type questions, carrying **3** marks each.
- (vi) In **Section D** – Questions no. **31 and 32** are case-based questions carrying **4** marks each.
- (vii) In **Section E** – Questions no. **33 to 35** are long answer (LA) type questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section B, 2 questions in Section C, 2 questions in Section D and 2 questions in Section E.
- (ix) Use of calculators **is not** allowed.

Section A (18 marks)

Questions no. 1 to 18 are Multiple Choice (MCQ) type Questions, carrying 1 mark each.

1. A compound $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ undergoes complete dissociation in water. The Van't Hoff factor ' i ' is:

[1 mark]

- (A) 9
- (B) 6
- (C) 3
- (D) 4

Correct Answer: (C) 3

Solution:

Concept:

- The van't Hoff factor i is the number of dissolved solute particles produced per formula unit when dissociation is complete.
- Water of crystallisation becomes part of the solvent and is not counted as an additional solute particle.

Step 1: Write the ionic dissociation On dissolving, the hydrated salt supplies one calcium ion and two chloride ions:



The six water molecules join the bulk water solvent.

Step 2: Count only solute particles Each formula unit therefore produces $1 + 2 = 3$ solute ions. Counting the six waters would incorrectly give 9; taking only their number gives 6. There is no fourth ion, so 4 is also incorrect.

Step 3: Conclusion $i = 3$. Hence, the correct option is (C).

Quick Tip to Solve: Count dissociated ions; never add waters of crystallisation to the solute-particle count.

2. For a zero order reaction of the type $A \rightarrow \text{products}$, the rate equation may be expressed as: [1 mark]

(A) $k = \frac{[A]_0 - [A]}{t}$

(B) $k = \frac{[A] - [A]_0}{t}$

(C) $k = \frac{[A]_0 - [A]}{2t}$

(D) $k = \frac{[A]_0 - [A]}{2} \cdot t$

Correct Answer: (A) $k = \frac{[A]_0 - [A]}{t}$

Solution:

Concept:

- For a zero order reaction, the rate is independent of reactant concentration: $-d[A]/dt = k$.
- Here $[A]_0$ is the initial concentration and $[A]$ is the concentration after time t .

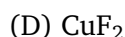
Step 1: Integrate the rate law Integrating between the initial state and time t gives $[A] - [A]_0 = -kt$, or $[A] = [A]_0 - kt$. Thus concentration decreases linearly with time while reactant remains.

Step 2: Rearrange and check the printed alternatives Rearrangement gives $k = ([A]_0 - [A])/t$. Option (B) has the wrong sign and would give a negative rate constant. Option (C) introduces an unjustified factor of 2. Option (D) multiplies by time rather than dividing and has incorrect dimensions.

Step 3: Conclusion $k = \frac{[A]_0 - [A]}{t}$. Hence, the correct option is (A).

Quick Tip to Solve: For zero order, divide the concentration lost by elapsed time; check that the rate constant is positive.

3. Which of the following Cu^{2+} halide is not known? [1 mark]



Correct Answer: (B) CuI_2

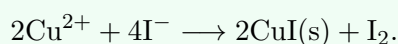
Solution:

Concept:

- Copper(II) can oxidise iodide to iodine, while itself being reduced to copper(I).
- The formation of sparingly soluble copper(I) iodide favours this redox reaction.

Step 1: Identify the unstable halide In a proposed CuI_2 , the iodide ions act as a reducing agent towards Cu^{2+} . Copper(II) iodide is therefore not a stable known halide under ordinary conditions.

Step 2: Write the redox change and compare The net reaction is



Quick Tip to Solve: Remember that iodide reduces copper(II) and precipitates copper(I) iodide.

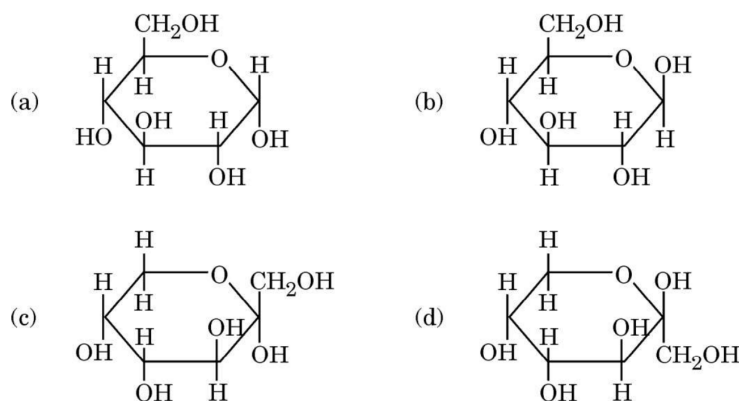
Thus iodide yields copper(I) iodide and iodine instead of the proposed copper(II) salt. The fluoride, chloride and bromide listed are known copper(II) halides and do not fit the question.

Step 3: Conclusion CuI_2 is not known as a stable copper(II) halide. Hence, the correct option is (B).

Quick Tip to Solve: Remember that iodide reduces copper(II) and precipitates copper(I) iodide.

4. Which of the following structures represents α -D-glucose?

[1 mark]



(A) Structure (a)

(B) Structure (b)

(C) Structure (c)

(D) Structure (d)

Correct Answer: (A) Structure (a)

Solution:

Concept:

- In a Haworth representation of D-glucose, the terminal CH_2OH group attached to C5 points above the ring.
- The alpha anomer has its anomeric hydroxyl at C1 on the opposite side from this CH_2OH group.

Step 1: Locate the anomeric carbon The anomeric carbon of glucopyranose is C1, immediately next to the ring oxygen on the right in the upper two structures. The upper structures have the glucose hydroxyl pattern: C2 down, C3 up and C4 down.

Step 2: Distinguish alpha from beta In structure (a), the C5 CH_2OH group is up and the C1 hydroxyl is down, so these groups are trans. In (b), the anomeric hydroxyl is up, giving beta-D-glucose. The lower structures place CH_2OH on the anomeric carbon and do not show the required glucopyranose arrangement.

Step 3: Conclusion Structure (a) represents α -D-glucose. Hence, the correct option is (A).

Quick Tip to Solve: For D-glucose in the usual Haworth orientation, alpha means the anomeric OH points down.

5. The compounds $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ exhibit: [1 mark]

- (A) Linkage isomerism
- (B) Geometrical isomerism
- (C) Ionization isomerism
- (D) Hydrate isomerism

Correct Answer: (D) Hydrate isomerism

Solution:

Concept:

- Hydrate isomerism is a form of solvate isomerism in which water occurs either inside or outside the coordination sphere.
- The square brackets identify ligands directly bonded to the metal; water outside them is water of crystallisation.

Step 1: Compare the coordination spheres The three complexes contain respectively six, five and four coordinated water molecules. As coordinated water decreases, the numbers of coordinated chloride ligands increase from zero to one to two.

Step 2: Compare the waters outside the brackets The corresponding numbers of uncoordinated waters are zero, one and two, while the overall composition remains $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. This exchange of water between the coordination sphere and crystal identifies hydrate isomerism. No ambidentate ligand changes its donor atom, and no geometrical arrangement is being compared.

Step 3: Conclusion The compounds exhibit hydrate isomerism. Hence, the correct option is (D).

Quick Tip to Solve: Count water molecules inside and outside the brackets to recognise hydrate isomerism immediately.

6. Which of the following alkenes on acid catalysed hydration gives a tertiary alcohol? [1 mark]

- (A) 2-Butene
- (B) 2-Methylpropene
- (C) Propene
- (D) 1-Butene

Correct Answer: (B) 2-Methylpropene

Solution:

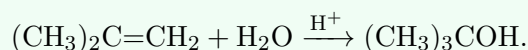
Concept:

- Acid catalysed hydration adds water across the alkene double bond according to Markovnikov orientation.
- A tertiary alcohol has the carbon bearing OH attached to three other carbon atoms.

Step 1: Hydrate the branched alkene Protonation of 2-methylpropene forms the tertiary tert-butyl

Quick Tip to Solve: Draw the Markovnikov alcohol and count the carbon neighbours of the carbon carrying OH.

carbocation. Water attacks this centre, and loss of a proton gives



The product is 2-methylpropan-2-ol.

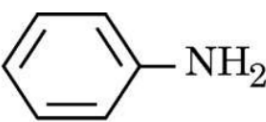
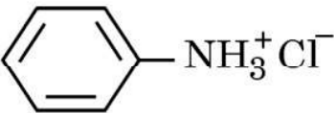
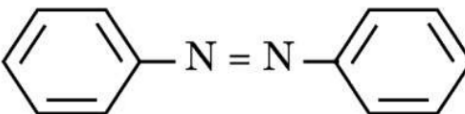
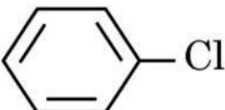
Step 2: Check the remaining alkenes The hydroxyl-bearing carbon in this product is bonded to three methyl groups. In contrast, 2-butene and 1-butene give butan-2-ol, while propene gives propan-2-ol. Each of those alcohols has its hydroxyl-bearing carbon attached to only two carbons and is secondary.

Step 3: Conclusion 2-Methylpropene gives a tertiary alcohol. Hence, the correct option is (B).

Quick Tip to Solve: Draw the Markovnikov alcohol and count the carbon neighbours of the carbon carrying OH.

7. When nitrobenzene is heated with tin and concentrated HCl, the product formed is:

[1 mark]

- (a) 
- (b) 
- (c) 
- (d) 

(A) $\text{C}_6\text{H}_5\text{NH}_2$ (Aniline)

(B) $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$ (Anilinium chloride)

(C) $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$ (Azobenzene)

(D) $\text{C}_6\text{H}_5\text{Cl}$ (Chlorobenzene)

Correct Answer: (B) $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$ (Anilinium chloride)

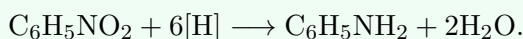
Solution:

Concept:

- Tin and concentrated hydrochloric acid reduce an aromatic nitro group to an amino group without replacing the benzene ring.
- In strongly acidic solution the amine is protonated, forming an anilinium salt; free aniline is obtained on subsequent basification.

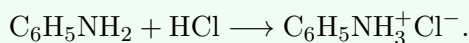
Quick Tip to Solve: For Sn/concentrated HCl, retain the ammonium salt unless an alkaline work-up is stated.

Step 1: Identify the reduction product The reduction converts $\text{C}_6\text{H}_5\text{NO}_2$ to the aniline framework:



This is complete reduction of the nitro group, not formation of an azo linkage.

Step 2: Account for the concentrated acid Because the stated medium contains concentrated HCl and no alkaline work-up is mentioned, the amine is protonated:



Thus the salt shown in (b) is present. Free aniline in (a) would require basification; neither azobenzene nor chlorobenzene is formed by these conditions.

Step 3: Conclusion The product is anilinium chloride, $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$. Hence, the correct option is (B).

Quick Tip to Solve: For Sn/concentrated HCl, retain the ammonium salt unless an alkaline work-up is stated.

8. Reaction of 1-phenyl-2-chloropropane with alcoholic KOH gives mainly:

[1 mark]

- (A) 1-phenylpropene
- (B) 3-phenylpropene
- (C) 1-phenylpropan-3-ol
- (D) 1-phenylpropan-2-ol

Correct Answer: (A) 1-phenylpropene

Solution:

Concept:

- Alcoholic KOH favours beta-elimination: a hydrogen on a carbon adjacent to the carbon bearing chlorine is removed along with the chlorine.
- The major alkene is favoured by greater substitution and, here, conjugation of its double bond with the phenyl ring.

Step 1: Identify the two elimination products The substrate is $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$. Removing a beta-hydrogen from the phenyl-adjacent carbon gives $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$; removing one from the terminal methyl carbon gives $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$.

Step 2: Compare stability and the other options The first alkene is more substituted and its double bond is conjugated with the benzene ring, so it is the major product. The second is 3-phenylpropene and is less favoured. The alcohols in (C) and (D) would require substitution rather than the elimination favoured by alcoholic KOH.

Step 3: Conclusion The major product is 1-phenylpropene, $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$. Hence, the correct option is (A).

Quick Tip to Solve: Draw both beta-elimination products and prefer the alkene conjugated with the phenyl ring.

9. Corrosion of iron is:

[1 mark]

- (A) a decomposition process
- (B) a photochemical process
- (C) an electrochemical process
- (D) a reduction process

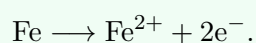
Correct Answer: (C) an electrochemical process

Solution:

Concept:

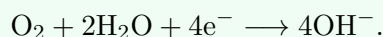
- Corrosion in moist air involves oxidation of iron at anodic sites and reduction of oxygen at cathodic sites.
- The wet surface acts as an electrolyte, while electrons move through the metal between these sites.

Step 1: Identify the oxidation at iron At an anodic region, iron loses electrons:



This dissolution is coupled to a reduction reaction elsewhere on the same metal surface.

Step 2: Identify the coupled reduction and reject alternatives In neutral aerated water, the cathodic reaction is



Subsequent reactions form hydrated iron(III) oxide, rust. Since both electrode reactions occur, corrosion is electrochemical. It is not merely decomposition, need not be initiated by light, and is not solely a reduction process.

Step 3: Conclusion Corrosion of iron is an electrochemical process. Hence, the correct option is (C).

Quick Tip to Solve: Look for coupled oxidation of the metal and reduction of oxygen on a moist surface.

10. The number of molecules that react with each other in an elementary reaction is a measure of the:

[1 mark]

- (A) activation energy of the reaction
- (B) order of the reaction
- (C) stoichiometry of the reaction
- (D) molecularity of the reaction

Correct Answer: (D) molecularity of the reaction

Solution:

Concept:

- Molecularity counts the reacting species participating in a single elementary reaction event.
- Reaction order is the sum of concentration exponents in the experimentally determined rate law.

Quick Tip to Solve: The words "number of reacting species in an elementary step" identify molecularity directly.

Step 1: Apply the definition to the wording The question specifies an elementary reaction and asks for the number of molecules reacting with one another. A single reacting molecule gives a unimolecular event, two give a bimolecular event, and three give a termolecular event.

Step 2: Distinguish the other quantities Activation energy is the energy barrier to reaction, not a count of molecules. Order refers to rate-law exponents; although it often equals molecularity for an elementary step, it is defined differently. Stoichiometry gives the quantitative proportions of reactants and products in a balanced equation, which can represent a multistep overall reaction.

Step 3: Conclusion The stated number is the molecularity of the reaction. Hence, the correct option is (D).

Quick Tip to Solve: The words "number of reacting species in an elementary step" identify molecularity directly.

11. On hydrolysis, which of the following carbohydrates gives glucose and galactose?

[1 mark]

- (A) Sucrose
- (B) Lactose
- (C) Maltose
- (D) Cellulose

Correct Answer: (B) Lactose

Solution:

Concept:

- Hydrolysis of a disaccharide breaks its glycosidic linkage to release its constituent monosaccharides.
- Lactose contains one glucose unit and one galactose unit.

Step 1: Identify the required constituent pair Lactose is the disaccharide formed from glucose and galactose. Its hydrolysis can be represented as



The products exactly match the pair named in the question.

Step 2: Check all remaining choices Sucrose gives glucose and fructose on hydrolysis. Maltose gives two glucose molecules. Cellulose is a polysaccharide built from glucose units, so complete hydrolysis yields glucose rather than the glucose-galactose pair. Thus none of these three options has the required composition.

Step 3: Conclusion Lactose gives glucose and galactose on hydrolysis. Hence, the correct option is (B).

Quick Tip to Solve: Remember lactose as glucose plus galactose; maltose contains only glucose units.

12. The deficiency of which of the following vitamins causes 'Rickets'?

[1 mark]

- (A) Vitamin A
- (B) Vitamin D
- (C) Vitamin B
- (D) Vitamin C

Correct Answer: (B) Vitamin D

Solution:

Concept:

- Vitamin D supports absorption and utilisation of calcium and phosphorus needed for bone mineralisation.
- Rickets is associated with inadequate mineralisation of growing bones in children.

Step 1: Connect the deficiency to bone formation When vitamin D is deficient, calcium absorption and normal mineralisation of bone are impaired. In children, the resulting soft, weak bones can become deformed; this condition is called rickets.

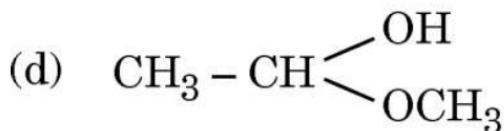
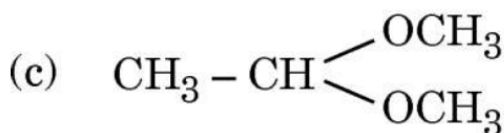
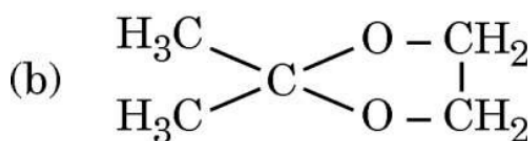
Step 2: Check the alternative vitamins Vitamin A deficiency is classically associated with night blindness. Deficiency of B-group vitamins causes disorders such as beriberi for vitamin B1, rather than the characteristic vitamin-D deficiency disease asked here. Vitamin C deficiency causes scurvy, involving impaired collagen formation and bleeding gums. These associations exclude (A), (C) and (D).

Step 3: Conclusion Deficiency of vitamin D causes rickets. Hence, the correct option is (B).

Quick Tip to Solve: Associate vitamin D with calcium absorption and bone mineralisation to identify rickets.

13. Which of the following is an 'Acetal'?

[1 mark]



- (A) Structure (a)
- (B) Structure (b)
- (C) $\text{CH}_3 - \text{CH}(\text{OCH}_3)_2$
- (D) $\text{CH}_3 - \text{CH}(\text{OH})(\text{OCH}_3)$

Correct Answer: (C) $\text{CH}_3\text{-CH}(\text{OCH}_3)_2$

Solution:

Concept:

- An aldehyde-derived acetal has two alkoxy groups on the same carbon, with that carbon also bonded to hydrogen and an organic group.
- A hemiacetal has one alkoxy group and one hydroxyl group on that carbon; the ketone-derived analogue with two alkoxy groups is a ketal.

Step 1: Inspect the functional carbon in option C Option (C) is $\text{CH}_3\text{CH}(\text{OCH}_3)_2$. Its central carbon is bonded to two methoxy groups, one hydrogen and one methyl group. This is the dimethyl acetal formed from ethanal and methanol.

Step 2: Compare the structures in the remaining options Option (A), $\text{CH}_3\text{CH}_2\text{OCH}_3$, is an ether with only one oxygen linkage. In (B), the carbon bearing both oxygen atoms also bears two methyl groups and no hydrogen; in the CBSE aldehyde/ketone distinction, it is a cyclic ketal. Option (D), $\text{CH}_3\text{CH}(\text{OH})(\text{OCH}_3)$, retains a hydroxyl group and is a hemiacetal.

Step 3: Conclusion $\text{CH}_3\text{CH}(\text{OCH}_3)_2$ is the acetal. Hence, the correct option is (C).

Quick Tip to Solve: Find a carbon bearing two alkoxy groups and one hydrogen; an OH on that carbon signals a hemiacetal.

14. The crystal field splitting energy in tetrahedral crystal field (Δ_t) is equal to:

[1 mark]

- (A) $\frac{4}{9}\Delta_0$
(B) $\frac{9}{4}\Delta_0$
(C) $\frac{4}{3}\Delta_0$
(D) $2\Delta_0$

Correct Answer: (A) $\frac{4}{9}\Delta_0$

Solution:

Concept:

- For the same metal ion and ligands, the tetrahedral splitting is related to octahedral splitting by $\Delta_t = \frac{4}{9}\Delta_o$.
- Tetrahedral splitting is smaller because there are fewer ligands and none lies directly along a d-orbital axis.

Step 1: Use the standard splitting relation The given quantity is the energy separation of the two sets of d orbitals in a tetrahedral field. Comparing it with the corresponding octahedral field gives

$$\Delta_t = \frac{4}{9}\Delta_o \approx 0.444\Delta_o.$$

Thus the required factor is less than unity.

Quick Tip to Solve: Check that the tetrahedral splitting is smaller, then select the standard factor 4/9.

Step 2: Check each proposed ratio Option (A) supplies exactly the factor 4/9. Option (B), 9/4, reverses the relationship. Options (C) and (D) give factors 4/3 and 2, respectively. All three alternatives make tetrahedral splitting larger than octahedral splitting, contrary to the standard relation.

Step 3: Conclusion $\Delta_t = \frac{4}{9}\Delta_o$. Hence, the correct option is (A).

Quick Tip to Solve: Check that the tetrahedral splitting is smaller, then select the standard factor 4/9.

15. Assertion (A): When NaCl is added to water, a depression in freezing point is observed.

Reason (R): The vapour pressure of solution is increased which causes depression in freezing point.

[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 non-volatile solute lowers the vapour pressure of the solvent and produces colligative effects.
- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality.

Step 1: Judge the assertion The assertion is true. Dissolved NaCl supplies solute particles (mainly Na^+ and Cl^- ions) and lowers the freezing point of water. Thus the solution freezes at a temperature below that of pure water.

Step 2: Judge the reason The reason is false. Adding a non-volatile solute decreases the vapour pressure of water; it does not increase it. The decreased chemical potential of liquid water shifts equilibrium with solid water to a lower temperature.

Step 3: Check the explanation and choices Because R makes the opposite claim about vapour pressure, it cannot explain A. Options (A) and (B) require a true reason, while (D) requires a false assertion; all three are excluded.

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

Quick Tip to Solve: Remember the direction: adding salt lowers both the vapour pressure and the freezing point of water.

16. Assertion (A): Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.

Reason (R): Acetylation decreases the activating effect of the amino group.

[1 mark]

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

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

Solution:

Concept:

- The $-NH_2$ group strongly activates the benzene ring towards electrophilic substitution.
- Acetylation converts $-NH_2$ into $-NHCOCH_3$, reducing its activating effect while retaining ortho/para direction.

Step 1: Judge the assertion The assertion is true. Direct bromination of aniline in bromine water readily gives 2,4,6-tribromoaniline. To obtain monobromination conveniently, aniline is first acetylated to acetanilide, then brominated, and the protecting acetyl group is hydrolysed.

Step 2: Judge the reason The reason is true. In acetanilide, the nitrogen lone pair is also delocalised towards the carbonyl group. It is therefore less available to activate the benzene ring than in free aniline.

Step 3: Connect the reason to the assertion The reduced activation controls substitution, giving predominantly para-bromoacetanilide on bromination. Hydrolysis then gives para-bromoaniline. This is exactly why acetyl protection permits convenient monobromination. Option (B) misses this causal link; (C) and (D) incorrectly reject true statements.

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

Quick Tip to Solve: For controlled bromination of aniline, protect as acetanilide, brominate, then hydrolyse the amide.

17. Assertion (A): Limiting molar conductivity (Λ_m°) is obtained by the extrapolation of the Λ_m versus $C^{1/2}$ curve of strong electrolyte.

Reason (R): Λ_m° for weak electrolytes is obtained by using Kohlrausch's law.

[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: (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

Solution:

Concept:

- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - K\sqrt{C}$; the intercept at $C = 0$ is the limiting molar conductivity.
- Kohlrausch's law states $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$, using independent limiting ionic contributions.

Step 1: Judge the assertion The assertion is true. Strong electrolytes are almost completely dissociated. Their low-concentration plot of molar conductivity against $\sqrt{C}$ is approximately linear, so extending it to zero concentration yields Λ_m° .

Step 2: Judge the reason The reason is also true. A weak electrolyte dissociates progressively on dilution; its conductivity plot is strongly curved and direct extrapolation is unreliable. Its limiting value is therefore calculated from suitable strong-electrolyte limiting values using Kohlrausch's law.

Step 3: Test whether R explains A R describes the method for weak electrolytes. It does not explain why the strong-electrolyte plot can be extrapolated: that follows from the strong-electrolyte concentration relation. Thus option (A) wrongly claims an explanatory link, and (C) and (D) wrongly label one statement false.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence, the correct option is (B).

Quick Tip to Solve: Separate the two methods: extrapolate strong electrolytes; combine ionic contributions for weak electrolytes.

18. Assertion (A): $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is positive (+ 0.34 V).

Reason (R): Copper has high $\Delta_a H^\circ$ and low $\Delta_{\text{hyd}} H^\circ$.

[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:

- The standard reduction potential compares $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ with the standard hydrogen electrode.
- Formation of aqueous metal ions involves atomisation and ionisation energy costs, opposed by energy released during hydration.

Step 1: Judge the assertion The assertion is true: the standard potential of the Cu^{2+}/Cu couple is +0.34 V. Consequently copper metal is relatively resistant to oxidation to aqueous Cu^{2+} under standard conditions.

Step 2: Judge the reason The reason is true in the intended energy-balance sense. Copper has a high atomisation enthalpy, while hydration supplies comparatively insufficient energy compensation. Here low hydration enthalpy means the magnitude of the energy released, since hydration itself is exothermic.

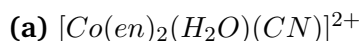
Step 3: Explain the potential and eliminate alternatives The energy required for atomisation and ionisation is not adequately offset by hydration. Copper therefore has little tendency to form aqueous ions by oxidation, consistent with a positive standard reduction potential. R supplies the stated explanation of A. Option (B) denies that link; (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: For copper, compare the energy needed to form gaseous ions with the energy recovered by hydration.

Section B (14 marks)

19. Write IUPAC names of the following:



[2 marks]

Solution:

Concept:

- Name ligands alphabetically, ignoring multiplicative prefixes; then name the metal and its oxidation state in Roman numerals.
- Water, ammonia and ethane-1,2-diamine (en) are neutral ligands; cyanido is CN^- . A cationic complex retains the ordinary metal name.

Step 1: Name complex (a) Let the cobalt oxidation state be x . The two en ligands and aqua ligand are neutral, while cyanido has charge -1 . Hence $x - 1 = +2$, giving $x = +3$. Alphabetical ligand order is aqua, cyanido, ethane-1,2-diamine. The two complex ligand names require the prefix bis. Thus the name is aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion.

Step 2: Name compound (b) The two chloride ions outside the brackets have total charge -2 , so the complex cation is $[Ni(NH_3)_6]^{2+}$. All six ammonia ligands are neutral, giving nickel oxidation state $+2$. Six ammine ligands are named hexaammine. Name the complex cation first and the chloride counterion second: hexaamminenickel(II) chloride.

Step 3: Conclusion (a) Aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion.
(b) Hexaamminenickel(II) chloride.

Quick Tip to Solve: Count only ligands inside the brackets; use outside chloride ions to determine the complex charge.

20. Name the cell which:

(a) was used in Apollo Space programme.

(b) is used in automobiles and inverters.

(c) is suitable for hearing aids and watches.

(d) does not give a steady potential and is used in transistors.

[2 marks]

Solution:

Concept:

- Choose a cell from its characteristic application, size, discharge behaviour and ability to be recharged.
- Fuel cells continuously consume supplied reactants; storage batteries can be recharged, while primary cells are normally discarded after use.

Step 1: Identify the Apollo cell (a) The hydrogen-oxygen fuel cell was used in the Apollo Space programme. Hydrogen is oxidised and oxygen is reduced, with the overall reaction $2H_2 + O_2 \rightarrow 2H_2O$.

Quick Tip to Solve: Match Apollo with a fuel cell, vehicles with a rechargeable lead battery, and tiny devices with a mercury cell.

It supplies electrical energy, and the water formed was useful to astronauts.

Step 2: Identify the rechargeable storage battery (b) The lead storage battery (lead-acid accumulator) is used in automobiles and inverters. It has a lead anode, a lead dioxide cathode and sulphuric acid electrolyte. Its discharge reaction can be reversed by charging, allowing repeated use.

Step 3: Identify the compact steady-potential cell (c) The mercury cell is suitable for hearing aids and watches. It is a small primary cell with a zinc-mercury amalgam anode and mercury(II) oxide cathode; its approximately constant potential makes it useful in such low-current devices.

Step 4: Identify the transistor cell (d) The dry cell, or Leclanche cell, is used in transistors. It contains a zinc container and a carbon rod surrounded by manganese dioxide. Its electrolyte paste composition changes during discharge, so it does not provide a steady potential throughout use.

Step 5: Conclusion (a) Hydrogen-oxygen fuel cell; (b) lead storage battery; (c) mercury cell; (d) dry (Leclanche) cell.

Quick Tip to Solve: Match Apollo with a fuel cell, vehicles with a rechargeable lead battery, and tiny devices with a mercury cell.

21(a). What type of deviation from Raoult's law is shown by a mixture of ethanol and acetone? Give reason. [2 marks]

Solution:

Concept:

- Raoult's law gives $p_i = x_i p_i^\circ$, where x_i is the liquid mole fraction and p_i° is the vapour pressure of pure component i .
- Positive deviation occurs when unlike-molecule attractions are weaker overall than those in the pure liquids, allowing molecules to escape more readily.

Step 1: Identify the interactions before mixing Pure ethanol molecules associate through intermolecular hydrogen bonding between their hydroxyl groups. These attractive forces hold ethanol molecules together and reduce their tendency to enter the vapour phase.

Step 2: Explain the effect of acetone Adding acetone disrupts the hydrogen-bonded association of ethanol molecules. Although ethanol can interact with acetone, the resulting unlike-molecule interactions are weaker overall than the original interactions in the pure liquids. Molecules therefore escape more readily, so the observed vapour pressure is greater than the value predicted by Raoult's law: $p_{\text{observed}} > p_{\text{Raoult}}$.

Step 3: Conclusion The ethanol-acetone mixture shows **positive deviation from Raoult's law**, because acetone disrupts ethanol's hydrogen bonding and increases the escaping tendency of the molecules.

Quick Tip to Solve: For ethanol mixed with acetone, connect disruption of ethanol hydrogen bonding directly to higher vapour pressure and positive deviation.

21(b). Define Azeotrope. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. [2 marks]

Solution:

Concept:

- An azeotrope is a liquid mixture that boils at a constant temperature and has the same composition in its liquid and vapour phases at a given pressure.
- Negative deviation from Raoult's law means that the mixture's vapour pressure is lower than the ideal value because unlike-molecule attractions are stronger.

Step 1: Define an azeotrope At the azeotropic composition, the vapour formed on boiling has the same composition as the liquid mixture. Consequently, boiling does not change the composition of the remaining liquid, and the mixture distils at a constant temperature. Its components cannot be separated by fractional distillation at that pressure.

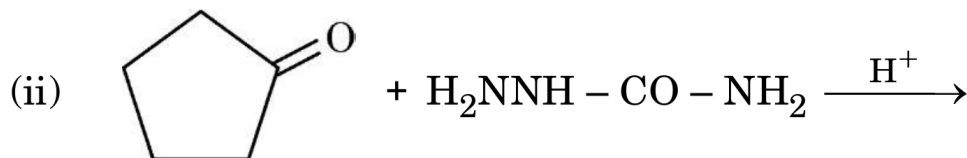
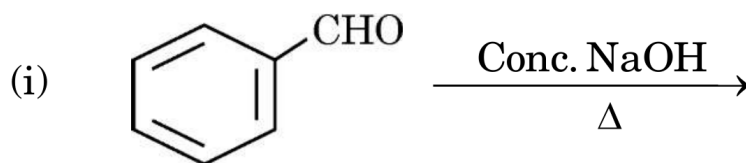
Step 2: Relate negative deviation to boiling temperature Stronger attractions between unlike molecules lower the vapour pressure below that predicted by Raoult's law. A higher temperature is therefore needed to make the vapour pressure equal to the external pressure. A sufficiently large negative deviation produces a maximum in the boiling-temperature curve, giving a maximum-boiling azeotrope. Nitric acid and water form a standard example of this type.

Step 3: Conclusion An azeotrope has identical liquid and vapour compositions and boils at a constant temperature. Negative deviation produces a **maximum-boiling azeotrope**; an example is **nitric acid and water**.

Quick Tip to Solve: Remember the inverse relation: negative vapour-pressure deviation corresponds to a higher boiling temperature and a maximum-boiling azeotrope.

22(a). Write the products of the following reactions:

[2 marks]

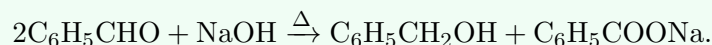


Solution:

Concept:

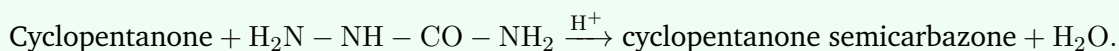
- Aldehydes without an α -hydrogen undergo the Cannizzaro reaction in concentrated alkali: one molecule is oxidised while another is reduced.
- Semicarbazide, $\text{H}_2\text{N} - \text{NH} - \text{CO} - \text{NH}_2$, condenses with a carbonyl group through its terminal amino group to form a semicarbazone and water.

Step 1: Identify the products of reaction (i) The printed reactant is benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$. It has no α -hydrogen and undergoes disproportionation in concentrated sodium hydroxide. The reduced product is benzyl alcohol and the oxidised product remains as sodium benzoate in the alkaline reaction mixture:



Benzoic acid would require a subsequent acidification, which is not shown here.

Step 2: Identify the product of reaction (ii) The five-membered cyclic ketone shown is cyclopentanone. Its carbonyl oxygen is replaced by $=\text{N} - \text{NH} - \text{CO} - \text{NH}_2$ on condensation with semicarbazide in the presence of acid:



The five-membered carbon ring is retained; the former carbonyl carbon bears the exocyclic $\text{C} = \text{N} - \text{NH} - \text{CO} - \text{NH}_2$ group.

Step 3: Conclusion (i) **Benzyl alcohol and sodium benzoate.**

(ii) **Cyclopentanone semicarbazone**, with $\text{C} = \text{N} - \text{NH} - \text{CO} - \text{NH}_2$ at the original carbonyl position.

Quick Tip to Solve: Count the ring vertices before naming a cyclic ketone, and retain the carboxylate salt when a Cannizzaro reaction has no acid work-up.

22(b). Do the following conversions in not more than two steps:

(i) Toluene to Benzoic acid

(ii) Benzaldehyde to 1-Phenylethanol

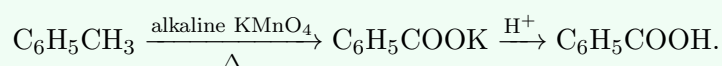
[2 marks]

Solution:

Concept:

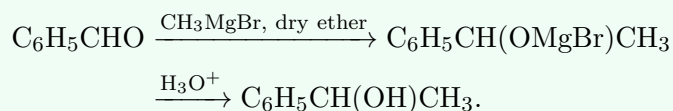
- Hot alkaline potassium permanganate oxidises an alkyl side chain having a benzylic hydrogen to a carboxylate group; acidification gives the carboxylic acid.
- A Grignard reagent RMgX adds R to the carbonyl carbon. Hydrolysis of the magnesium alkoxide gives an alcohol.

Step 1: Convert toluene into benzoic acid First heat toluene with alkaline KMnO_4 to oxidise its methyl side chain to potassium benzoate. Then acidify to obtain benzoic acid:



Oxidation changes the side chain while retaining the benzene ring. Acidification protonates the carboxylate ion, so the final product is the acid rather than its salt.

Step 2: Convert benzaldehyde into 1-phenylethanol Add methylmagnesium bromide to benzaldehyde in dry ether, then hydrolyse the resulting magnesium alkoxide with dilute acid:



The methyl group supplies the extra carbon atom required in the target. Acid hydrolysis supplies the hydroxyl hydrogen, yielding the secondary alcohol 1-phenylethanol.

Step 3: Conclusion (i) Use **hot alkaline KMnO_4 , followed by acidification.**

(ii) Use **CH_3MgBr in dry ether, followed by acidic hydrolysis.** Each conversion requires two steps.

Quick Tip to Solve: Compare carbon counts first: benzaldehyde needs one added methyl carbon, so choose methylmagnesium bromide followed by hydrolysis.

23. The rate constant for the first order decomposition of N_2O_5 is given by the following equation:

$$\log k = 23.6 - \frac{2 \times 10^4 \text{ K}}{T}$$

Calculate E_a for this reaction.

[$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

[2 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For a common logarithm, $\log k = \log A - \frac{E_a}{2.303RT}$. Thus the coefficient of $1/T$ is $-E_a/(2.303R)$.

Step 1: Compare the temperature-dependent terms The printed expression uses $\log k$, so the common-logarithm form must be used, rather than the natural-logarithm form. Comparing $\log k = 23.6 - (2 \times 10^4 \text{ K})/T$ with the Arrhenius equation gives

$$\frac{E_a}{2.303R} = 2 \times 10^4 \text{ K}.$$

The constant 23.6 represents $\log A$ and is not needed to calculate the activation energy.

Step 2: Substitute the gas constant Using $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$,

$$\begin{aligned} E_a &= 2.303 \times 8.314 \times 2 \times 10^4 \\ &= 3.8294 \times 10^5 \text{ J mol}^{-1}. \end{aligned}$$

The kelvin in the coefficient cancels the inverse-kelvin unit in R .

Step 3: Conclusion The activation energy is $E_a \approx 3.83 \times 10^5 \text{ J mol}^{-1} = 383 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: When the equation contains $\log k$, multiply the coefficient of $1/T$ by $2.303R$; for $\ln k$, multiply by R .

24. An alkyl halide (A) of molecular formula $\text{C}_6\text{H}_{13}\text{Cl}$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12} . Both alkenes on hydrogenation give 2,3-dimethylbutane. Write the structures of (A), (B) and (C). [2 marks]

Solution:

Concept:

- Alcoholic KOH causes β -elimination: chlorine is removed from the α -carbon and hydrogen from an adjacent β -carbon, producing a double bond.
- Hydrogenation adds H_2 across a double bond without changing the carbon skeleton. Both alkenes must therefore have the skeleton of 2,3-dimethylbutane.

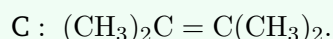
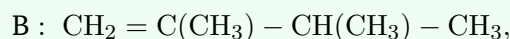
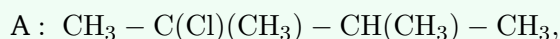
Step 1: Identify the alkyl chloride The required carbon skeleton is $\text{CH}_3 - \text{CH}(\text{CH}_3) - \text{CH}(\text{CH}_3) - \text{CH}_3$. Place chlorine on one of the equivalent central carbons to obtain $\text{CH}_3 - \text{C}(\text{Cl})(\text{CH}_3) - \text{CH}(\text{CH}_3) - \text{CH}_3$,

Quick Tip to Solve: Keep the hydrogenation product carbon skeleton fixed, then locate chlorine where two nonequivalent beta-hydrogen sites are available.

namely 2-chloro-2,3-dimethylbutane. Its formula is $C_6H_{13}Cl$. This position has two distinct kinds of neighbouring carbon bearing hydrogen.

Step 2: Eliminate hydrogen from each distinct beta position Removal of a hydrogen from either equivalent methyl group next to the chlorine-bearing carbon gives $CH_2 = C(CH_3) - CH(CH_3) - CH_3$, 2,3-dimethylbut-1-ene. Removal from the neighbouring methine carbon gives $(CH_3)_2C = C(CH_3)_2$, 2,3-dimethylbut-2-ene. Each has formula C_6H_{12} , and adding hydrogen across either double bond gives 2,3-dimethylbutane. The more substituted internal alkene is the major elimination product.

Step 3: Conclusion The structures are



The labels B and C can be interchanged.

Quick Tip to Solve: Keep the hydrogenation product carbon skeleton fixed, then locate chlorine where two nonequivalent beta-hydrogen sites are available.

25. Write the mechanism of acid dehydration of ethanol to yield ethene.

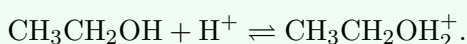
[2 marks]

Solution:

Concept:

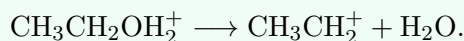
- Heating ethanol with concentrated H_2SO_4 at about 443 K produces ethene by acid-catalysed dehydration.
- Protonation converts the poor leaving group $-OH$ into $-OH_2^+$, which can leave as water; the acid catalyst is regenerated.

Step 1: Protonate the alcohol oxygen A lone pair on oxygen accepts a proton from the acid. The resulting protonated alcohol is an oxonium ion:



This activation is necessary because an unprotonated hydroxide ion is a poor leaving group.

Step 2: Remove water In the standard textbook representation, the carbon-oxygen bond breaks with its electron pair moving to oxygen. Water leaves and the ethyl carbocation is represented as the intermediate:



This is the slow step in the usual board-level mechanism.

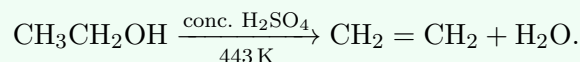
Step 3: Lose a beta proton and form the double bond A base such as water removes a hydrogen from the adjacent methyl carbon. The electrons of that carbon-hydrogen bond form the carbon-carbon double bond:



Quick Tip to Solve: Write protonation first: water can leave from an oxonium ion, whereas the unprotonated hydroxyl group is a poor leaving group.

The proton is returned to the reaction medium, completing the catalytic cycle.

Step 4: Conclusion The overall dehydration is



Ethene is formed and the acid catalyst is regenerated.

Quick Tip to Solve: Write protonation first: water can leave from an oxonium ion, whereas the unprotonated hydroxyl group is a poor leaving group.

Section C (15 marks)

26. Account for the following:

(a) Benzyl chloride is highly reactive towards $\text{S}_{\text{N}}1$ reaction.

(b) $(\pm)$ -Butan-2-ol is optically inactive, though it contains a chiral carbon atom.

(c) Chloroform is stored in closed dark coloured bottles.

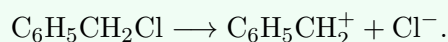
[3 marks]

Solution:

Concept:

- An $\text{S}_{\text{N}}1$ reaction depends on carbocation formation; resonance stabilisation makes ionisation easier.
- A racemic mixture contains equal amounts of two enantiomers whose optical rotations cancel.
- Chloroform can undergo oxidation in air in the presence of light to form poisonous phosgene, COCl_2 .

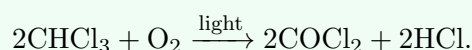
Step 1: (a) Reactivity of benzyl chloride Benzyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, loses chloride to form the benzyl carbocation:



The empty orbital at the benzylic carbon conjugates with the aromatic ring. The positive charge is delocalised over the benzylic carbon and the ortho and para positions through resonance. Stabilisation of this carbocation favours the ionisation step and accounts for the high reactivity towards $\text{S}_{\text{N}}1$.

Step 2: (b) Optical inactivity of racemic butan-2-ol Carbon 2 of $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$ is attached to four different groups: H, OH, CH_3 and C_2H_5 . Each pure enantiomer is optically active. However, the symbol $(\pm)$ specifies an equimolar mixture of the two enantiomers. Their rotations have equal magnitudes and opposite signs, so the net rotation is zero. This optical inactivity is due to external compensation, not absence of a chiral centre.

Step 3: (c) Storage of chloroform In the presence of light, atmospheric oxygen slowly oxidises chloroform to highly poisonous carbonyl chloride, or phosgene:



A tightly closed bottle restricts contact with air and its oxygen. A dark-coloured bottle restricts light, thereby suppressing this harmful oxidation. Both storage precautions address the conditions required

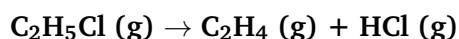
Quick Tip to Solve: Distinguish a chiral molecule from a racemic sample: the molecule can rotate light while equal amounts of its enantiomers cancel in the sample.

for phosgene formation.

Step 4: Conclusion (a) The resonance-stabilised benzyl carbocation favours S_N1 . (b) Equal opposite rotations in the racemic mixture cancel. (c) Closed, dark bottles suppress light-assisted aerial oxidation of chloroform to poisonous phosgene.

Quick Tip to Solve: Distinguish a chiral molecule from a racemic sample: the molecule can rotate light while equal amounts of its enantiomers cancel in the sample.

27. The following data were obtained during the first order thermal decomposition of C_2H_5Cl at a constant volume:



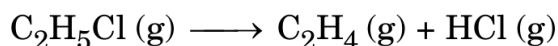
Experiment 1: Time = 0 s, Total pressure = 0.4 atm

Experiment 2: Time = 100 s, Total pressure = 0.6 atm

Calculate the rate constant.

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

[3 marks]



Experiment	Time (s^{-1})	Total pressure (atm)
1	0	0.4
2	100	0.6

Solution:

Concept:

- For a first-order reaction, $k = \frac{2.303}{t} \log \frac{p_0}{p_A}$, where p_0 is the initial reactant pressure and p_A is its partial pressure at time t .
- At constant volume and temperature, pressure is proportional to the number of moles. Each mole of ethyl chloride decomposes into two moles of gaseous products, so total pressure increases with decomposition.

Step 1: Relate the total pressure to decomposition Initially only ethyl chloride is present, with $p_0 = 0.4$ atm. Let x be the pressure corresponding to the amount decomposed after 100 s. The remaining reactant pressure is $p_0 - x$, while each product has pressure x . Thus

$$p_t = (p_0 - x) + x + x = p_0 + x, \quad x = 0.6 - 0.4 = 0.2 \text{ atm.}$$

Step 2: Find the remaining reactant pressure The first-order equation uses the partial pressure of undecomposed reactant, not the measured total pressure. Hence

$$p_A = p_0 - x = 0.4 - 0.2 = 0.2 \text{ atm.}$$

Quick Tip to Solve: For one gaseous reactant giving two gaseous products, first calculate its remaining pressure as $2p_0 - p_t$.

Half of the original ethyl chloride remains.

Step 3: Apply the integrated rate equation Substitute $t = 100$ s and the reactant pressures:

$$k = \frac{2.303}{100} \log \frac{0.4}{0.2} = \frac{2.303 \times 0.3010}{100} = 0.00693203 \text{ s}^{-1}.$$

The pressure ratio is dimensionless, and the first-order rate constant has units of inverse time.

Step 4: Conclusion The rate constant is $k = 6.93 \times 10^{-3} \text{ s}^{-1}$.

Quick Tip to Solve: For one gaseous reactant giving two gaseous products, first calculate its remaining pressure as $2p_0 - p_t$.

28. If benzoic acid ($M = 122 \text{ g mol}^{-1}$) is associated into a dimer when dissolved in benzene and the osmotic pressure of a solution of 6.1 g of benzoic acid in 100 mL benzene is 6.5 atm at 27°C , then what is the percentage association of benzoic acid?

(Given: $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- Osmotic pressure obeys $\pi = iCRT$, where i is the van't Hoff factor and C is the concentration calculated using the normal molar mass.
- For association into dimers, $i = 1 - \alpha/2$, where α is the fraction of original acid molecules that associate. Association reduces the total number of solute particles.

Step 1: Calculate the analytical concentration The amount of benzoic acid before accounting for association is

$$n = \frac{6.1 \text{ g}}{122 \text{ g mol}^{-1}} = 0.050 \text{ mol}.$$

With $V = 100 \text{ mL} = 0.100 \text{ L}$, the concentration is $C = 0.050/0.100 = 0.50 \text{ mol L}^{-1}$. The absolute temperature is $T = 27 + 273 = 300 \text{ K}$.

Step 2: Find the particle reduction factor If the acid did not associate, its osmotic pressure would be

$$\pi_0 = CRT = 0.50 \times 0.0821 \times 300 = 12.315 \text{ atm}.$$

The observed pressure is smaller, consistent with association. Hence

$$i = \frac{\pi}{\pi_0} = \frac{6.5}{12.315} = 0.5278.$$

This factor compares the actual number of solute particles with the number that would be present without association.

Step 3: Convert the factor into percentage association For $2\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons (\text{C}_6\text{H}_5\text{COOH})_2$, take an initial amount n . If a fraction α associates, free molecules amount to $n(1 - \alpha)$, while dimers amount

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; the factor of two arises because two monomers form one particle.

to $n\alpha/2$. Their total is $n(1 - \alpha/2)$, giving

$$\begin{aligned}\alpha &= 2(1 - i) \\ &= 2(1 - 0.5278) = 0.9444.\end{aligned}$$

Multiplying this fraction by 100 gives the percentage of original acid molecules associated.

Step 4: Conclusion The percentage association of benzoic acid is 94.4% approximately.

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; the factor of two arises because two monomers form one particle.

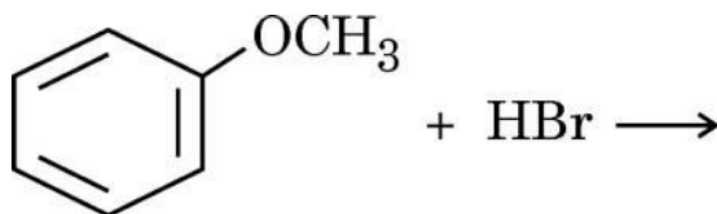
29(a). (i) Write hydroboration-oxidation reaction with an example.

(ii) Write the products of the following reaction:



(iii) Why is p-nitrophenol more acidic than phenol?

[3 marks]

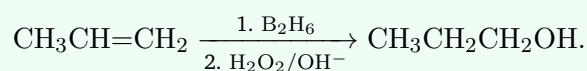


Solution:

Concept:

- Hydroboration followed by oxidation adds water across an alkene in the anti-Markovnikov orientation: the hydroxyl group appears on the less substituted carbon.
- In an aryl methyl ether, hydrogen bromide cleaves the alkyl-oxygen bond; the aryl-oxygen bond resists substitution.
- Acidity increases when the conjugate base is stabilised. A para nitro group withdraws electron density by inductive and resonance effects.

Step 1: Explain hydroboration-oxidation with an example An alkene first reacts with diborane, B_2H_6 , followed by oxidation using hydrogen peroxide in alkaline medium. Boron attaches preferentially to the less substituted carbon; oxidation replaces the carbon-boron bond by a carbon-oxygen bond. For example, propene gives propan-1-ol:

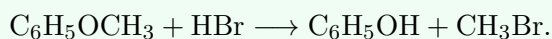


This is anti-Markovnikov hydration and does not involve a carbocation rearrangement.

Step 2: Identify the products of anisole cleavage The ether oxygen is protonated by HBr , after which bromide attacks the unhindered methyl carbon by an $\text{S}_{\text{N}}2$ process. The products are phenol and

Quick Tip to Solve: In anisole cleavage retain the phenyl-oxygen bond; for acidity comparisons always compare the stability of the conjugate bases.

bromomethane:



Cleavage occurs at the methyl–oxygen bond. The phenyl–oxygen bond has partial double-bond character through resonance, and substitution at the aromatic sp^2 carbon is not the normal ether-cleavage route.

Step 3: Compare the acidity of the two phenols Loss of H^+ from phenol produces phenoxide, whereas p -nitrophenol produces p -nitrophenoxide. The para $-\text{NO}_2$ group exerts both an electron-withdrawing inductive effect and a resonance effect. It delocalises and stabilises the negative charge of the conjugate base more effectively than in unsubstituted phenoxide. This increased conjugate-base stability favours proton loss, making p -nitrophenol more acidic.

Step 4: Conclusion (i) Hydroboration–oxidation of propene gives propan-1-ol. (ii) The products are phenol and bromomethane. (iii) Nitro-group stabilisation of the conjugate base increases acidity.

Quick Tip to Solve: In anisole cleavage retain the phenyl–oxygen bond; for acidity comparisons always compare the stability of the conjugate bases.

OR

29(b). (i) What happens when phenol reacts with

(1) Conc. HNO_3 , and

(2) CHCl_3 in presence of aqueous NaOH followed by acidification?

Write equations only.

(ii) Why does the reaction of CH_3ONa with $(\text{CH}_3)_3\text{C-Br}$ give 2-methylpropene and not $(\text{CH}_3)_3\text{C-OCH}_3$?

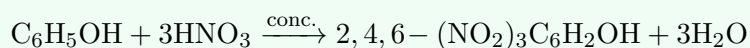
[3 marks]

Solution:

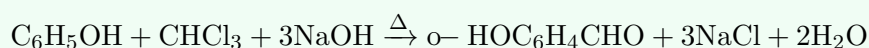
Concept:

- Phenol undergoes electrophilic substitution readily because its $-\text{OH}$ group activates the benzene ring and directs substitution to ortho and para positions.
- The Reimer–Tiemann reaction introduces a formyl group, $-\text{CHO}$, predominantly at the ortho position of phenol. A tertiary halide reacts with a strong base mainly by elimination.

Step 1: (i)(1) Reaction with concentrated nitric acid



Step 2: (i)(2) Reaction with chloroform and aqueous alkali

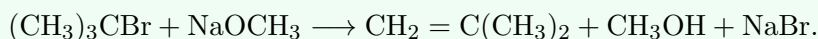


Aqueous NaOH , followed by acidification: $\text{o- HOC}_6\text{H}_4\text{CHO}$

Step 3: (ii) Explain elimination with a tertiary halide In $(\text{CH}_3)_3\text{CBr}$, the carbon bonded to bromine is

Quick Tip to Solve: For Williamson ether synthesis choose a primary alkyl halide; a tertiary halide with an alkoxide gives elimination.

tertiary and sterically hindered. Backside attack by methoxide, required for the S_N2 step of Williamson ether synthesis, is strongly hindered. Methoxide instead acts as a strong base and removes a hydrogen from a neighbouring methyl group while bromide leaves. This β -elimination forms the alkene:



Thus, using a tertiary alkyl halide favours elimination over the nucleophilic substitution needed to produce the ether.

Step 4: Conclusion The products in (i) are 2,4,6-trinitrophenol (picric acid) and predominantly 2-hydroxybenzaldehyde (salicylaldehyde), respectively. In (ii), steric hindrance prevents efficient S_N2 ether formation, and methoxide gives 2-methylpropene by elimination.

Quick Tip to Solve: For Williamson ether synthesis choose a primary alkyl halide; a tertiary halide with an alkoxide gives elimination.

30. Answer any three of the following questions:

- Explain the type of hybridization in $[\text{Fe}(\text{CN})_6]^{3-}$ on the basis of valence bond theory. (Given: Atomic number of Fe = 26)
- Draw the geometrical isomers of $[\text{PtCl}_2(\text{en})_2]^{2+}$ ion.
- $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why?
- Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give one example of ambidentate ligand.

[3 marks]

Solution:

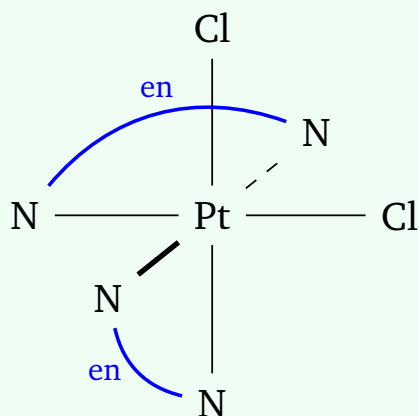
Concept:

- Valence bond theory assigns hybridisation using the metal oxidation state, its electronic configuration and the pairing caused by ligands. The number of unpaired electrons determines magnetic behaviour.
- Ethylenediamine, en, is a bidentate ligand with two nitrogen donor atoms. Ambidentate ligands can bind through either of two different donor atoms.

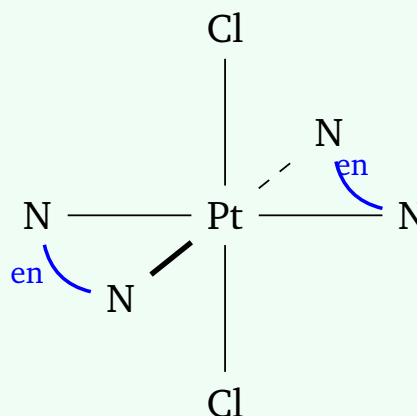
Step 1: (a) Hybridisation of hexacyanidoferrate(III) For $[\text{Fe}(\text{CN})_6]^{3-}$, let the oxidation state of Fe be x . Then $x - 6 = -3$, so $x = +3$. Fe has configuration $[\text{Ar}]3d^64s^2$; thus Fe^{3+} is $[\text{Ar}]3d^5$. The strong-field CN^- ligands cause pairing in the $3d$ orbitals. Five electrons occupy three $3d$ orbitals as two pairs and one unpaired electron. The two vacant $3d$ orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrid orbitals. The complex is inner-orbital octahedral and has one unpaired electron.

Step 2: (b) Geometrical isomers Two en ligands supply four donor atoms and two chloride ligands supply two more, giving octahedral coordination. In the cis isomer the two Cl ligands are adjacent, at 90° ; in the trans isomer they are opposite, at 180° . Each blue arc in the drawing joins the two nitrogen donors belonging to one en ligand. The bold bond points towards the viewer and the dashed bond points away.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; for cis/trans compare the positions of the two chloride ligands.



cis: adjacent Cl ligands



trans: opposite Cl ligands

Octahedral cis and trans isomers; each en joins a pair of adjacent nitrogen donors.

Step 3: (c) Compare the nickel complexes In $[\text{NiCl}_4]^{2-}$, Ni is +2 and has a $3d^8$ configuration. Chloride is a weak-field ligand; the tetrahedral sp^3 complex retains two unpaired electrons and is paramagnetic. In $[\text{Ni}(\text{CO})_4]$, neutral CO gives Ni oxidation state zero. CO causes pairing and electron redistribution so that the metal has a filled $3d^{10}$ set. Four empty sp^3 hybrid orbitals accept ligand lone pairs. All electrons are paired, making this tetrahedral complex diamagnetic.

Step 4: (d) Isomerism due to an ambidentate ligand Attachment of an ambidentate ligand through different donor atoms produces linkage isomerism. For example, NO_2^- can coordinate through nitrogen as a nitro ligand, $\text{M} - \text{NO}_2$, or through oxygen as a nitrito ligand, $\text{M} - \text{ONO}$.

Step 5: Conclusion (a) d^2sp^3 , inner-orbital octahedral. (b) cis and trans geometrical isomers, as drawn. (c) Two unpaired electrons in $[\text{NiCl}_4]^{2-}$, none in $[\text{Ni}(\text{CO})_4]$. (d) Linkage isomerism; an example of an ambidentate ligand is NO_2^- .

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; for cis/trans compare the positions of the two chloride ligands.

Section D (8 marks)

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

31(i). Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups - monosaccharides, oligosaccharides and polysaccharides. Monosaccharides are held together by glycosidic linkages to form disaccharides like sucrose, maltose or polysaccharides like starch and cellulose.

Another biomolecule: proteins are polymers of α -amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. Structure and shape of proteins can be studied at four different levels i.e. primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

Answer the following questions:

What is the difference between a glycosidic linkage and peptide linkage?

[1 mark]

Solution:

Concept:

- A linkage joins monomer units in a larger biomolecule; its functional group distinguishes carbohydrate linkages from protein linkages.
- Both types can arise by condensation with loss of water, but the atoms forming the linkage differ.

Step 1: Identify the carbohydrate linkage A glycosidic linkage is an oxygen bridge, $C - O - C$, joining two monosaccharide units through the anomeric carbon of at least one unit. It occurs in disaccharides such as maltose and in polysaccharides.

Step 2: Identify the protein linkage A peptide linkage is an amide bond, $-CO - NH-$, formed between the carboxyl group of one α -amino acid and the amino group of another, with elimination of a water molecule. It joins amino-acid residues in proteins.

Step 3: Conclusion A glycosidic linkage is the $C - O - C$ bridge between sugar units; a peptide linkage is the $-CO - NH-$ bond between amino-acid residues.

Quick Tip to Solve: Identify the bridge: an oxygen between sugar units is glycosidic, whereas the carbonyl-nitrogen bond in proteins is peptide.

31(ii). Which amino acids are called essential amino acids?

[1 mark]

Solution:

Concept:

- Amino acids are the building units of proteins, and the body must obtain an adequate supply for protein synthesis.
- The term essential refers to the dietary requirement resulting from the body's inability to synthesise the amino acid in sufficient quantity.

Quick Tip to Solve: In a definition question connect essential with dietary supply, and explicitly state the inability to synthesise sufficiently.

Step 1: Use the physiological criterion Essential amino acids are those which the human body cannot synthesise, or cannot synthesise in amounts sufficient to meet its needs. Their classification depends on this inability, rather than on whether they occur in a particular protein.

Step 2: State how they are obtained They must therefore be supplied through the diet. For example, valine and lysine are essential amino acids. Amino acids that the body can synthesise sufficiently are termed non-essential, although they too are needed to make proteins.

Step 3: Conclusion Essential amino acids are amino acids that the body cannot synthesise adequately and must obtain from food.

Quick Tip to Solve: In a definition question connect essential with dietary supply, and explicitly state the inability to synthesise sufficiently.

31(iii). What are the common types of secondary structures of proteins? Write any two forces which stabilise the secondary and tertiary structures of protein. [2 marks]

Solution:

Concept:

- Secondary structure describes regular local folding of a polypeptide backbone; tertiary structure describes its overall three-dimensional folding.
- Hydrogen bonding involves attraction between a hydrogen attached to an electronegative atom and another electronegative atom. Disulphide linkages join two cysteine side chains.

Step 1: Identify the common secondary structures The two common forms are the α -helix and the β -pleated sheet. In an α -helix, the polypeptide chain coils into a regular helix. In a β -pleated sheet, extended segments of the chain lie alongside one another to form a sheet-like arrangement. Both depend on hydrogen bonding between backbone C = O and N – H groups.

Step 2: State two stabilising interactions Hydrogen bonds stabilise the secondary structures and also help stabilise tertiary folding. Disulphide linkages, –S – S–, between cysteine residues stabilise the tertiary structure by connecting different parts of a folded chain. Other tertiary interactions include ionic attractions, van der Waals forces and hydrophobic interactions; disulphide linkages are not the characteristic stabiliser of the secondary backbone arrangement.

Step 3: Conclusion The common secondary structures are the α -helix and β -pleated sheet. Two stabilising interactions are hydrogen bonds and disulphide linkages.

Quick Tip to Solve: Name both regular folds, then connect hydrogen bonds to the backbone and disulphide links to tertiary folding.

31(iii). Define denaturation of protein with an example. During denaturation which structures of protein lose their biological activity? [2 marks]

Solution:

Concept:

- A protein has a definite amino-acid sequence (primary structure) and a characteristic folded shape needed for biological activity.
- Denaturation disrupts the interactions maintaining the folded structure without ordinarily breaking the peptide bonds of the primary structure.

Step 1: Define denaturation and give an example Denaturation is the loss of the native conformation and biological activity of a protein when it is subjected to heat, a change in pH or suitable chemical agents. These conditions disturb the interactions that maintain its folded shape. For example, boiling an egg causes the albumin in egg white to denature and coagulate, producing the familiar opaque solid.

Step 2: Identify the affected structural levels During denaturation, the secondary and tertiary structures are disrupted: the regular local folding and the overall three-dimensional shape are lost. Consequently, the protein loses biological activity, since its function depends on this native shape. Its primary structure, namely the amino-acid sequence joined by peptide bonds, remains intact under ordinary denaturing conditions. Thus, denaturation should not be confused with hydrolysis of the polypeptide chain.

Step 3: Conclusion Denaturation is the loss of a protein's native shape and biological activity, as in coagulation of egg-white albumin on boiling. Secondary and tertiary structures are disrupted; primary structure remains intact.

Quick Tip to Solve: Remember boiled egg white: folding is destroyed, but denaturation does not ordinarily cut peptide bonds.

32. Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in an aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

Answer the following questions :

[4 marks]

32(i). Arrange the following in the increasing order of their pK_b values in aqueous solution: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$.

[1 mark]

Solution:

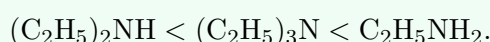
Concept:

- For a base, $pK_b = -\log_{10} K_b$; greater basic strength means a smaller pK_b .
- In aqueous ethylamines, electron donation, solvation of the conjugate acid and steric effects together determine basicity.

Step 1: Compare the aqueous basic strengths For ethyl-substituted amines in aqueous solution, the basicity order is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$. The secondary amine has a favourable combination of electron donation and solvation. The tertiary ethylamine is still more basic than the primary ethylamine; simply applying a universal primary-secondary-tertiary order would be incorrect.

Step 2: Convert basicity into the requested order Since the logarithm has a negative sign in the definition of pK_b , reverse the basic-strength order to obtain increasing pK_b . The strongest base comes first, followed by the tertiary amine, and the weakest of these three comes last.

Step 3: Conclusion Increasing pK_b :



Quick Tip to Solve: For aqueous ethylamines use secondary > tertiary > primary basicity, then reverse it for increasing pK_b .

32(ii). Aniline on nitration gives a substantial amount of m-nitroaniline, though amino group is o/p directing. Why?

[1 mark]

Solution:

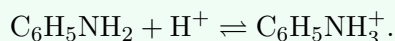
Concept:

- The free $-NH_2$ group donates its lone pair to the benzene ring and directs electrophilic substitution to ortho and para positions.
- Protonation removes the available lone pair and changes the directing influence of the amino

Quick Tip to Solve: Before applying a directing rule in strong acid, replace aniline by its protonated anilinium form.

group.

Step 1: Identify the species in the nitrating mixture The strongly acidic nitrating mixture protonates a substantial proportion of aniline to the anilinium ion:



Nitrogen in this ion no longer has a lone pair available for resonance donation to the ring.

Step 2: Apply the directing effect of the protonated group The positively charged $-\text{NH}_3^+$ group is electron withdrawing and meta directing. Nitration of the anilinium ion therefore produces the meta isomer. The ortho/para directing rule applies to free aniline; it cannot be applied unchanged to the protonated form present in strongly acidic solution.

Step 3: Conclusion A substantial amount of *m*-nitroaniline forms because aniline is protonated to the meta-directing anilinium ion in the strongly acidic nitrating mixture.

Quick Tip to Solve: Before applying a directing rule in strong acid, replace aniline by its protonated anilinium form.

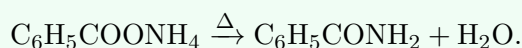
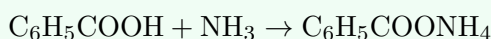
32(iii). An aromatic compound 'A' of molecular formula $\text{C}_7\text{H}_6\text{O}_2$ on treatment with aqueous ammonia and heating forms compound 'B'. Compound 'B' on heating with Br_2 and aqueous KOH gives a compound 'C' of molecular formula $\text{C}_6\text{H}_7\text{N}$. Write the structures of A, B and C. [2 marks]

Solution:

Concept:

- A carboxylic acid reacts with ammonia to give an ammonium carboxylate, which forms a primary amide on heating.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon from the carbon skeleton.

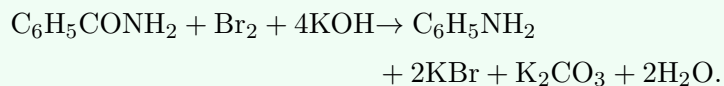
Step 1: Identify the aromatic acid and its amide The aromatic compound with formula $\text{C}_7\text{H}_6\text{O}_2$ that forms an amide on treatment with aqueous ammonia and heating is benzoic acid. Thus A has the condensed structure $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{OH}$. Ammonia first gives ammonium benzoate, and heating produces benzamide B, whose structure is $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH}_2$:



Step 2: Identify the Hofmann degradation product Benzamide undergoes Hofmann bromamide degradation with bromine and aqueous potassium hydroxide. The carbonyl carbon is lost, leaving the phenyl group directly bonded to the amino group. Hence C is aniline, $\text{C}_6\text{H}_5 - \text{NH}_2$, whose formula is

Quick Tip to Solve: In Hofmann degradation delete the amide carbonyl carbon and attach NH_2 directly to the remaining group.

C_6H_7N , as required. The balanced reaction is



Step 3: Conclusion A: benzoic acid, $C_6H_5 - C(=O) - OH$; B: benzamide, $C_6H_5 - C(=O) - NH_2$; C: aniline, $C_6H_5 - NH_2$.

Quick Tip to Solve: In Hofmann degradation delete the amide carbonyl carbon and attach NH_2 directly to the remaining group.

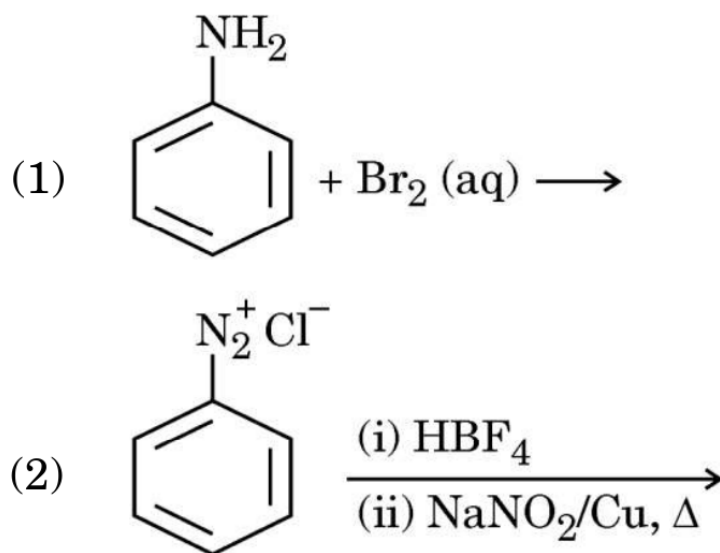
OR

32(iii). Complete the following reactions giving main products:

(1) Aniline + $Br_2(aq) \rightarrow$

(2) Benzenediazonium chloride $C_6H_5N_2^+Cl^- \xrightarrow[(ii) NaNO_2/Cu, \Delta]{(i) HBF_4}$

[2 marks]



Solution:

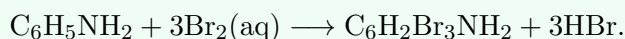
Concept:

- The amino group strongly activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- A diazonium group can be replaced by a nitro group using sodium nitrite and copper after converting the diazonium chloride into its tetrafluoroborate.

Step 1: (1) Bromination of aniline In bromine water, the strong activating effect of $-NH_2$ allows substitution at both ortho positions and the para position without a Lewis-acid catalyst. The main

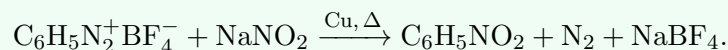
Quick Tip to Solve: Read the final diazonium-replacement reagent: sodium nitrite with copper introduces a nitro group even when HBF_4 is used first.

product is the white precipitate of 2,4,6-tribromoaniline:



Bromine occupies positions 2, 4 and 6 relative to the amino group.

Step 2: (2) Replacement of the diazonium group Treatment of benzenediazonium chloride with HBF_4 first gives benzenediazonium tetrafluoroborate. Heating this salt with sodium nitrite in the presence of copper replaces the diazonium group with $-\text{NO}_2$, liberating nitrogen:



Nitrite/copper introduces a nitro group; heating the tetrafluoroborate alone would instead give fluorobenzene.

Step 3: Conclusion Products: (1) 2,4,6-tribromoaniline; (2) nitrobenzene.

Quick Tip to Solve: Read the final diazonium-replacement reagent: sodium nitrite with copper introduces a nitro group even when HBF_4 is used first.

Section E (15 marks)

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

(1) Zn^{2+} salts are colourless while Ni^{2+} salts are coloured.

(2) Cr^{2+} is a strong reducing agent.

(3) Transition metals and their compounds show catalytic activities.

(ii) Write the ionic equations for the oxidizing action of MnO_4^- in acidic medium with

(1) I^- ion, and

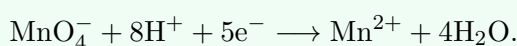
(2) Fe^{2+} ion.

[5 marks]

Solution:

Concept:

- Colour in many transition-metal ions arises from absorption of visible light during transitions between split d-orbital energy levels; partially filled d orbitals are needed for d–d transitions.
- A reducing agent donates electrons and is itself oxidised. Stability of the resulting electronic configuration favours oxidation.
- Transition-metal catalysts provide an alternative pathway of lower activation energy through variable oxidation states, intermediate formation or surface adsorption.
- In acidic medium, permanganate is reduced from manganese(VII) to manganese(II):

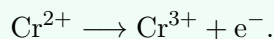


Step 1: (i)(1) Compare zinc(II) and nickel(II) Zinc has configuration $[\text{Ar}]3\text{d}^{10}4\text{s}^2$, so Zn^{2+} is $[\text{Ar}]3\text{d}^{10}$. Its d subshell is completely filled, and d–d transitions are not available. Consequently, ordinary

Quick Tip to Solve: Start each acidic permanganate equation with its five-electron reduction half-reaction, then match the electrons lost by the other ion.

zinc(II) salts with colourless counterions are colourless. Nickel has configuration $[\text{Ar}]3d^84s^2$, so Ni^{2+} is $[\text{Ar}]3d^8$. In a ligand field its partially filled d orbitals split into different energy levels. Absorption of selected visible wavelengths promotes d electrons, and the remaining transmitted light gives the observed colour of nickel(II) salts.

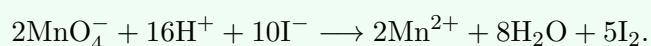
Step 2: (i)(2) Explain the reducing action of chromium(II) Chromium(II) has configuration $[\text{Ar}]3d^4$. It readily loses one electron:



The resulting chromium(III) ion has the more stable $3d^3$ configuration; in an octahedral field it has the favourable t_{2g}^3 arrangement. Thus chromium(II) readily undergoes oxidation and supplies electrons to another species, making it a strong reducing agent.

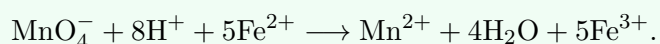
Step 3: (i)(3) Explain catalytic activity Transition metals can exhibit several oxidation states because the energies of their outer s and d electrons are close. Their compounds can form intermediate species and transfer electrons through a cycle of oxidation-state changes, after which the catalyst is regenerated. Metal surfaces also adsorb reactant molecules, bring them together and weaken their bonds. These effects provide a reaction pathway with a lower activation energy and increase the reaction rate.

Step 4: (ii)(1) Oxidation of iodide Iodide is oxidised to iodine, with the half-reaction $2\text{I}^{-} \longrightarrow \text{I}_2 + 2e^{-}$. Multiply the permanganate reduction half-reaction by 2 and the iodide oxidation half-reaction by 5. Adding them cancels ten electrons and gives



Both sides contain two manganese atoms, eight oxygen atoms, sixteen hydrogen atoms and ten iodine atoms. The net charge on either side is +4.

Step 5: (ii)(2) Oxidation of iron(II) Iron(II) loses one electron to form iron(III): $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^{-}$. Multiply this oxidation half-reaction by 5 and add it to the permanganate reduction half-reaction:



The atoms balance, and the total charge is +17 on each side. Acid supplies the hydrogen ions needed to convert permanganate oxygen into water.

Step 6: Conclusion Zinc(II) has a filled d subshell, while nickel(II) permits visible-light d–d transitions. Chromium(II) readily loses an electron to form stable chromium(III). Variable oxidation states, intermediate formation and adsorption explain catalytic activity. In acidic medium, permanganate oxidises iodide to iodine and iron(II) to iron(III), according to the balanced ionic equations derived above.

Quick Tip to Solve: Start each acidic permanganate equation with its five-electron reduction half-reaction, then match the electrons lost by the other ion.

- 33(b).** (i) Name two oxometal anions of the 3d series of the transition metals in which the metal exhibits the oxidation state equal to its group number.
 (ii) What is the effect of increasing pH on a solution of $\text{K}_2\text{Cr}_2\text{O}_7$?
 (iii) Why is Cu^+ not stable in aqueous solution?
 (iv) Name a member of Lanthanoid series which is well-known to exhibit +4 oxidation state.
 (v) Name two elements of 3d series which show anomalous electronic configuration. [5 marks]

Solution:**Concept:**

- In an oxometal anion, oxygen normally has oxidation state -2 ; the sum of oxidation states equals the charge on the ion.
- Chromate and dichromate interconvert through an acid-base equilibrium. Increasing pH lowers $[\text{H}^+]$ and favours chromate.
- Aqueous stability depends on hydration as well as electronic configuration. The large hydration enthalpy of Cu^{2+} favours disproportionation of Cu^+ .
- Half-filled and completely filled subshells can favour anomalous configurations; cerium can form the stable $4f^0$ configuration in its +4 state.

Step 1: (i) Identify oxometal anions and check oxidation states Two examples are chromate, CrO_4^{2-} , and permanganate, MnO_4^- . For chromate, let the chromium oxidation state be x :

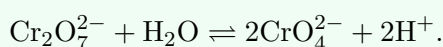
$$x + 4(-2) = -2 \Rightarrow x = +6.$$

Chromium belongs to group 6. Similarly, for permanganate,

$$x + 4(-2) = -1 \Rightarrow x = +7.$$

Manganese belongs to group 7. Thus, both metals have oxidation states equal to their respective group numbers.

Step 2: (ii) Apply the chromate-dichromate equilibrium The relevant equilibrium is



Increasing pH removes hydrogen ions, so the equilibrium shifts to the right by Le Chatelier's principle. Orange dichromate is converted into yellow chromate; hence the solution changes from orange to yellow. In alkaline medium the conversion can also be written as



Step 3: (iii) Explain the instability of aqueous copper(I) Although Cu^+ has a completely filled $3d^{10}$ subshell, it is unstable in aqueous solution and disproportionates:

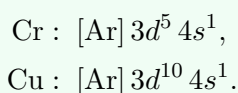


Quick Tip to Solve: For oxoanions, calculate the metal oxidation state from oxygen and the ionic charge; remember that alkali makes dichromate yellow and both Cr and Cu have a single 4s electron.

One copper(I) ion is oxidised to copper(II), while the other is reduced to copper metal. The much greater, more negative hydration enthalpy of Cu^{2+} , compared with Cu^+ , compensates for the energy needed to remove the second electron and makes this process favourable in water.

Step 4: (iv) Name the lanthanoid exhibiting the +4 state Cerium, Ce, is a well-known lanthanoid that exhibits the +4 oxidation state. On forming Ce^{4+} , it attains the noble-gas configuration $[\text{Xe}]$, with an empty 4f subshell. This helps explain the occurrence of cerium(IV), for example in CeO_2 .

Step 5: (v) Name the elements with anomalous configurations Chromium and copper show anomalous ground-state electronic configurations:



These differ from the simple filling predictions $[\text{Ar}] 3d^4 4s^2$ and $[\text{Ar}] 3d^9 4s^2$, respectively. The small energy difference between the 3d and 4s subshells allows the additional stability associated with half-filled $3d^5$ and filled $3d^{10}$ arrangements to favour the observed configurations.

Step 6: Conclusion (i) Chromate, CrO_4^{2-} , and permanganate, MnO_4^- ; (ii) orange dichromate converts to yellow chromate as pH increases; (iii) Cu^+ disproportionates because aqueous Cu^{2+} is strongly stabilised by hydration; (iv) cerium; (v) chromium and copper.

Quick Tip to Solve: For oxoanions, calculate the metal oxidation state from oxygen and the ionic charge; remember that alkali makes dichromate yellow and both Cr and Cu have a single 4s electron.

34. (a) Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(b) Which acid of the following pair is a stronger acid?

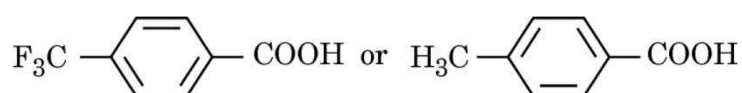
$p\text{-CF}_3\text{-C}_6\text{H}_4\text{-COOH}$ or $p\text{-CH}_3\text{-C}_6\text{H}_4\text{-COOH}$.

(c) Write the chemical equation involved in Rosenmund's reduction.

(d) Why are α -hydrogen atoms of aldehydes and ketones acidic in nature?

(e) Write a chemical test to distinguish between Benzaldehyde and Benzoic acid.

[5 marks]



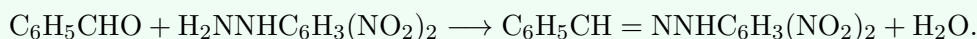
Solution:

Concept:

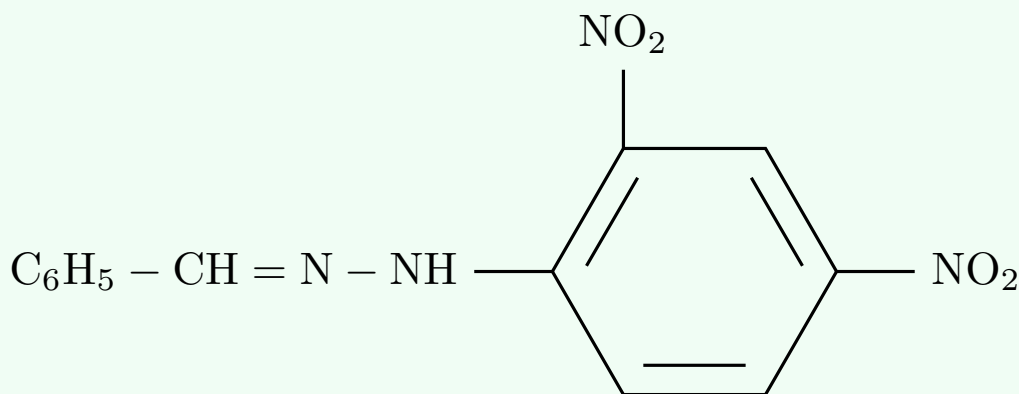
- Aldehydes condense with 2,4-dinitrophenylhydrazine through their carbonyl group to form a hydrazone, containing the linkage $\text{C} = \text{N} - \text{NH}$, with loss of water.
- An electron-withdrawing substituent stabilises a carboxylate ion and increases acidity; an electron-donating substituent has the opposite effect.
- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen and poisoned palladium on barium sulphate. An enolate ion is stabilised by resonance, accounting for the acidity of carbonyl compounds' α -hydrogens.

Quick Tip to Solve: In a hydrazone, retain the aldehydic H and replace only carbonyl O by N-NH; for the distinguishing test, look for CO_2 with sodium hydrogen carbonate.

Step 1: (a) Form the benzaldehyde hydrazone The carbonyl oxygen of benzaldehyde is replaced by the = N – NH group of the reagent. The terminal –NH₂ group reacts, while the nitrogen bonded to the dinitrophenyl ring retains one hydrogen:



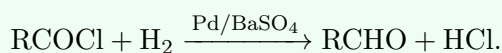
In the product, the two nitro groups are at positions 2 and 4 relative to the ring carbon attached to –NH–. The aldehydic hydrogen remains on the carbon of the CH = N group. The structure is drawn below.



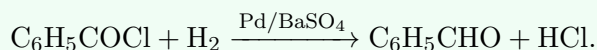
Benzaldehyde 2,4-dinitrophenylhydrazone; nitro groups occupy positions 2 and 4.

Step 2: (b) Compare the substituted benzoic acids The –CF₃ group exerts a strong electron-withdrawing inductive effect, which stabilises the negative charge of the conjugate-base carboxylate ion. In contrast, –CH₃ is electron-donating and destabilises that negative charge. Thus loss of a proton is favoured more strongly for the trifluoromethyl-substituted acid. Both substituents are para to –COOH, as shown in the question, so the decisive comparison is their opposite electronic effects.

Step 3: (c) Write Rosenmund's reduction The general reaction is

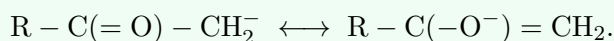


For example, benzoyl chloride gives benzaldehyde:



The palladium catalyst is poisoned to reduce its activity and prevent further reduction of the newly formed aldehyde to the primary alcohol.

Step 4: (d) Explain the acidity of alpha hydrogens An α-hydrogen is attached to the carbon adjacent to the carbonyl carbon. The electron-withdrawing carbonyl group favours its removal as a proton. The resulting enolate conjugate base is resonance-stabilised, with negative charge delocalised between the α-carbon and oxygen:

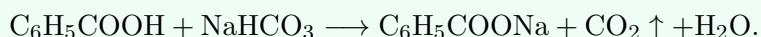


Here R may be hydrogen for an aldehyde or an alkyl group for a ketone. Stabilisation of this conjugate

Quick Tip to Solve: In a hydrazone, retain the aldehydic H and replace only carbonyl O by N-NH; for the distinguishing test, look for CO₂ with sodium hydrogen carbonate.

base explains why these hydrogens are more acidic than ordinary alkane hydrogens.

Step 5: (e) Distinguish benzaldehyde from benzoic acid Add aqueous sodium hydrogen carbonate, NaHCO_3 , to separate samples. Benzoic acid produces brisk effervescence of carbon dioxide:

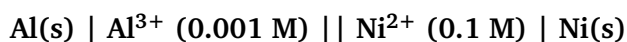


Benzaldehyde gives no effervescence because it has no carboxylic acid group and does not liberate carbon dioxide from hydrogen carbonate. The released gas turns limewater milky, confirming that it is carbon dioxide.

Step 6: Conclusion (a) The product is $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{NHC}_6\text{H}_3(\text{NO}_2)_2$, with nitro groups at positions 2 and 4. (b) *p*-Trifluoromethylbenzoic acid is stronger. (c) Rosenmund reduction gives RCHO from RCOCl . (d) Enolate resonance stabilisation makes α -hydrogens acidic. (e) Only benzoic acid effervesces with aqueous NaHCO_3 .

Quick Tip to Solve: In a hydrazone, retain the aldehydic H and replace only carbonyl O by N-NH; for the distinguishing test, look for CO_2 with sodium hydrogen carbonate.

35(a). (i) Calculate the emf of the following cell at 298 K:



[Given: $E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.66 \text{ V}$, $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$, $\log 10 = 1$]

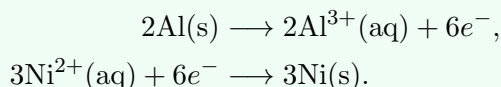
(ii) With the help of a graph explain why it is not possible to determine Λ_m° for a weak electrolyte by extrapolating the molar conductivity (Λ_m) versus $C^{1/2}$ curve as for strong electrolyte. [5 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons in the balanced cell reaction and Q is its reaction quotient.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$. A weak electrolyte has concentration-dependent ionisation, so its conductivity curve is strongly nonlinear.

Step 1: (i) Identify the electrodes and balance the cell reaction Nickel has the more positive reduction potential, so nickel ions are reduced at the cathode and aluminium is oxidised at the anode. The half-reactions are



Hence the overall reaction is $2\text{Al} + 3\text{Ni}^{2+} \longrightarrow 2\text{Al}^{3+} + 3\text{Ni}$, with $n = 6$. The standard emf is

$$E^\circ_{\text{cell}} = (-0.25) - (-1.66) = 1.41 \text{ V}.$$

Step 2: (i) Apply the Nernst equation at the given concentrations Pure solids have unit activity and

Quick Tip to Solve: Balance the overall cell reaction before choosing n and the powers in Q ; here both come from the six-electron reaction.

do not occur in the reaction quotient. Using the supplied molar concentrations for the ions,

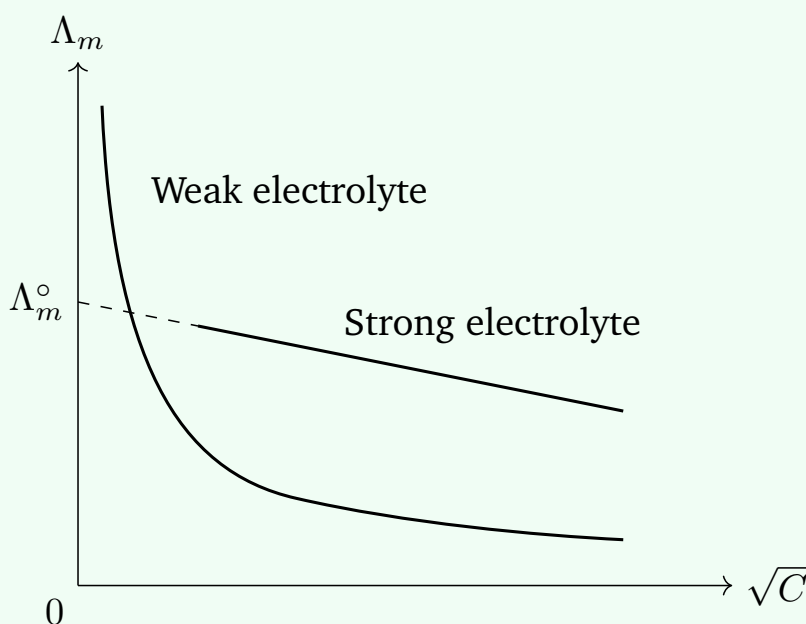
$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = 10^{-3}.$$

Thus $\log Q = -3$, and substitution gives

$$E_{\text{cell}} = 1.41 - \frac{0.0591}{6}(-3) = 1.41 + 0.02955 = 1.43955 \text{ V}.$$

The correction is positive because the present quotient is below unity; the given concentrations favour the forward cell reaction relative to standard conditions.

Step 3: (ii) Compare the conductivity curves The graph is schematic: the solid straight line represents a strong electrolyte at low concentration; its dashed extension reaches the vertical axis at Λ_m° . Strong electrolytes are essentially completely ionised, and their small increase in molar conductivity on dilution arises mainly from reduced interionic interactions. Therefore plotting Λ_m against $\sqrt{C}$ allows a reliable straight-line extrapolation to $C = 0$. For a weak electrolyte, dilution increases the degree of ionisation greatly, producing many more ions per mole. Its molar conductivity therefore rises steeply as $\sqrt{C}$ approaches zero, as shown by the curved line. The accessible data do not give a straight line whose intercept can be determined by the same extrapolation. Moreover, measurements become difficult at extremely low concentrations. Its limiting molar conductivity is instead obtained using Kohlrausch's law of independent migration of ions, by combining suitable strong-electrolyte limiting conductivities.



Schematic molar conductivity curves; the dashed line shows strong-electrolyte extrapolation.

Step 4: Conclusion (i) The cell emf at 298 K is 1.440 V (approximately). (ii) The weak-electrolyte Λ_m versus $\sqrt{C}$ curve is nonlinear because ionisation increases strongly on dilution, so the straight-line extrapolation used for strong electrolytes is unavailable.

Quick Tip to Solve: Balance the overall cell reaction before choosing n and the powers in Q ; here both come from the six-electron reaction.

35(b). (i) The molar conductivities of NH_4^+ and Cl^- ion are $73.8 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.2 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The conductivity of $0.1 \text{ M NH}_4\text{Cl}$ is $1.29 \times 10^{-2} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation.

(ii) Calculate the half-cell potential at 298 K for the reaction $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$ if $[\text{Zn}^{2+}] = 0.1 \text{ M}$ and $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$, where κ is conductivity in S cm^{-1} and c is concentration in mol L^{-1} . The factor 1000 converts litres to cubic centimetres.
- Kohlrausch's law gives $\Lambda_m^\circ = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ$. The conductivity-based degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- For a reduction half-reaction, the Nernst equation at 298 K is $E = E^\circ - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. A pure solid has unit activity.

Step 1: (i) Calculate the molar conductivity The given concentration is $c = 0.1 \text{ mol L}^{-1}$ and the conductivity is $\kappa = 1.29 \times 10^{-2} \text{ S cm}^{-1}$. Therefore,

$$\Lambda_m = \frac{1000 \times 1.29 \times 10^{-2}}{0.1} = 129 \text{ S cm}^2 \text{ mol}^{-1}.$$

This is the molar conductivity at the stated concentration, rather than the limiting value. Conductivity alone measures conductance per unit cell geometry; dividing by concentration expresses it per mole of electrolyte.

Step 2: (i) Determine the limiting value and the dissociation ratio Each formula unit of NH_4Cl gives one ammonium ion and one chloride ion. Hence their limiting ionic molar conductivities are added with coefficients of unity:

$$\Lambda_m^\circ = 73.8 + 76.2 = 150.0 \text{ S cm}^2 \text{ mol}^{-1}.$$

Using the relation requested for the conductivity calculation,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{129}{150} = 0.86, \quad 100\alpha = 86\%.$$

This ratio is dimensionless because both molar conductivities have the same units. Ammonium chloride is a strong electrolyte; here 0.86 is the apparent conductivity-based dissociation ratio. At finite concentration, reduced ionic mobility also lowers conductivity, so the ratio need not represent a literal fraction of undissociated formula units.

Step 3: (ii) Write the reaction quotient for the reduction For $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}(s)$, two electrons are transferred, so $n = 2$. Electrons are omitted from the reaction quotient and solid zinc has unit activity. Taking the ion activity as its concentration relative to 1 mol L^{-1} ,

$$Q = \frac{1}{[\text{Zn}^{2+}]} = \frac{1}{0.1} = 10.$$

Quick Tip to Solve: Use 1000 when conductivity is in S per centimetre and concentration is in mol per litre ; for zinc reduction, put the ion concentration in the denominator of Q .

Thus dilution of zinc ions increases Q and makes the reduction potential more negative than its standard value.

Step 4: (ii) Substitute in the Nernst equation With $E^\circ = -0.76 \text{ V}$ and $\log 10 = 1$,

$$\begin{aligned} E &= -0.76 - \frac{0.0591}{2} \log 10 \\ &= -0.76 - 0.02955 \\ &= -0.78955 \text{ V.} \end{aligned}$$

The negative correction has the expected sign for a zinc-ion concentration below the standard concentration.

Step 5: Conclusion (i) $\Lambda_m = 129 \text{ S cm}^2 \text{ mol}^{-1}$ and the calculated conductivity-based degree of dissociation is $\alpha = 0.86 = 86\%$. (ii) The zinc reduction half-cell potential is $E \approx -0.790 \text{ V}$ at 298 K.

Quick Tip to Solve: Use 1000 when conductivity is in S per centimetre and concentration is in mol per litre; for zinc reduction, put the ion concentration in the denominator of Q .