CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-5-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **five** sections – **Section A, B, C, D and E**.

(iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29 and 30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is not allowed.

Section A (16 marks)

Questions no. ***1 to 16*** *are Multiple Choice type Questions, carrying* ***1*** *mark each.* $16 \times 1 = 16$

1. While doing qualitative analysis in chemistry lab, Abhishek added yellow coloured potassium chromate solution into a test tube. He was surprised to see the colour of the solution changing immediately to orange. He realised that the test tube was not clean and contained a few drops of some liquid. Which of the following substances will be the most likely liquid to be present in the test tube before adding potassium chromate solution? [1 mark]

(A) Sodium hydrogen carbonate solution

(B) Methyl orange solution

(C) Sodium hydroxide solution

(D) HCl solution

Correct Answer: (D) HCl solution

Solution:

Concept:

- Chromate ions, CrO_4^{2-}, are yellow; dichromate ions, $Cr_2O_7^{2-}$, are orange.
- Increasing H^+ concentration shifts the chromate-dichromate equilibrium towards dichromate.

Step 1: Apply the colour equilibrium The relevant equilibrium is

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O.$$

Added acid supplies hydrogen ions, so the equilibrium shifts to the right and the yellow solution becomes orange.

Step 2: Check the four liquids HCl provides the required acidic medium. Sodium hydroxide and sodium hydrogen carbonate are basic and favour yellow chromate rather than orange dichromate. Methyl orange is an indicator; its own colour is not the chemical explanation for conversion of chromate into dichromate. Thus the observed immediate change points to residual HCl.

Step 3: Conclusion The liquid was HCl solution: option (D).

Quick Tip to Solve: For a yellow chromate solution turning orange, look for the option that supplies hydrogen ions.

2. The role of a catalyst is to change: [1 mark]

(A) equilibrium constant

(B) enthalpy of reaction

(C) Gibbs energy of reaction

(D) activation energy of reaction

Correct Answer: (D) activation energy of reaction

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy, E_a.
- Reaction thermodynamic quantities depend on reactants and products, not on the pathway.

Step 1: Identify the kinetic effect Activation energy is the energy barrier that reacting species must overcome. A catalyst lowers this barrier by providing a different pathway, increasing the reaction rate at the same temperature. It speeds both forward and reverse reactions.

Step 2: Reject thermodynamic changes The equilibrium constant depends on temperature and the standard Gibbs energy change, $\Delta_r G^\circ = -RT \ln K$. A catalyst does not change the initial or final states, so neither the reaction enthalpy nor its Gibbs energy changes. It makes equilibrium arrive sooner without changing its composition. Hence options (A), (B) and (C) do not describe its role.

Step 3: Conclusion A catalyst changes the activation energy of reaction: option (D).

Quick Tip to Solve: Separate rate from equilibrium: a catalyst changes the energy barrier, while reactant and product energies stay fixed.

3. Match the type of cell given in Column I with their use given in Column II.

Column I	*Column II*
i. Lead storage cell	**a. Wall clock**
ii. Mercury cell	**b. Apollo Space Programme**
iii. Dry cell	**c. Wrist watch**
iv. Fuel cell	**d. Inverter**

[1 mark]

(A) i-a, ii-b, iii-c, iv-d

(B) i-d, ii-c, iii-a, iv-b

(C) i-c, ii-d, iii-b, iv-a

(D) i-b, ii-a, iii-d, iv-c

Correct Answer: (B) i-d, ii-c, iii-a, iv-b

Solution:

Concept:

- A cell is selected for an application according to its rechargeability, output and operating requirements.

Quick Tip to Solve: Anchor the two distinctive uses first: rechargeable lead storage for an inverter and fuel cells for Apollo.

- Lead storage cells are secondary cells; dry and mercury cells are primary cells, while fuel cells receive reactants continuously.

Step 1: Match common portable and backup uses A lead storage cell is rechargeable and can supply substantial current, so it is used in an inverter: i-d. A mercury cell provides a nearly constant voltage in a compact form and is associated with wrist watches: ii-c. A dry cell is commonly used in a wall clock: iii-a.

Step 2: Match the space application and check options A hydrogen-oxygen fuel cell was used in the Apollo Space Programme, supplying electricity with water as a reaction product: iv-b. Together these give i-d, ii-c, iii-a, iv-b. Only option (B) contains all four matches. Options (A), (C) and (D) interchange the applications and fail the cell-by-cell matching.

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

Quick Tip to Solve: Anchor the two distinctive uses first: rechargeable lead storage for an inverter and fuel cells for Apollo.

4. CH_3CH_2OH can be converted to CH_3CHO by: [1 mark]

(A) catalytic hydrogenation

(B) treatment with $LiAlH_4$

(C) treatment with PCC

(D) treatment with $KMnO_4$

Correct Answer: (C) treatment with PCC

Solution:

Concept:

- Ethanol is a primary alcohol; controlled oxidation converts it into ethanal.
- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde without normally continuing to a carboxylic acid.

Step 1: Recognise the required transformation The conversion removes two hydrogen atoms from ethanol while retaining the two-carbon skeleton:

$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO.$$

The product is ethanal, an aldehyde, so a controlled oxidising reagent is required.

Step 2: Evaluate each reagent PCC gives the required aldehyde and is the selective choice. Catalytic hydrogenation and lithium aluminium hydride are reducing conditions, so options (A) and (B) cannot perform this alcohol-to-aldehyde oxidation. Potassium permanganate is a strong oxidising agent and ordinarily oxidises a primary alcohol further to a carboxylic acid; it is not the selective reagent for stopping at ethanal.

Step 3: Conclusion Ethanol is converted to ethanal by treatment with PCC: option (C).

Quick Tip to Solve: When a primary alcohol must stop at the aldehyde stage, choose PCC over a strong oxidant such as permanganate.

5. The IUPAC name for $CH_3 - CH_2 - N(CH_3) - CH_2 - CH_2 - CH_3$ is: [1 mark]

(A) N-methylpentan-2-amine

(B) N-ethyl-N-methylpropan-1-amine

(C) N,N-diethylpropan-1-amine

(D) N,N-dimethylpropan-1-amine

Correct Answer: (B) N-ethyl-N-methylpropan-1-amine

Solution:

Concept:

- For an unsymmetrical tertiary amine, choose the longest carbon chain attached to nitrogen as the parent alkanamine.
- Other groups attached directly to nitrogen are indicated with the locant N.

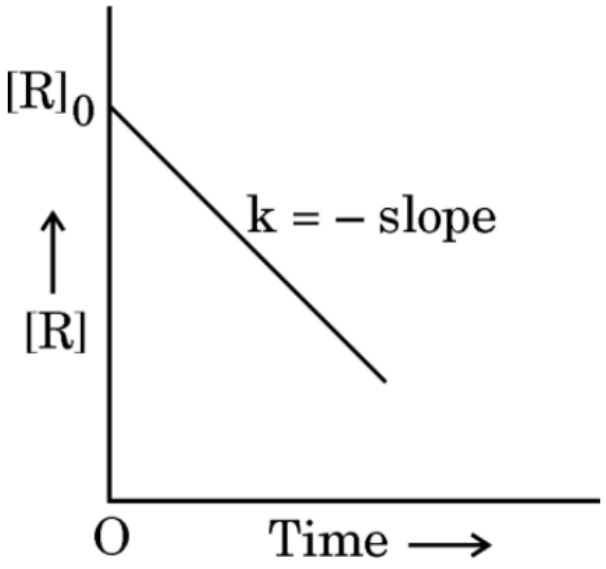
Step 1: Choose the parent chain The nitrogen is attached to three alkyl groups: ethyl, CH_3CH_2-; methyl, CH_3-; and propyl, $-CH_2CH_2CH_3$. The longest continuous chain attached to nitrogen has three carbon atoms, and nitrogen is attached at carbon 1. The parent name is therefore propan-1-amine.

Step 2: Name the nitrogen substituents and compare The remaining substituents on nitrogen are ethyl and methyl, cited alphabetically as N-ethyl and N-methyl. Option (A) incorrectly treats the separate chains as a pentane chain. Option (C) would require two ethyl substituents, and option (D) two methyl substituents, neither of which is present in the printed structure.

Step 3: Conclusion The IUPAC name is N-ethyl-N-methylpropan-1-amine: option (B).

Quick Tip to Solve: Do not join carbon chains through nitrogen; take the longest attached chain as the parent and use N for the others.

6. A plot between concentration of reactant [R] and time 't' is shown below. Which of the given order of reaction is indicated by the graph? [1 mark]



(A) Third order

(B) Second order

(C) First order

(D) Zero order

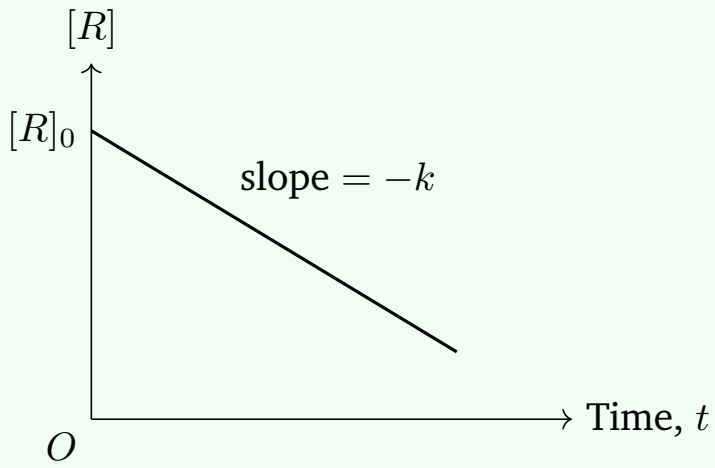
Correct Answer: (D) Zero order

Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$.
- Its integrated rate law is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration and k is the rate constant.

Step 1: Compare the graph with the rate law The printed graph plots reactant concentration directly against time and shows a straight line descending from $[R]_0$. Comparing $[R] = [R]_0 - kt$ with $y = c + mx$, its intercept is $[R]_0$ and its slope is $-k$, exactly as labelled in the graph.



Concentration-time plot for a zero-order reaction

Step 2: Exclude other reaction orders For a first-order reaction, a straight line is obtained by plotting $\ln[R]$ against time, while $[R]$ itself decays exponentially. For second order the linear plot is $1/[R]$ against time, and for third order it is $1/[R]^2$ against time. These orders therefore do not give the displayed linear fall of untransformed concentration with time.

Step 3: Conclusion The graph indicates a zero-order reaction: option (D).

Quick Tip to Solve: Check the vertical-axis variable first: a straight descending line of [R] itself against time identifies zero order.

7. The treatment of ethyl bromide with alcoholic silver nitrite gives: [1 mark]

(A) ethyl nitrite

(B) nitroethane

(C) nitromethane

(D) ethene

Correct Answer: (B) nitroethane

Solution:

Concept:

- Nitrite is an ambident nucleophile: it can form a bond through nitrogen or oxygen.
- With predominantly covalent silver nitrite, alkyl halides give nitroalkanes, containing a carbon–nitrogen bond.

Step 1: Identify the attacking atom In silver nitrite, the oxygen is associated with silver; substitution of bromide therefore occurs through nitrogen. Ethyl bromide retains its two-carbon ethyl group.

Step 2: Compare the products The reaction is

$$CH_3CH_2Br + AgNO_2 \longrightarrow CH_3CH_2NO_2 + AgBr.$$

Ethyl nitrite would contain a carbon–oxygen bond and is associated with alkali-metal nitrites. Nitromethane has only one carbon, while ethene is an elimination product, not the substitution product here.

Step 3: Conclusion The product is nitroethane. Hence, the correct option is (B).

Quick Tip to Solve: For an alkyl halide, distinguish AgNO2 (nitroalkane) from KNO2 (alkyl nitrite).

8. Which of the following aqueous solutions will have the highest freezing point? [1 mark]

(A) 1.0 M KCl

(B) 1.0 M Na_2SO_4

(C) 1.0 M Glucose

(D) 1.0 M $AlCl_3$

Correct Answer: (C) 1.0 M Glucose

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the solvent constant and m molality.
- More dissolved particles produce a larger depression and thus a lower freezing point.

Step 1: Count solute particles Glucose is a nonelectrolyte, so its factor is $i = 1$. In the usual complete-dissociation comparison, KCl gives two ions, sodium sulphate gives three, and aluminium chloride gives four: their factors are approximately 2, 3 and 4.

Quick Tip to Solve: Highest freezing point means the smallest depression: select the solute with the fewest particles.

Step 2: Compare freezing points For the given equal-concentration aqueous solutions, the standard colligative-property comparison identifies glucose as producing the fewest solute particles. Its freezing-point depression is therefore the smallest, and its freezing point the highest. Each electrolyte option lowers the freezing point more than glucose. The given molarity is used for this qualitative textbook comparison; an exact numerical depression would require molality.

Step 3: Conclusion The 1.0 M glucose solution has the highest freezing point. Hence, the correct option is (C).

Quick Tip to Solve: Highest freezing point means the smallest depression: select the solute with the fewest particles.

9. Which of the following aldehydes will undergo Cannizzaro reaction? [1 mark]

(A) CH_3–$CH(CH_3)$–CHO

(B) $(CH_3)_3C$–CHO

(C) CH_3–CH_2–CHO

(D) CH_3–$CH(CH_3)$–$CH(CH_3)$–CHO

Correct Answer: (B) $(CH_3)_3C$–CHO

Solution:

Concept:

- The Cannizzaro reaction is disproportionation of an aldehyde without any alpha-hydrogen in concentrated alkali.
- The alpha-carbon is the carbon directly bonded to the aldehyde carbon; inspect hydrogens on that carbon.

Step 1: Inspect the eligible aldehyde In $(CH_3)_3CCHO$, the carbon next to $-CHO$ is bonded to three methyl groups and the aldehyde carbon. It consequently has no hydrogen. One molecule can be oxidised to a carboxylate while another is reduced to an alcohol.

Step 2: Eliminate the remaining choices In option (A), the alpha-carbon is $CH(CH_3)$, so it has one hydrogen. In (C), it is CH_2, with two hydrogens. In (D), the $CH(CH_3)$ group immediately adjacent to $-CHO$ also has one hydrogen. These compounds do not meet the no-alpha-hydrogen requirement for the usual Cannizzaro reaction.

Step 3: Conclusion Only $(CH_3)_3CCHO$ qualifies. Hence, the correct option is (B).

Quick Tip to Solve: Ignore hydrogens on the aldehyde carbon; count only those on the immediately adjacent carbon.

10. In which of the following groups are both ions coloured in aqueous solution?

I. Cu^{+} II. Ti^{4+} III. Co^{2+} IV. Fe^{2+}

[Atomic number: Cu = 29, Ti = 22, Co = 27, Fe = 26] [1 mark]

(A) I and II

(B) II and III

(C) III and IV

(D) I and IV

Correct Answer: (C) III and IV

Solution:

Concept:

- In aqueous transition-metal ions, partially filled d orbitals permit d–d transitions and commonly give colour.
- For cations, remove the outer 4s electrons before the 3d electrons when finding the configuration.

Step 1: Find the d-electron counts The ionic configurations are Cu^{+} : $[Ar]3d^{10}$, Ti^{4+} : $[Ar]3d^{0}$, Co^{2+} : $[Ar]3d^{7}$, and Fe^{2+} : $[Ar]3d^{6}$. Copper(I) has a full d subshell and titanium(IV) has an empty one.

Step 2: Select a pair of coloured ions Co(II) and Fe(II) both have partially filled d subshells; their aqueous ions are coloured, typically pink and pale green, respectively. Cu(I) and Ti(IV) do not show the usual d–d colour in aqueous solution. Thus (A) has two colourless ions, (B) contains colourless Ti(IV), and (D) contains colourless Cu(I).

Step 3: Conclusion Both III and IV are coloured. Hence, the correct option is (C).

Quick Tip to Solve: Calculate the ionic d count first: d0 and d10 fail the usual aqueous d–d colour test.

11. Which of the following molecules is chiral in nature? [1 mark]

(A) 1-chloropropane

(B) 2-chloropropane

(C) 1-chlorobutane

(D) 2-chlorobutane

Correct Answer: (D) 2-chlorobutane

Solution:

Concept:

- A tetrahedral carbon attached to four different groups is a stereogenic centre and can give chirality.
- For these simple alkyl halides, check whether the carbon bearing chlorine has four different substituents.

Step 1: Check 2-chlorobutane The structure is $CH_3CH(Cl)CH_2CH_3$. Its second carbon bears hydrogen, chlorine, methyl and ethyl. These are four distinct groups, so it gives a pair of non-superimposable mirror images.

Quick Tip to Solve: Compare the two carbon chains at the chlorine-bearing carbon: methyl and ethyl are different.

Step 2: Check the other molecules In 1-chloropropane and 1-chlorobutane, the chlorine-bearing carbon is CH_2Cl, with two identical hydrogens, and neither chain has another stereogenic centre. In 2-chloropropane, the middle carbon has two identical methyl groups. All three therefore fail the four-different-groups test and are achiral.

Step 3: Conclusion 2-chlorobutane is chiral. Hence, the correct option is (D).

Quick Tip to Solve: Compare the two carbon chains at the chlorine-bearing carbon: methyl and ethyl are different.

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12. CH_3CH_2CHO and CH_3CH_2COOH can be distinguished by: [1 mark]

(A) Sodium bicarbonate test

(B) Hinsberg test

(C) Iodoform test

(D) Lucas test

Correct Answer: (A) Sodium bicarbonate test

Solution:

Concept:

- Carboxylic acids react with sodium bicarbonate to release carbon dioxide; aldehydes do not.
- A distinguishing test must give visibly different observations for the two compounds.

Step 1: Apply the bicarbonate test Propanoic acid reacts as

$$CH_3CH_2COOH + NaHCO_3 \longrightarrow CH_3CH_2COONa + H_2O + CO_2 \uparrow.$$

It produces brisk effervescence of carbon dioxide, whereas propanal shows no such effervescence.

Step 2: Reject the other tests The Hinsberg test distinguishes classes of amines, and the Lucas test distinguishes classes of alcohols; neither suits this pair. The iodoform test requires a methyl ketone or a suitable precursor such as ethanal. Propanal has no methyl carbonyl group, and propanoic acid also gives no iodoform precipitate, so this test cannot distinguish them.

Step 3: Conclusion The sodium bicarbonate test distinguishes the compounds. Hence, the correct option is (A).

Quick Tip to Solve: Look for the COOH group: bicarbonate gives visible CO2 bubbles with the acid alone.

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13. Assertion (A): The boiling points of alkyl halides decrease in the order $RI > RBr > RCl > RF$.
Reason (R): The van der Waals forces of attraction decrease in the order $RI > RBr > RCl > RF$.

[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:

- For the same alkyl group, boiling point depends on the strength of intermolecular attractions.
- From fluorine to iodine, electron-cloud size and polarizability increase, strengthening dispersion forces.

Step 1: Judge the assertion The assertion is true for alkyl halides with the same alkyl group: the boiling points decrease as $RI > RBr > RCl > RF$. More energy is needed to separate the molecules of the heavier, more polarizable halides.

Step 2: Judge the reason The reason is true. The increasingly large electron clouds from F to I are more easily distorted, so London dispersion contributions to van der Waals attraction increase towards the iodide. Written in descending order, these attractions are $RI > RBr > RCl > RF$.

Step 3: Test the explanatory link Stronger intermolecular forces require more thermal energy for vaporisation. The stated force order therefore directly explains the stated boiling-point order. Option (B) incorrectly denies this link; (C) and (D) incorrectly classify one statement as false.

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

Quick Tip to Solve: Keep the alkyl group fixed, then rank halogen polarizability to rank dispersion and boiling point.

14. Assertion (A): For measuring resistance of an ionic solution an AC source is used.

Reason (R): Concentration of ionic solution will change if DC source is used. [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:

- Ions carry current through an electrolyte; a steady direct current can cause electrolysis.
- An alternating current reverses direction periodically, reducing net electrolysis and electrode polarisation.

Step 1: Judge the assertion The assertion is true. An AC source is used in measuring the resistance of an ionic solution so that the measurement reflects the electrical resistance of the solution under substantially unchanged conditions.

Step 2: Judge the reason The reason is true. With a DC source, ions migrate continuously towards the electrodes and electrode reactions can consume or produce species. This can change ionic concentration near the electrodes and cause polarisation, altering the measured resistance.

Step 3: Connect the statements AC reverses the direction of current repeatedly and avoids the sustained electrode reactions and concentration changes associated with DC. Thus the reason directly explains the use of AC. Option (B) misses this explanatory link, while (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: For electrolyte resistance measurements, link AC to avoiding sustained electrolysis and concentration changes.

15. Assertion (A): Henry's law constant (K_H) decreases with increase in temperature.

Reason (R): As the temperature increases, solubility of gases in liquids decreases. [1 mark]

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

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

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is gas pressure and x is its mole fraction in the liquid.
- At fixed gas pressure, a larger K_H corresponds to a smaller dissolved mole fraction.

Step 1: Judge the assertion For a fixed pressure, $K_H = p/x$. On increasing temperature, the dissolved mole fraction generally decreases, so this ratio increases. Therefore Henry's law constant increases, rather than decreases, with temperature; the assertion is false.

Step 2: Judge the reason The reason is true: gases generally become less soluble in liquids as temperature rises. Dissolution of most gases is exothermic, so heating favours their escape from the liquid.

Step 3: Select the logical combination Since the assertion is false and the reason is true, option (D) fits. Options (A) and (B) require a true assertion, while option (C) requires a false reason, so none of those codes applies.

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

Quick Tip to Solve: Rearrange Henry's law to $K_H = p/x$: lower solubility at fixed pressure means a larger constant.

16. Assertion (A): The solubility of aldehydes and ketones in water decreases with increase in size of the alkyl group.

Reason (R): Aldehydes and ketones have dipole-dipole interaction. [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:

- The polar carbonyl oxygen can accept hydrogen bonds from water.
- An alkyl group is hydrophobic; a larger alkyl portion reduces the relative influence of the polar carbonyl group.

Step 1: Judge the assertion The assertion is true. Lower aldehydes and ketones dissolve readily in water because their carbonyl oxygen forms hydrogen bonds with water molecules. As the alkyl group grows, the nonpolar, hydrophobic portion becomes larger and aqueous solubility decreases.

Step 2: Judge the reason The reason is true. The polar $C = O$ bond gives aldehydes and ketones permanent molecular dipoles, so dipole-dipole attractions occur between their molecules.

Step 3: Check the explanation The existence of dipole-dipole attraction alone does not explain why increasing alkyl-group size reduces water solubility. The required explanation is the growing hydrophobic alkyl portion relative to the water-interacting carbonyl group. Thus (A) assigns an incorrect explanatory link; (C) and (D) wrongly treat one of the true statements as false.

Step 4: Conclusion Both statements are true, but the reason is not the correct explanation of the assertion. Hence, the correct option is (B).

Quick Tip to Solve: For solubility trends, compare the size of the hydrophobic alkyl part with the water-interacting carbonyl group.

Section B (10 marks)

17. For KCl solution, the conductivity (κ, in S cm^{-1}) and molar conductivity (Λ_m, in S cm^2 mol^{-1}) at 298.15 K at different concentrations are given:

Concentration (mol/L)	Conductivity (S cm^{-1})	Molar Conductivity (S cm^2 mol^{-1})
1.000	0.1113	111.3
0.100	0.0129	129.0
0.010	0.00141	141.0

Based on the data given above, give plausible reason for the variation of conductivity and molar conductivity with concentration. [2 marks]

Solution:

Concept:

- Conductivity κ measures the conductance contribution of ions per unit volume of solution.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when c is in $\mathrm{mol\,L^{-1}}$ and κ in $\mathrm{S\,cm^{-1}}$.
- KCl is a strong electrolyte; dilution mainly reduces interionic interactions rather than causing a large increase in dissociation.

Step 1: Explain the conductivity trend On dilution from 1.000 to $0.010\,\mathrm{mol\,L^{-1}}$, κ decreases from 0.1113 to $0.00141\,\mathrm{S\,cm^{-1}}$. The number of potassium and chloride ions present per unit volume decreases. Although ionic mobility improves on dilution, the reduction in charge carriers per unit volume dominates, so conductivity falls.

Step 2: Explain the molar conductivity trend Over the same dilution, Λ_m rises from 111.3 through 129.0 to $141.0\,\mathrm{S\,cm^2\,mol^{-1}}$. The ions become farther apart, reducing interionic electrostatic interactions that hinder their motion. Their mobility therefore increases, so the conductance associated with one mole of KCl increases. For example, at the lowest concentration,

$$\Lambda_m = \frac{1000(0.00141)}{0.010} = 141.0\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Step 3: Conclusion On dilution, conductivity decreases because there are fewer ions per unit volume, while molar conductivity increases because reduced interionic interactions increase ionic mobility.

Quick Tip to Solve: Distinguish ions per unit volume for conductivity from the conductance of one mole for molar conductivity.

18(a). Calculate the elevation of boiling point of a solution when 3 g of $CaCl_2$ (Molar mass = 111 g mol^{-1}) was dissolved in 260 g of water, assuming that $CaCl_2$ undergoes complete dissociation. (K_b for water = 0.52 K kg mol^{-1}) [2 marks]

Solution:

Concept:

- Elevation of boiling point is $\Delta T_b = iK_bm$, where m is solute molality and i is the van't Hoff factor.
- Complete dissociation of $CaCl_2$ produces three ions per formula unit, hence $i = 3$.

Step 1: Determine the particle factor Calcium chloride dissociates as

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-.$$

One mole of calcium chloride therefore gives three moles of dissolved ions. With complete dissociation as stipulated, the particle factor is $i = 3$; using $i = 1$ would underestimate the colligative effect.

Step 2: Calculate the molality The solvent mass must be in kilograms. The amount of calcium chloride and molality are

$$n = \frac{3}{111} = 0.027027\,\text{mol},$$
$$m = \frac{0.027027}{0.260} = 0.10395\,\text{mol kg}^{-1}.$$

The denominator is the mass of water, not the mass of the complete solution.

Step 3: Apply the boiling-point elevation formula Substituting $K_b = 0.52\,\text{K kg mol}^{-1}$,

$$\Delta T_b = 3 \times 0.52 \times \frac{3}{111 \times 0.260} = 0.16216\,\text{K}.$$

The kilogram and mole units cancel, leaving a temperature difference in kelvin.

Step 4: Conclusion The elevation of boiling point is $\boxed{\Delta T_b \approx 0.162\,\text{K}}$.

Quick Tip to Solve: Count all ions formed on complete dissociation and use the solvent mass in kilograms in the molality.

OR

18(b). Liquids 'X' and 'Y' form an ideal solution. The vapour pressure of pure 'X' and pure 'Y' are 120 mm Hg and 160 mm Hg respectively. Calculate the vapour pressure of the solution containing equal moles of 'X' and 'Y'. [2 marks]

Solution:

Concept:

- For an ideal solution, Raoult's law gives $p_i = x_i p_i^0$, where x_i is the liquid-phase mole fraction and p_i^0 is the vapour pressure of pure component i.
- The total vapour pressure is the sum of the partial pressures: $P = p_X + p_Y$, with $x_X + x_Y = 1$.

Quick Tip to Solve: For an ideal binary solution with equal mole fractions, take the arithmetic mean of the two pure-liquid vapour pressures.

Step 1: Determine both mole fractions The solution contains equal moles of the two liquids. Taking $n_X = n_Y = n$, we obtain

$$x_X = \frac{n}{n+n} = \frac{1}{2}, \qquad x_Y = \frac{1}{2}.$$

Equal moles mean equal mole fractions; no molar masses or liquid volumes are needed.

Step 2: Calculate and add the partial pressures Using the given pure-liquid vapour pressures,

$$\begin{aligned} p_X &= \tfrac{1}{2}(120) = 60\,\text{mm Hg}, \\ p_Y &= \tfrac{1}{2}(160) = 80\,\text{mm Hg}, \\ P &= 60 + 80 = 140\,\text{mm Hg}. \end{aligned}$$

The two liquids both contribute vapour. Adding the pure-liquid pressures directly would ignore their dilution in the solution.

Step 3: Conclusion The vapour pressure of the solution is $\boxed{140\,\text{mm Hg}}$.

Quick Tip to Solve: For an ideal binary solution with equal mole fractions, take the arithmetic mean of the two pure-liquid vapour pressures.

19(a). Define rate constant. [1 mark]

Solution:

Concept:

- The rate law relates reaction rate to reactant concentrations: $r = k[A]^m[B]^n$. Here k is the rate constant and m, n are the experimentally determined partial orders.
- At a specified temperature, k is independent of reactant concentrations; its units depend on the overall order.

Step 1: Identify the proportionality constant The rate constant is the proportionality constant in the experimentally determined rate law. It connects the measured rate with the concentration factors for that reaction.

Step 2: State the unit-concentration definition When the concentration of each reactant appearing in the rate law is unity, the concentration factors are unity and the rate is numerically equal to k. This definition is understood at a fixed temperature; it does not mean that k and rate necessarily have identical units.

Step 3: Conclusion The rate constant is the proportionality constant in the rate law, numerically equal to the reaction rate when each reactant concentration is unity at a given temperature.

Quick Tip to Solve: Define k through the rate law, and include the condition of unit reactant concentrations at a fixed temperature.

19(b). Identify the reaction order which has a rate constant of 4.5×10^{-5} L mol^{-1} s^{-1}. [1 mark]

Solution:

Concept:

- For overall order n, the rate-constant units are $[k] = (\text{mol L}^{-1})^{1-n}\text{s}^{-1}$.
- The rate has units mol L^{-1}s^{-1}; divide by the concentration factor to find the units of k.

Step 1: Rewrite the given units The given constant is $k = 4.5 \times 10^{-5}\,\text{L mol}^{-1}\text{s}^{-1}$. Its units can be written as $(\text{mol L}^{-1})^{-1}\text{s}^{-1}$, so the concentration exponent is -1.

Step 2: Compare the concentration exponent Equating this exponent to $1 - n$,

$$1 - n = -1 \quad \Rightarrow \quad n = 2.$$

The numerical magnitude of the constant does not decide the order. A first-order constant has units s^{-1}, whereas a zero-order constant has units of concentration per time.

Step 3: Conclusion The reaction is $\boxed{\text{second order}}$.

Quick Tip to Solve: Use the units, not the numerical value: $\text{L mol}^{-1}\,\text{s}^{-1}$ identifies a second-order rate constant.

20. Write the mechanism of dehydration of ethyl alcohol with conc. H_2SO_4 at 413 K. [2 marks]

Solution:

Concept:

- At $413\,\text{K}$, ethanol undergoes acid-catalysed intermolecular dehydration to form diethyl ether.
- Protonation converts the poor leaving group $-\text{OH}$ into water. A second ethanol molecule attacks the primary carbon, and the acid catalyst is regenerated.

Step 1: Protonate the ethanol oxygen The oxygen lone pair accepts a proton supplied by concentrated sulphuric acid:

$$\text{C}_2\text{H}_5\text{OH} + \text{H}^+ \rightleftharpoons \text{C}_2\text{H}_5\text{OH}_2^+.$$

The resulting protonated alcohol has a good leaving group, H_2O.

Step 2: Attack by a second ethanol molecule The oxygen of another ethanol molecule attacks the ethyl carbon of protonated ethanol as water leaves, forming protonated ether:

$$\text{C}_2\text{H}_5\text{OH} + \text{C}_2\text{H}_5\text{OH}_2^+ \longrightarrow (\text{C}_2\text{H}_5)_2\text{OH}^+ + \text{H}_2\text{O}.$$

This is a substitution at a primary carbon; formation of a free primary carbocation is unnecessary.

Step 3: Regenerate the acid catalyst The protonated ether loses a proton:

$$(\text{C}_2\text{H}_5)_2\text{OH}^+ \longrightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{H}^+.$$

Thus the catalyst is restored and two ethanol molecules together eliminate one water molecule.

Quick Tip to Solve: At 413 K, show protonation, attack by a second ethanol molecule, and deprotonation to obtain ether.

Step 4: Conclusion The product at $413\,\text{K}$ is diethyl ether:

$$2C_2H_5OH \xrightarrow[413\,\text{K}]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$

Quick Tip to Solve: At 413 K, show protonation, attack by a second ethanol molecule, and deprotonation to obtain ether.

21(a). Give a simple chemical test to distinguish between 3-pentanone and 2-pentanone. [1 mark]

Solution:

Concept:

- The iodoform test detects the methyl ketone group CH_3CO-, using iodine and aqueous sodium hydroxide.
- A positive test produces a yellow precipitate of iodoform, CHI_3.

Step 1: Apply the iodoform test Warm separate samples with iodine and aqueous $NaOH$. 2-Pentanone, $CH_3COCH_2CH_2CH_3$, contains a methyl group directly attached to its carbonyl carbon and gives a yellow precipitate of CHI_3.

Step 2: Compare the other ketone 3-Pentanone, $CH_3CH_2COCH_2CH_3$, has ethyl groups on both sides of the carbonyl group. It has no CH_3CO- group and gives no yellow iodoform precipitate under the same test conditions.

Step 3: Conclusion Use the iodoform test: 2-pentanone gives yellow CHI_3; 3-pentanone gives no yellow precipitate.

Quick Tip to Solve: Inspect the groups directly bonded to the carbonyl carbon: only 2-pentanone has the CH3CO group needed for iodoform.

21(b). Write an equation for Clemmensen reduction. [1 mark]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group.
- The reagents are amalgamated zinc, $Zn(Hg)$, and concentrated hydrochloric acid.

Step 1: State the reagents and transformation In the acidic Clemmensen reduction, $>C=O$ is reduced to $>CH_2$. The carbon skeleton remains intact, and the reaction proceeds beyond the alcohol stage.

Step 2: Write a representative balanced equation Using acetone as a ketone example,

$$CH_3COCH_3 + 4[H] \xrightarrow{Zn(Hg),\ \text{conc. HCl}} CH_3CH_2CH_3 + H_2O.$$

Quick Tip to Solve: Remember the acidic pair Zn(Hg)/concentrated HCl, and replace the carbonyl oxygen by two hydrogens.

Here $[H]$ represents reducing hydrogen equivalents supplied by the reagent system. The carbonyl oxygen leaves as water and propane is formed.

Step 3: Conclusion An equation for Clemmensen reduction is

$$CH_3COCH_3 + 4[H] \xrightarrow{\text{Zn(Hg), conc. HCl}} CH_3CH_2CH_3 + H_2O.$$

Quick Tip to Solve: Remember the acidic pair Zn(Hg)/concentrated HCl, and replace the carbonyl oxygen by two hydrogens.

Section C (21 marks)

22. For the reaction A + B → Products, the following initial rates were obtained at various initial concentrations of reactants:

Sl. No.	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate/mol L^{-1} s^{-1}
1	0.1	0.1	0.05
2	0.2	0.1	0.10
3	0.1	0.2	0.05

Determine the order of the reaction with respect to A and B and overall order of the reaction.

[3 marks]

Solution:

Concept:

- The initial-rate law is $r = k[A]^m[B]^n$, where r is the reaction rate, k the rate constant, and m, n the orders with respect to A and B.
- Compare experiments in which only one reactant concentration changes. The overall order is $m + n$; it need not equal the sum of stoichiometric coefficients.

Step 1: Determine the order with respect to A Compare experiments 1 and 2: $[B] = 0.1\,\text{mol L}^{-1}$ remains constant, while $[A]$ doubles from 0.1 to $0.2\,\text{mol L}^{-1}$. The rate also doubles from 0.05 to $0.10\,\text{mol L}^{-1}\text{s}^{-1}$. Dividing the two rate laws gives

$$\frac{0.10}{0.05} = \left(\frac{0.2}{0.1}\right)^m, \qquad 2 = 2^m.$$

Therefore $m = 1$.

Step 2: Determine the order with respect to B Compare experiments 1 and 3: $[A] = 0.1\,\text{mol L}^{-1}$ remains constant, while $[B]$ doubles. The measured initial rate stays at $0.05\,\text{mol L}^{-1}\text{s}^{-1}$. Thus

$$\frac{0.05}{0.05} = \left(\frac{0.2}{0.1}\right)^n, \qquad 1 = 2^n.$$

Hence $n = 0$: changing B has no effect on the rate in these experiments.

Step 3: Combine the experimentally determined exponents The rate expression is $r = k[A]^1[B]^0 = k[A]$. Adding the exponents gives $m + n = 1 + 0 = 1$. As a consistency check, $k = r/[A] = 0.05/0.1 =$

Quick Tip to Solve: For each comparison, hold one concentration fixed before taking the rate ratio.

$0.50\,s^{-1}$; all three experiments give this same value.

Step 4: Conclusion The reaction is first order with respect to A, zero order with respect to B, and first order overall.

Quick Tip to Solve: For each comparison, hold one concentration fixed before taking the rate ratio.

23(a)(i). Shweta mixed two liquids A and B of 10 mL each. After mixing, the volume of the solution was found to be 20.2 mL.

Why was there a volume change after mixing the liquids? [1 mark]

Solution:

Concept:

- In a non-ideal solution, unlike-molecule interactions A–B differ from the like-molecule interactions A–A and B–B.
- Weaker A–B attractions can produce expansion on mixing, so $\Delta V_{mix} > 0$.

Step 1: Calculate the observed volume change The sum of the separate volumes is $10 + 10 = 20$ mL, but the final volume is 20.2 mL. Hence $\Delta V_{mix} = 20.2 - 20 = +0.2$ mL.

Step 2: Explain the molecular cause The A–B intermolecular attractions formed on mixing are weaker than the A–A and B–B attractions in the pure liquids. Molecules are therefore held less closely in the mixture, giving expansion and a non-additive volume.

Step 3: Conclusion The volume increases because weaker A–B attractions cause expansion on mixing; this solution shows positive deviation from ideal behaviour.

Quick Tip to Solve: A final volume larger than the sum signals expansion and weaker unlike-molecule attractions.

23(a)(ii). Shweta mixed two liquids A and B of 10 mL each. After mixing, the volume of the solution was found to be 20.2 mL.

Will there be an increase or decrease of temperature after mixing? [1 mark]

Solution:

Concept:

- Mixing with weaker A–B attractions is endothermic: $\Delta H_{mix} > 0$.
- Breaking stronger like-molecule attractions requires more energy than is released by forming the weaker unlike-molecule attractions.

Step 1: Identify the interaction change The expansion from 20 to 20.2 mL indicates that A–B attractions in the mixture are weaker than the A–A and B–B attractions in the separate liquids.

Step 2: Relate mixing to temperature Net energy is absorbed during mixing. This energy is taken from the liquids and their immediate surroundings, so the freshly mixed solution cools, before subsequent heat exchange with the environment restores thermal equilibrium.

Quick Tip to Solve: Weaker attractions on mixing imply positive enthalpy of mixing and initial cooling.

Step 3: Conclusion The temperature decreases after mixing because the mixing process is endothermic.

Quick Tip to Solve: Weaker attractions on mixing imply positive enthalpy of mixing and initial cooling.

23(a)(iii). Shweta mixed two liquids A and B of 10 mL each. After mixing, the volume of the solution was found to be 20.2 mL.

Give one example for this type of solution. [1 mark]

Solution:

Concept:

- A solution with weaker unlike-molecule attractions than like-molecule attractions exhibits positive deviation from Raoultś law.
- Such mixtures commonly have $\Delta H_{\text{mix}} > 0$ and $\Delta V_{\text{mix}} > 0$.

Step 1: Select a suitable pair of liquids An example is a mixture of ethanol and acetone. Pure ethanol molecules are held together by an extensive network of intermolecular hydrogen bonds.

Step 2: Explain why it fits the observed behaviour Adding acetone disrupts the hydrogen-bonded arrangement of ethanol. The resulting interactions between the unlike molecules are weaker overall than the original attractions, allowing molecules to escape more readily into the vapour and producing positive deviation.

Step 3: Conclusion A mixture of ethanol and acetone is an example of this type of solution.

Quick Tip to Solve: For positive deviation, remember acetone with ethanol: ethanol hydrogen bonding is disrupted.

OR

23(b)(i). How does sprinkling of salt help in clearing the snow covered roads in hilly areas? [1 mark]

Solution:

Concept:

- A dissolved non-volatile solute lowers the freezing point of a solvent; this is freezing-point depression.
- For a dilute solution, $\Delta T_f = iK_f m$, where i is the vant́ Hoff factor, K_f the cryoscopic constant, and m the molality.

Step 1: Form a salt solution on the icy surface Salt dissolves in the thin film of water present on snow or ice. Dissolved ions lower the chemical potential of water, so the resulting brine has a lower freezing point than pure water.

Step 2: Explain snow removal At temperatures where pure water would freeze but the brine remains liquid, the snow melts to form more salt solution. Thus the freezing-point depression helps remove the snow covering the road.

Quick Tip to Solve: Connect salt on snow directly to freezing-point depression, not to a rise in temperature.

Step 3: Conclusion Sprinkling salt lowers the freezing point of water, causing snow to melt and helping clear the roads.

Quick Tip to Solve: Connect salt on snow directly to freezing-point depression, not to a rise in temperature.

23(b)(ii). What happens when red blood cells are kept in 0.5% (mass/vol) NaCl solution? Justify your answer. [1 mark]

Solution:

Concept:

- Osmosis is the movement of water through a semipermeable membrane from lower solute concentration to higher solute concentration.
- A 0.9% (mass/volume) NaCl solution is approximately isotonic with red blood cells; a more dilute solution is hypotonic.

Step 1: Compare the solution with the cell interior The supplied 0.5% NaCl solution is more dilute than the approximately 0.9% NaCl solution isotonic with red blood cells. Its osmotic pressure is lower than that inside the cells.

Step 2: Determine the direction and consequence of osmosis Water enters the cells through their semipermeable membranes by endosmosis. The increased water content makes the red blood cells swell, and sufficiently extensive swelling ruptures the cell membranes, causing haemolysis.

Step 3: Conclusion The red blood cells swell and may burst (haemolysis) because water enters them by endosmosis in the hypotonic 0.5% NaCl solution.

Quick Tip to Solve: Compare with 0.9 percent NaCl: a lower concentration sends water into red blood cells.

23(b)(iii). Write an application of reverse osmosis. [1 mark]

Solution:

Concept:

- Osmosis is the flow of solvent through a semipermeable membrane from dilute solution towards concentrated solution.
- In reverse osmosis, pressure greater than the osmotic pressure is applied on the solution side to reverse the solvent flow.

Step 1: Choose a practical application Reverse osmosis is used for desalination of seawater to obtain fresh water suitable for drinking.

Step 2: Explain how the separation occurs High pressure forces water from the saline side through a semipermeable membrane. The membrane allows water to pass while retaining dissolved salts on the saline side, thereby reducing the salt content of the collected water.

Step 3: Conclusion An application is desalination of seawater to obtain fresh drinking water.

Quick Tip to Solve: For a reverse-osmosis application, name desalination and identify water as the substance passing through the membrane.

24(a). Based on Valence Bond Theory, explain the geometry and magnetic character of $[NiCl_4]^{2-}$. [Atomic number: Ni = 28] [2 marks]

Solution:

Concept:

- The oxidation state of nickel follows from the total charge: $x + 4(-1) = -2$, so $x = +2$.
- Valence Bond Theory relates the available hybrid orbitals to geometry; unpaired electrons determine paramagnetism.

Step 1: Determine the electronic configuration Nickel has atomic number 28 and ground-state configuration $[\mathrm{Ar}]3d^8 4s^2$. Removal of the two $4s$ electrons gives Ni^{2+} : $[\mathrm{Ar}]3d^8$. The five $3d$ orbitals contain three paired electron pairs and two unpaired electrons.

Step 2: Identify hybridisation and geometry Chloride is a weak-field ligand, so it does not cause additional pairing of the $3d$ electrons. One empty $4s$ orbital and three empty $4p$ orbitals form four sp^3 hybrid orbitals. Each accepts a lone pair from a chloride ligand. Their tetrahedral arrangement gives tetrahedral geometry.

Step 3: Explain magnetic character The two unpaired $3d$ electrons remain in the complex. Consequently it is attracted by a magnetic field and is paramagnetic. The spin-only value is $\mu = \sqrt{n(n+2)} = \sqrt{8} \approx 2.83\,\mathrm{BM}$ for $n = 2$.

Step 4: Conclusion $[\mathrm{NiCl_4}]^{2-}$ is sp^3-hybridised, tetrahedral and paramagnetic with two unpaired electrons.

Quick Tip to Solve: First obtain the metal oxidation state; weak-field chloride leaves the two unpaired electrons of nickel(II) intact.

24(b). Draw the possible isomers of $[Co(en)_2Cl_2]^+$. [1 mark]

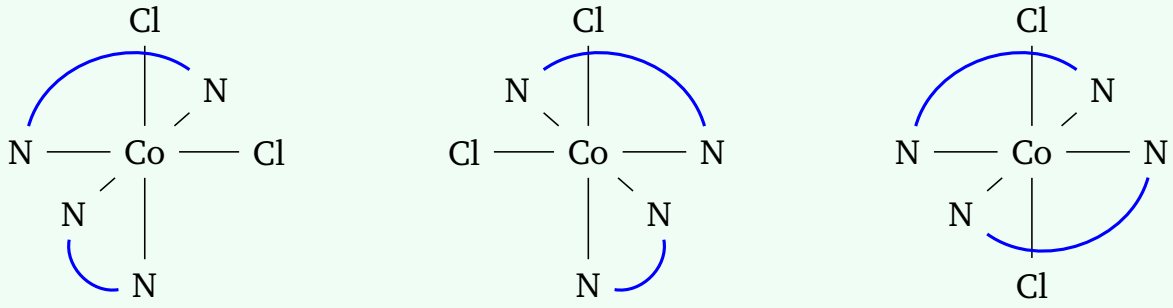
Solution:

Concept:

- Ethylenediamine (en) is bidentate: two en ligands supply four nitrogen donor atoms, giving coordination number six with the two chlorides.
- In an octahedral complex, adjacent chloride positions give cis geometry and opposite chloride positions give trans geometry.

Step 1: Draw the geometrical isomers The octahedral arrangements are shown below. Each blue en connection joins the two nitrogen atoms of one chelating ethylenediamine ligand. In cis the two Cl ligands are adjacent ($90°$); in trans they are opposite ($180°$).

Quick Tip to Solve: Place the two chloride ligands first: adjacent means cis, opposite means trans; connect each en only to adjacent donor sites.



Octahedral cis optical pair and trans form; en connects its two nitrogen donors.

Step 2: Include the optical forms The cis arrangement has two nonsuperimposable mirror-image forms, both drawn. These are its optical isomers. The trans arrangement has symmetry and is optically inactive. Thus there are two geometrical forms, and three stereoisomers when the two optical forms of cis are counted separately. All drawings represent the cation $[\mathrm{Co(en)_2Cl_2}]^+$.

Step 3: Conclusion The possible geometrical isomers are cis and trans; cis additionally exists as a pair of optical isomers.

Quick Tip to Solve: Place the two chloride ligands first: adjacent means cis, opposite means trans; connect each en only to adjacent donor sites.

25(a). Among the following, which will have inversion of configuration on reaction with aqueous alkali and why?

(i) 1-chloropropane OR (ii) 2-chloro-2-methylpropane [1 mark]

Solution:

Concept:

- An S_N2 substitution occurs by backside attack of the nucleophile and inversion of the local tetrahedral arrangement.
- Steric crowding suppresses backside attack at a tertiary carbon.

Step 1: Identify the substrate for backside attack 1-Chloropropane is a primary haloalkane. Its carbon bearing chlorine is accessible to $\mathrm{OH^-}$, so substitution proceeds predominantly by the S_N2 pathway. Attack opposite the C–Cl bond reverses the arrangement at the reacting carbon.

Step 2: Contrast the tertiary substrate 2-Chloro-2-methylpropane has a tertiary carbon surrounded by three methyl groups, which hinder S_N2 attack. In aqueous alkali it favours S_N1 substitution through a planar carbocation and does not give obligatory inversion. Although 1-chloropropane is achiral, the inversion here refers to the substitution geometry, not an observable change in optical rotation.

Step 3: Conclusion 1-Chloropropane is the expected choice, because its S_N2 reaction involves backside attack and inversion at the reacting carbon.

Quick Tip to Solve: Primary halides allow backside attack; distinguish inversion of the reacting geometry from optical activity of the molecule.

25(b). Which of the following (A) or (B) will be the major product in the reaction given below? Give a suitable reason for your answer.

$CH_3 - CH_2 - CH(Br) - CH_3$ + alc. KOH $\rightarrow$

$CH_3 - CH_2 - CH = CH_2$ (A) + $CH_3 - CH = CH - CH_3$ (B) [2 marks]

Solution:

Concept:

- Alcoholic KOH favours elimination of hydrogen halide from a haloalkane, forming a carbon–carbon double bond.
- Saytzeffś rule predicts that the more substituted alkene is the major product of such elimination.

Step 1: Identify the two elimination products The substrate is 2-bromobutane. Removal of a hydrogen from the terminal beta carbon gives but-1-ene (A), while removal from the internal beta carbon gives but-2-ene (B). In each case bromide leaves from the carbon originally bearing Br. The products correspond to the two available neighbouring carbon atoms.

Step 2: Compare alkene stability But-1-ene, $CH_3CH_2CH{=}CH_2$, is monosubstituted at its double bond. But-2-ene, $CH_3CH{=}CHCH_3$, is disubstituted. The two alkyl groups stabilise the double bond in but-2-ene by their electron-releasing inductive effect and hyperconjugation. Therefore the more substituted internal alkene is favoured, in agreement with Saytzeffś rule. The question asks which constitutional product predominates, so the comparison is between A and B.

Step 3: Conclusion Product (B), $CH_3CH{=}CHCH_3$ (but-2-ene), is the major product because it is the more substituted and more stable alkene.

Quick Tip to Solve: For alcoholic KOH, compare the substitution of each possible double bond; the more substituted alkene usually predominates.

26(a). Write the chemical equation for Williamson's synthesis. [1 mark]

Solution:

Concept:

- Williamson synthesis forms an ether by reaction of a sodium alkoxide with an alkyl halide.
- The alkoxide ion is a nucleophile; it displaces the halide ion from a suitable primary alkyl halide.

Step 1: Write the general equation For alkyl groups R and $R\prime$, and a halogen X, the reaction is

$$\mathrm{RONa} + \mathrm{R\prime X} \longrightarrow \mathrm{ROR\prime} + \mathrm{NaX}.$$

The ether contains the oxygen of the alkoxide and the alkyl group supplied by the halide.

Step 2: Illustrate the synthesis For example, sodium ethoxide reacts with bromoethane to form ethoxyethane:

$$\mathrm{C_2H_5ONa} + \mathrm{C_2H_5Br} \longrightarrow \mathrm{C_2H_5OC_2H_5} + \mathrm{NaBr}.$$

A primary halide favours nucleophilic substitution and avoids the competing elimination associated with hindered halides.

Quick Tip to Solve: Place the alkoxide oxygen between the two alkyl groups and combine sodium with the halide.

Step 3: Conclusion The required equation is $\mathrm{RONa} + \mathrm{R\prime X} \longrightarrow \mathrm{ROR\prime} + \mathrm{NaX}$.

Quick Tip to Solve: Place the alkoxide oxygen between the two alkyl groups and combine sodium with the halide.

26(b). Give a method to separate o-nitrophenol and p-nitrophenol. Explain the principle involved.

[2 marks]

Solution:

Concept:

- Steam distillation separates substances that differ in their volatility in steam.
- Intramolecular hydrogen bonding occurs within one molecule; intermolecular hydrogen bonding associates different molecules.

Step 1: Choose the separation method The mixture is separated by steam distillation. Pass steam through the mixture and collect the condensed vapour. The more steam-volatile o-nitrophenol distils with steam, while p-nitrophenol remains predominantly in the distillation flask. Thus the distillate supplies the ortho isomer and the residue supplies the para isomer.

Step 2: Explain the difference in volatility In o-nitrophenol, the adjacent hydroxyl and nitro groups form an intramolecular hydrogen bond. This reduces association between different molecules and makes the compound more volatile. In p-nitrophenol, the two groups are too far apart for this internal bond; intermolecular hydrogen bonding produces molecular association. More energy is required to separate those associated molecules, so the para isomer is less volatile and does not readily distil with steam.

Step 3: Conclusion Separate the isomers by steam distillation: o-nitrophenol distils because of intramolecular hydrogen bonding, whereas intermolecularly associated p-nitrophenol remains behind.

Quick Tip to Solve: Associate ortho with an internal hydrogen bond and steam volatility; para forms bonds between molecules.

27. Identify P, Q and R in the following reaction sequence:

$$\mathrm{P} \xrightarrow{\mathrm{NH_3}} \mathrm{CH_3COO^-NH_4^+} \xrightarrow{\Delta} \mathrm{Q}$$

$$\mathrm{P} \xrightarrow{\mathrm{PCl_5}} \mathrm{R}$$

[3 marks]

Solution:

Concept:

- A carboxylic acid reacts with ammonia to form an ammonium carboxylate salt.
- Heating an ammonium carboxylate eliminates water and forms the corresponding amide.
- Phosphorus pentachloride replaces the hydroxyl group of a carboxylic acid with chlorine to form

Quick Tip to Solve: Trace both arrows from P independently: ammonia then heat gives an amide, while PCl5 gives an acyl chloride.

an acyl chloride.

Step 1: Identify P from the ammonium salt The given salt is ammonium ethanoate, $CH_3COO^-NH_4^+$. Its carboxylate ion is obtained by removal of the acidic hydrogen from ethanoic acid. Therefore P is CH_3COOH, ethanoic acid (acetic acid). Its reaction with ammonia is

$$CH_3COOH + NH_3 \longrightarrow CH_3COO^-NH_4^+.$$

This first step is an acid-base reaction; the two-carbon skeleton is retained.

Step 2: Identify Q on heating the salt Heating ammonium ethanoate removes one molecule of water to produce ethanamide (acetamide):

$$CH_3COO^-NH_4^+ \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Hence Q is CH_3CONH_2. The product is an amide, containing the $-CONH_2$ group, rather than a nitrile.

Step 3: Identify R from the separate branch The printed lower branch starts from P, ethanoic acid, and uses PCl_5. It converts the acid into ethanoyl chloride (acetyl chloride):

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl.$$

Hence R is CH_3COCl. The carbonyl oxygen remains attached to carbon; chlorine replaces the acid hydroxyl group. The by-products balance the phosphorus, oxygen, chlorine and hydrogen atoms.

Step 4: Conclusion $\boxed{P = CH_3COOH, \quad Q = CH_3CONH_2, \quad R = CH_3COCl}$.

Quick Tip to Solve: Trace both arrows from P independently: ammonia then heat gives an amide, while PCl5 gives an acyl chloride.

28(a). Name the vitamin whose deficiency causes pernicious anaemia. [1 mark]

Solution:

Concept:

- Vitamins are required in small quantities for normal metabolism; a specific deficiency produces characteristic symptoms.
- Vitamin B_{12}, also called cobalamin, is a water-soluble member of the vitamin B complex.

Step 1: Recognise the deficiency association The standard vitamin-deficiency association for pernicious anaemia is vitamin B_{12}. This vitamin supports normal red blood cell formation; inadequate availability disrupts that process.

Step 2: State the specific vitamin The required name is cobalamin, or vitamin B_{12}. Merely writing vitamin B is insufficient because the B complex contains several distinct vitamins. The adjective pernicious distinguishes this association from the general anaemia associated with iron deficiency.

Step 3: Conclusion The vitamin is $\boxed{\text{Vitamin } B_{12} \text{ (cobalamin)}}$.

Quick Tip to Solve: Use the specific term pernicious to recall vitamin B12, and write the subscript 12 clearly.

28(b). Write any two differences between globular and fibrous proteins. [2 marks]

Solution:

Concept:

- Protein chains fold into structures whose shape influences their physical properties and biological roles.
- Globular proteins are compact and approximately spherical, whereas fibrous proteins have extended thread-like structures.

Step 1: Compare their shapes Globular proteins have polypeptide chains folded into compact, roughly spherical structures. Fibrous proteins have polypeptide chains arranged in elongated, fibre-like structures. For example, insulin is globular, while keratin is fibrous. This gives the first required difference: compact spherical shape versus long thread-like shape.

Step 2: Compare their solubility Globular proteins are generally soluble in water because their folded surfaces interact favourably with the surrounding aqueous medium. Fibrous proteins are generally insoluble in water and form tough structural materials. This gives the second required difference: generally water-soluble versus generally water-insoluble. The word generally allows for variations among proteins while stating the standard textbook comparison clearly.

Step 3: Conclusion Two differences: globular proteins are compact and spherical and generally soluble in water; fibrous proteins are elongated and fibre-like and generally insoluble in water.

Quick Tip to Solve: Use the paired properties shape and water solubility; give both sides of each comparison.

Section D (8 marks)

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

29(a). Werner's coordination theory in 1893 was the first attempt to explain the bonding in coordination complexes. It must be remembered that this theory was put forward before the electron had been discovered by J.J. Thomson in 1897, and before the electronic theory of valency. Werner did not have any of the modern instrumental techniques and all his studies were made using simple experimental techniques. Werner was able to explain the nature of bonding in complexes and he concluded that in complexes, the metal shows two different sorts of valency: primary and secondary. Primary valences are normally ionisable whereas secondary valences are non ionisable.

Answer the following questions:

One mole of $CrCl_3 \cdot 4H_2O$ precipitates one mole of AgCl when treated with excess of $AgNO_3$ solution. Write (i) the structural formula of the complex, and (ii) the secondary valency of Cr. [2 marks]

Solution:

Concept:

- Primary valency is the oxidation state; secondary valency is the coordination number, namely the number of donor atoms bonded directly to the metal.
- Only ionisable chloride outside the coordination sphere reacts immediately with excess silver

Quick Tip to Solve: First count chloride ions precipitated as AgCl; only these belong outside the square brackets.

nitrate: $Ag^+ + Cl^- \longrightarrow AgCl(s)$.

Step 1: Identify the ionisable chloride One mole of the compound produces one mole of $AgCl$. Thus exactly one of its three chloride ions lies outside the coordination sphere. The remaining two chloride ions are coordinated to chromium and do not behave as free chloride ions in this test.

Step 2: Place the ligands inside the sphere The four water molecules and the two coordinated chloride ions surround chromium. The formula is therefore $[Cr(H_2O)_4Cl_2]Cl$. Chromium is in oxidation state $+3$; the complex ion has charge $+3 - 2 = +1$, balanced by the one external Cl^-. Each water molecule and chloride ligand is monodentate, giving $4 + 2 = 6$ donor atoms directly bonded to Cr.

Step 3: Conclusion (i) Structural formula: $\boxed{[Cr(H_2O)_4Cl_2]Cl}$. (ii) Secondary valency of chromium: $\boxed{6}$.

Quick Tip to Solve: First count chloride ions precipitated as AgCl; only these belong outside the square brackets.

29(b). What is the difference between a complex and a double salt? [1 mark]

Solution:

Concept:

- A double salt dissociates completely into its constituent simple ions in water.
- A coordination complex retains its complex ion in solution; coordinated ligands remain attached to the central metal.

Step 1: Describe a double salt For example, Mohŕs salt dissociates in water to give Fe^{2+}, NH_4^+ and SO_4^{2-} ions. These constituent ions give their usual characteristic tests.

Step 2: Describe a complex For example, $K_4[Fe(CN)_6]$ gives K^+ and $[Fe(CN)_6]^{4-}$ in solution. The complex ion retains its identity and does not furnish free Fe^{2+} and CN^- for their usual tests.

Step 3: Conclusion A double salt loses its identity by complete dissociation into simple ions, whereas a complex retains its coordination entity in solution.

Quick Tip to Solve: Compare the ions formed in water: simple constituent ions versus an intact complex ion.

29(c). Arrange the following complexes in the increasing order of conductivity of their solution: $[Cr(NH_3)_3Cl_3]$, $[Cr(NH_3)_6]Cl_3$, $[Cr(NH_3)_5Cl]Cl_2$ [1 mark]

Solution:

Concept:

- For this comparison under similar solution conditions, conductivity increases with the number of ions produced by dissociation.
- Ligands inside square brackets remain bound; chloride ions outside the brackets are ionisable counterions.

Step 1: Count particles in solution $[Cr(NH_3)_3Cl_3]$ is a neutral complex with no counterions and

Quick Tip to Solve: Count only chlorides outside brackets and add one for the charged complex ion.

produces essentially no ions. $[Cr(NH_3)_5Cl]Cl_2$ produces one complex cation and two chloride ions: three ions in total.

Step 2: Compare the remaining complex $[Cr(NH_3)_6]Cl_3$ produces one complex cation and three chloride ions: four ions in total. Consequently its solution has the greatest conductivity of the three in the standard ion-count comparison.

Step 3: Conclusion Increasing conductivity:

$$[Cr(NH_3)_3Cl_3] < [Cr(NH_3)_5Cl]Cl_2 < [Cr(NH_3)_6]Cl_3.$$

Quick Tip to Solve: Count only chlorides outside brackets and add one for the charged complex ion.

OR

29(c). Write two differences between primary and secondary valences in coordination compounds.

[1 mark]

Solution:

Concept:

- Werner distinguished ionisable primary valencies from non-ionisable secondary valencies.
- Primary valency equals the oxidation state, whereas secondary valency equals the coordination number.

Step 1: Compare ionisation Primary valencies are normally ionisable and are satisfied by negative ions. Secondary valencies are non-ionisable and are satisfied by ligands, which may be neutral molecules or negative ions.

Step 2: Compare directionality Primary valencies are non-directional. Secondary valencies are directed in space, so their arrangement determines the geometry of the coordination entity, for example octahedral geometry for six suitably arranged donor atoms.

Step 3: Conclusion Two differences are: primary valencies are ionisable and non-directional; secondary valencies are non-ionisable and directional.

Quick Tip to Solve: Remember primary as oxidation state and secondary as the directed ligand coordination number.

30(a). **Carbohydrates are polyhydroxy aldehydes or ketones that represent enormous structural diversity in terms of the arrangement of atoms in space, resulting in hundreds of stereoisomers. Although the chemical properties of most stereoisomers may not be very different, their metabolic rate and utilization in biological systems is significantly different and known to influence the overall carbohydrate metabolism. Structural variants, which arise due to a different arrangement of atoms in three-dimensional space are known as stereoisomers. The number of stereoisomers can be theoretically estimated by using the formula 2^n, where 'n' is the number of stereocenters or asymmetric (chiral) carbon atoms in a molecule. Out of these stereoisomers, there are some structures, which are mirror images of each other, and they are referred to as enantiomers.**

Answer the following questions:

Give chemical reactions to show the presence of an aldehydic group and straight chain in glucose.

[2 marks]

Solution:

Concept:

- Mild oxidation with bromine water converts an aldehyde group $-\mathrm{CHO}$ into $-\mathrm{COOH}$.
- Prolonged heating with excess HI reduces glucose to n-hexane, establishing an unbranched chain of six carbon atoms.

Step 1: Establish the aldehydic group Glucose is oxidised by bromine water to gluconic acid. Using its open-chain formula, the balanced reaction is

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O}$$

$$\longrightarrow \mathrm{COOH(CHOH)_4CH_2OH + 2HBr.}$$

This mild oxidising agent changes the terminal aldehyde group to a carboxyl group, showing the presence of $-\mathrm{CHO}$ in the open-chain form of glucose.

Step 2: Establish the straight carbon chain On prolonged heating with excess hydrogen iodide, glucose gives n-hexane:

$$\mathrm{C_6H_{12}O_6 + 14HI \xrightarrow{\Delta} CH_3(CH_2)_4CH_3 + 6H_2O + 7I_2.}$$

The product contains six carbon atoms joined in a continuous unbranched chain. Since reduction removes oxygen without altering the carbon skeleton, all six carbon atoms in glucose lie in a straight chain.

Step 3: Conclusion Bromine-water oxidation to gluconic acid establishes the aldehydic group; reduction with hot excess HI to n-hexane establishes the straight six-carbon chain.

Quick Tip to Solve: Use bromine water for the aldehyde evidence and hot excess HI for the carbon-skeleton evidence.

30(b). Define anomers. [1 mark]

Solution:

Concept:

- Cyclisation of a sugar creates an anomeric carbon from the carbonyl carbon of its open-chain form.
- Anomers are cyclic stereoisomers that differ only in configuration at this anomeric carbon.

Step 1: Locate the difference In glucose, the aldehyde carbon C-1 becomes the anomeric carbon when the cyclic hemiacetal forms. The configurations at all other stereocentres remain the same in the two anomers.

Step 2: Give an example α-D-glucopyranose and β-D-glucopyranose are anomers. They differ in the orientation of the hydroxyl group at C-1: in the usual Haworth representation it is down in the alpha form and up in the beta form.

Step 3: Conclusion Anomers are cyclic sugar stereoisomers differing only in configuration at the anomeric carbon, such as the alpha and beta forms of D-glucopyranose.

Quick Tip to Solve: For glucose, compare C-1 only; differences at another stereocentre define other epimers.

OR

30(b). Draw the structure of β-D-Glucopyranose. [1 mark]

Solution:

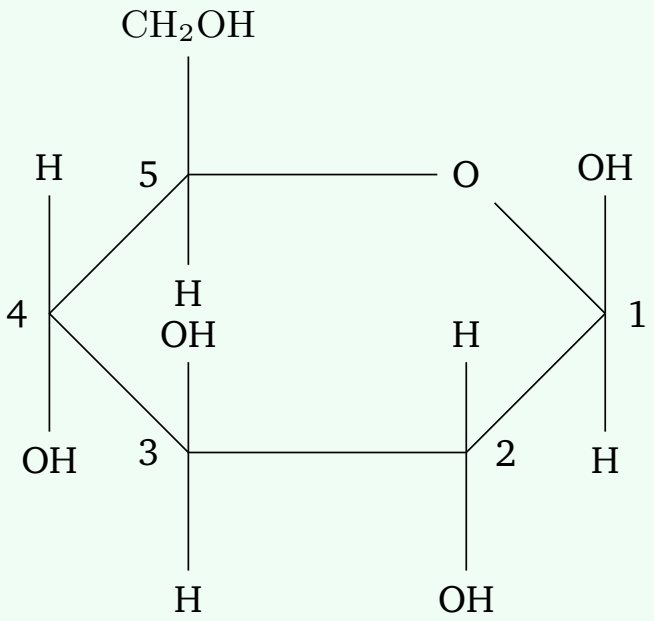
Concept:

- Glucopyranose is a six-membered cyclic hemiacetal formed by reaction of the C-5 hydroxyl group with the C-1 aldehyde group.
- In a D-sugar Haworth projection, the C-5 CH_2OH group is above the ring. The beta anomer has its C-1 hydroxyl group on the same side.

Step 1: Form the pyranose ring Draw a ring with five carbon atoms and one oxygen atom. Put oxygen at the upper right and number the carbons clockwise starting with C-1 at the right. From the configuration of D-glucose, the hydroxyl groups point down at C-2, up at C-3 and down at C-4.

Step 2: Choose the beta anomer Place the C-5 CH_2OH group upwards. For the beta anomer, put the C-1 OH group upwards too. The hydrogens at all five ring carbon atoms occupy the opposite positions to the indicated substituents. The labelled Haworth projection below gives the required complete structure.

Quick Tip to Solve: For beta-D-glucose, keep C-1 OH and C-5 CH2OH up; C-2, C-3 and C-4 OH follow down, up, down.



Haworth projection of beta-D-glucopyranose

Step 3: Conclusion The structure shown is β-D-glucopyranose; the C-1 OH and C-5 CH_2OH groups are on the same side of the ring.

Quick Tip to Solve: For beta-D-glucose, keep C-1 OH and C-5 CH2OH up; C-2, C-3 and C-4 OH follow down, up, down.

30(c). Sucrose is known as invert sugar. Explain. [1 mark]

Solution:

Concept:

- Optical rotation of a mixture is the combined rotation of its components; dextrorotation is positive and laevorotation is negative.
- Sucrose hydrolysis gives equimolar D-glucose and D-fructose. Fructose has a larger negative specific rotation than the positive specific rotation of glucose.

Step 1: Hydrolyse sucrose On hydrolysis with dilute acid or the enzyme invertase, sucrose gives glucose and fructose:

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6\ (\text{glucose}) + C_6H_{12}O_6\ (\text{fructose}).$$

Sucrose itself is dextrorotatory, with specific rotation about $+66.5^\circ$.

Step 2: Explain the inversion of rotation Glucose is dextrorotatory (about $+52.5^\circ$), whereas fructose is laevorotatory (about -92.4°). Their equimolar hydrolysis mixture is therefore laevorotatory, since the negative rotation due to fructose predominates. The change from positive rotation of sucrose to negative rotation of its hydrolysis products is called inversion.

Quick Tip to Solve: Compare the magnitudes of glucose and fructose rotations: the larger negative fructose rotation determines the mixture sign.

Step 3: Conclusion Thus hydrolysis of sucrose inverts the direction of optical rotation. The glucose-fructose mixture obtained is called invert sugar.

Quick Tip to Solve: Compare the magnitudes of glucose and fructose rotations: the larger negative fructose rotation determines the mixture sign.

Section E (15 marks)

31(a). (i) In a chemistry practical class, the teacher gave his students an amine 'X' having molecular formula C_2H_7N, and asked the students to identify the type of amine. One of the students, Neeta, observed that it reacts with $C_6H_5SO_2Cl$, to give a compound which dissolves in NaOH solution. Can you help Neeta to identify the compound 'X'?

(ii) Arrange the following in the increasing order of their pK_b value in aqueous phase:

$C_6H_5NH_2$, $(CH_3)_2NH$, NH_3, CH_3NH_2, $(CH_3)_3N$

(iii) Aniline on nitration gives considerable amount of meta product along with ortho and para products. Why?

(iv) Convert aniline to:

(I) p-bromoaniline

(II) phenol [5 marks]

Solution:

Concept:

- The Hinsberg reagent $C_6H_5SO_2Cl$ gives a primary amine sulphonamide containing an acidic N-H bond, which dissolves in alkali.
- $pK_b = -\log K_b$: stronger bases have smaller pK_b. Aqueous basicity depends on electron donation and solvation.
- Protonation converts aniline into the meta-directing anilinium ion. Acetylation protects the amino group during selective bromination.
- Diazotisation of a primary aromatic amine at 273-278 K gives a diazonium salt, which hydrolyses to phenol on warming.

Step 1: (i) Identify amine X The product dissolves in NaOH, so it must retain an acidic N-H bond. This is the Hinsberg response of a primary amine. Of the amines having formula C_2H_7N, ethylamine is primary, while dimethylamine is secondary. Hence X is ethylamine, $CH_3CH_2NH_2$.

$$C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHC_2H_5 + HCl.$$

NaOH removes the sulphonamide proton, forming a soluble sodium salt. The secondary-amine product would have no N-H bond and would not show this alkali solubility.

Step 2: (ii) Arrange increasing pKb In water, dimethylamine is the strongest base in this list, followed by methylamine and trimethylamine. Alkyl groups donate electron density, but hydration and steric effects also influence the conjugate acids; hence three methyl groups do not make trimethylamine the strongest aqueous base. Ammonia is weaker than these methylamines. Aniline is weakest because its

Quick Tip to Solve: For increasing pKb, reverse aqueous basicity; protect aniline before monobromination and diazotise it before conversion to phenol.

nitrogen lone pair is delocalised into the aromatic ring. Increasing pK_b, the reverse of basic strength, is therefore

$$(CH_3)_2NH < CH_3NH_2 < (CH_3)_3N < NH_3 < C_6H_5NH_2.$$

Step 3: (iii) Explain the meta nitration product The strongly acidic nitrating mixture protonates a substantial fraction of aniline:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

The anilinium group $-NH_3^+$ is electron withdrawing and meta directing, so this fraction gives meta-nitroaniline. Unprotonated aniline retains its electron-donating, ortho/para-directing $-NH_2$ group and gives ortho and para products. This explains the considerable meta product along with the ortho and para products.

Step 4: (iv)(I) Convert aniline into p-bromoaniline First protect the amino group by acetylation using acetic anhydride. Brominate acetanilide with Br_2 in acetic acid to obtain predominantly para-bromoacetanilide, then hydrolyse the acetyl group:

$$\begin{aligned} C_6H_5NH_2 &\xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3 \\ &\xrightarrow{Br_2/CH_3COOH} p\text{-}BrC_6H_4NHCOCH_3 \\ &\xrightarrow{H_3O^+,\ \text{heat}} p\text{-}BrC_6H_4NH_2. \end{aligned}$$

Protection moderates activation and avoids direct bromination giving 2,4,6-tribromoaniline.

Step 5: (iv)(II) Convert aniline into phenol Treat aniline with $NaNO_2/HCl$ at 273-278 K to form benzenediazonium chloride. Warm this salt with water:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O,$$
$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\text{warm}} C_6H_5OH + N_2 + HCl.$$

Keep the diazotisation cold because the diazonium salt decomposes at higher temperatures; warm only for the hydrolysis step.

Step 6: Conclusion X is ethylamine. Increasing pK_b is dimethylamine, methylamine, trimethylamine, ammonia, aniline. Anilinium ion accounts for meta nitration. Acetylation-bromination-hydrolysis gives p-bromoaniline, while diazotisation followed by aqueous hydrolysis gives phenol.

Quick Tip to Solve: For increasing pKb, reverse aqueous basicity; protect aniline before monobromination and diazotise it before conversion to phenol.

OR

31(b)(i). Arun heated a mixture of ethylamine and $CHCl_3$ with ethanolic KOH, which forms a foul smelling gas. Write the chemical equation involved. [1 mark]

Solution:

Concept:

- Primary amines react with chloroform and alcoholic alkali on heating to form isocyanides; this is the carbylamine reaction.
- The isocyanide group is $-N \equiv C$, with nitrogen bonded to the alkyl group. Isocyanides have a characteristic foul smell.

Step 1: Identify the reacting amine Ethylamine, $C_2H_5NH_2$, is a primary amine, so it gives the carbylamine test. Its ethyl group is retained in the product; the carbon of chloroform becomes the terminal carbon of the isocyanide group.

Step 2: Write the balanced reaction On heating with chloroform and ethanolic potassium hydroxide,

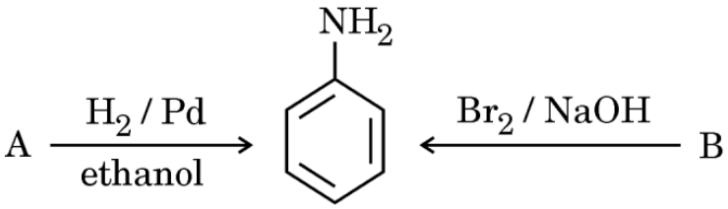
$$C_2H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{ethanol}]{\Delta} C_2H_5NC + 3KCl + 3H_2O.$$

The three chlorine atoms form three units of potassium chloride, and the oxygen and hydrogen balance as three water molecules.

Step 3: Conclusion The foul-smelling product is ethyl isocyanide, C_2H_5NC, formed by the carbylamine reaction.

Quick Tip to Solve: Write the product as RNC, not RCN: the carbylamine test makes an isocyanide.

31(b)(ii). Identify A and B in the following reactions: [2 marks]



Solution:

Concept:

- Catalytic hydrogenation converts a nitro group $-NO_2$ to an amino group $-NH_2$ without changing the benzene ring under the stated conditions.
- Hofmann bromamide degradation converts $RCONH_2$ to RNH_2 with one fewer carbon atom, using $Br_2/NaOH$.

Step 1: Identify A from catalytic reduction The central product is aniline, $C_6H_5NH_2$. Hydrogen in the presence of palladium in ethanol reduces nitrobenzene to aniline. Therefore the precursor on the

Quick Tip to Solve: For a Hofmann reaction, add a CONH2 group to R in the product RNH2 to recover the starting amide.

left is nitrobenzene:

$$C_6H_5NO_2 + 3H_2 \xrightarrow[\text{ethanol}]{Pd} C_6H_5NH_2 + 2H_2O.$$

The nitro nitrogen remains attached to the same phenyl group while its oxygen atoms are removed as water.

Step 2: Identify B from Hofmann degradation The arrow from B to aniline has $Br_2/NaOH$, the reagents for Hofmann bromamide degradation. To obtain $C_6H_5NH_2$, the starting amide must be benzamide, $C_6H_5CONH_2$:

$$C_6H_5CONH_2 + Br_2 + 4NaOH \longrightarrow C_6H_5NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is lost as carbonate, so benzamide has one more carbon than aniline.

Step 3: Conclusion $\boxed{A = C_6H_5NO_2 \text{ (nitrobenzene)}, \quad B = C_6H_5CONH_2 \text{ (benzamide)}}$.

Quick Tip to Solve: For a Hofmann reaction, add a CONH2 group to R in the product RNH2 to recover the starting amide.

31(b)(iii). Convert aniline to:

(I) benzene

(II) sulphanilic acid [2 marks]

Solution:

Concept:

- Aniline undergoes diazotisation with nitrous acid generated from $NaNO_2/HCl$ at 273–278 K.
- Hypophosphorous acid, H_3PO_2, replaces a diazonium group by hydrogen; heating aniline with concentrated sulphuric acid gives para-sulphonation.

Step 1: (I) Convert aniline to benzene First diazotise aniline at low temperature to obtain benzenediazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\,K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Then reduce the diazonium salt with hypophosphorous acid in water:

$$C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl.$$

The diazonium group is replaced by hydrogen, and nitrogen gas is evolved.

Step 2: (II) Convert aniline to sulphanilic acid Treat aniline with concentrated sulphuric acid to form anilinium hydrogensulphate, then heat to 453–473 K:

$$C_6H_5NH_2 + H_2SO_4 \longrightarrow [C_6H_5NH_3]^+HSO_4^-.$$

Quick Tip to Solve: To remove NH2 from aniline, first make a diazonium salt; for sulphanilic acid remember hot concentrated sulphuric acid.

$$[C_6H_5NH_3]^+HSO_4^- \xrightarrow{453\text{–}473\,K} p\text{-}H_2NC_6H_4SO_3H + H_2O.$$

The sulphonation product is para-aminobenzenesulphonic acid, called sulphanilic acid; it exists predominantly as a zwitterion.

Step 3: Conclusion Benzene is obtained by diazotisation followed by H_3PO_2 reduction. Sulphanilic acid is obtained by heating aniline with concentrated H_2SO_4.

Quick Tip to Solve: To remove NH2 from aniline, first make a diazonium salt; for sulphanilic acid remember hot concentrated sulphuric acid.

32(a)(i). When pyrolusite ore is fused with KOH, in presence of air, a dark green coloured product 'A' is obtained which changes to purple coloured compound 'B' in acidic medium.

(I) Write the formulae of 'A' and 'B'.

(II) Write the ionic equation for the reaction when compound 'B' reacts with Fe^{2+} in acidic medium.

[2 marks]

Solution:

Concept:

- Alkaline oxidation of MnO_2 produces green manganate(VI), MnO_4^{2-}; acidification causes disproportionation to permanganate and manganese dioxide.
- In acidic medium, permanganate is reduced from manganese(VII) to manganese(II), accepting five electrons; each Fe^{2+} loses one electron.

Step 1: (I) Identify the green and purple compounds Pyrolusite is MnO_2. Fusion with potassium hydroxide in air gives potassium manganate:

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O.$$

Thus A is green K_2MnO_4. In acidic medium manganate disproportionates:

$$3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + MnO_2 + 2H_2O.$$

The purple compound B is potassium permanganate, $KMnO_4$.

Step 2: (II) Balance the reaction with iron(II) The reduction and oxidation half-reactions are

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O,$$

$$Fe^{2+} \longrightarrow Fe^{3+} + e^-.$$

Multiply the iron half-reaction by five and add them, cancelling the electrons:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O.$$

There are four oxygen atoms and eight hydrogen atoms on each side. The total charge on each side is $+17$, confirming the balance.

Quick Tip to Solve: For acidic permanganate, use 8 H+ and 5 electrons; this fixes the coefficient of Fe2+ as five.

Step 3: Conclusion $A = K_2MnO_4$ and $B = KMnO_4$. In acid, one permanganate ion oxidises five Fe^{2+} ions to Fe^{3+}, while forming Mn^{2+}.

Quick Tip to Solve: For acidic permanganate, use 8 H+ and 5 electrons; this fixes the coefficient of Fe2+ as five.

32(a)(ii). Give reasons:

(I) Ce^{4+} in aqueous solution is a good oxidising agent.

(II) The actinoid contraction is greater from element to element than lanthanoid contraction.

(III) $E^\circ_{Zn^{2+}/Zn}$ value is more negative than expected, whereas $E^\circ_{Cu^{2+}/Cu}$ is positive. [3 marks]

Solution:

Concept:

- An oxidising agent accepts electrons and is itself reduced. A favourable positive standard reduction potential indicates a strong tendency for reduction.
- Poor shielding by f electrons causes an increase in effective nuclear charge across the inner-transition series. Electrode potentials depend on the overall energy changes of atomisation, ionisation and hydration.

Step 1: I. Oxidising nature of cerium(IV) In aqueous solution, Ce^{4+} readily accepts an electron to form the more stable $+3$ oxidation state:

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}.$$

The standard reduction potential of this couple is strongly positive (about $+1.74\,V$). Thus reduction of Ce^{4+} is favourable, and it oxidises other species while itself changing to Ce^{3+}.

Step 2: II. Greater actinoid contraction Across the actinoid series, the nuclear charge increases while electrons are added to the $5f$ subshell. The $5f$ electrons shield the increasing nuclear charge less effectively than the $4f$ electrons do in the lanthanoid series. Consequently, the effective attraction of the nucleus for the outer electrons rises more sharply, giving a greater contraction from element to element.

Step 3: III. Electrode potentials of zinc and copper Zinc readily forms Zn^{2+}, whose $3d^{10}$ configuration is especially stable. The overall energetics therefore favour formation of aqueous Zn^{2+} and give the Zn^{2+}/Zn reduction couple an unusually negative potential. For copper, the high energy needed for atomisation and ionisation to Cu^{2+} is not compensated by the energy released on hydration. Oxidation of copper to aqueous Cu^{2+} is consequently unfavourable relative to the standard hydrogen electrode, so $E^\circ_{Cu^{2+}/Cu}$ is positive.

Step 4: Conclusion Cerium(IV) is reduced readily to cerium(III); poorer shielding by $5f$ electrons gives greater actinoid contraction; stable Zn^{2+} and the uncompensated energy cost of forming aqueous Cu^{2+} explain their contrasting reduction potentials.

Quick Tip to Solve: For electrode potentials, compare the complete atomisation-ionisation-hydration energy balance, not electronic configuration alone.

OR

32(b)(i). While studying the periodic properties, Arti came across an abnormal behaviour in the atomic size of Hf. She found that, even though Hf is placed below Zr in the same group, both have almost similar atomic sizes.

(I) Which phenomenon is responsible for the above behaviour? Define it.

(II) Mention any other consequence of the above phenomenon. [2 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii with increasing atomic number across the lanthanoid series.
- The added $4f$ electrons shield the nuclear charge poorly, so the effective nuclear attraction increases across the series.

Step 1: I. Identify and explain the phenomenon The phenomenon is **lanthanoid contraction**. It is the gradual decrease in atomic and ionic radii from lanthanum to lutetium as atomic number increases. Between zirconium and hafnium, the intervening lanthanoids fill the $4f$ subshell. Poor shielding by these electrons increases the effective nuclear charge and contracts the hafnium atom. This contraction nearly offsets the size increase expected from adding a new shell, so Zr and Hf have almost identical atomic radii.

Step 2: II. State another consequence The basic strength of lanthanoid hydroxides decreases across the series, from $La(OH)_3$ towards $Lu(OH)_3$. As the Ln^{3+} ionic radius decreases, its polarising power increases and the metal-oxygen bond gains covalent character. Thus the hydroxides become progressively less basic.

Step 3: Conclusion Lanthanoid contraction accounts for the nearly equal sizes of Zr and Hf. Another consequence is the decreasing basicity of lanthanoid hydroxides across the series.

Quick Tip to Solve: Remember the causal chain: poor 4f shielding, smaller ionic radius, greater polarising power and lower hydroxide basicity.

32(b)(ii). Give reasons for the following:

(I) Transition metals exhibit catalytic properties.

(II) Transition metals have high enthalpy of atomisation.

(III) Sc is a transition element, while Zn is not. [3 marks]

Solution:

Concept:

- Transition elements have an incompletely filled d subshell in their atoms or in at least one of their oxidation states.
- Variable oxidation states, surface adsorption and strong metallic bonding account for many characteristic properties of transition metals.

Quick Tip to Solve: Apply the transition-element definition to both the neutral atom and its ions; a d-zero ion does not disqualify Sc.

Step 1: I. Catalytic properties Transition metals can exhibit different oxidation states and form intermediate compounds with reactants. These intermediates provide an alternative reaction pathway of lower activation energy, after which the catalyst is regenerated. Their metal surfaces can also adsorb reactant molecules, bringing them together and weakening bonds before reaction; this contributes to their catalytic activity.

Step 2: II. High enthalpy of atomisation Transition metals generally have several unpaired electrons in their $(n-1)d$ subshell, in addition to their outer ns electrons. Participation of these electrons in metallic bonding produces strong interatomic attractions. Separating the solid into individual gaseous atoms requires breaking these strong metallic bonds, so the enthalpy of atomisation is high.

Step 3: III. Scandium versus zinc Scandium has the electronic configuration $[\mathrm{Ar}]\,3d^1 4s^2$. Its atom has an incompletely filled $3d$ subshell, so it satisfies the definition of a transition element, even though Sc^{3+} is $3d^0$. Zinc has configuration $[\mathrm{Ar}]\,3d^{10}4s^2$, and its usual ion Zn^{2+} is $[\mathrm{Ar}]\,3d^{10}$. The d subshell is complete in both the atom and its usual ion; therefore Zn is not a transition element.

Step 4: Conclusion Transition metals catalyse reactions through intermediate formation and adsorption, and strong metallic bonding gives high atomisation enthalpies. Sc qualifies because its atom is $3d^1$; Zn and Zn^{2+} both have complete $3d^{10}$ subshells.

Quick Tip to Solve: Apply the transition-element definition to both the neutral atom and its ions; a d-zero ion does not disqualify Sc.

33(a)(i). For a galvanic cell, the following half reactions are given. Decide, which will remain as reduction reaction and which will be reversed to become an oxidation reaction. Give reason for your answer.

(I) Cr^{3+} + 3e$^-$ → Cr(s); E° = −0.74 V

(II) Fe^{2+} + 2e$^-$ → Fe(s); E° = −0.44 V [2 marks]

Solution:

Concept:

- In a galvanic cell, the half-cell with the higher standard reduction potential undergoes reduction at the cathode; the other undergoes oxidation at the anode.
- For a spontaneous standard cell, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} > 0$, using reduction potentials for both electrodes.

Step 1: Compare the reduction potentials The iron couple has $E^\circ = -0.44\,\text{V}$, whereas the chromium couple has $E^\circ = -0.74\,\text{V}$. Since $-0.44 > -0.74$, reaction (II) has the greater tendency to occur as reduction. It remains

$$\mathrm{Fe}^{2+} + 2\mathrm{e}^- \longrightarrow \mathrm{Fe(s)}.$$

Iron is deposited at the cathode.

Step 2: Reverse chromium and verify spontaneity Reaction (I) must be reversed to supply electrons at the anode:

$$\mathrm{Cr(s)} \longrightarrow \mathrm{Cr}^{3+} + 3\mathrm{e}^-.$$

Quick Tip to Solve: Compare signed potentials: the less negative reduction potential is higher and identifies the cathode.

The resulting standard cell potential is

$$E^\circ_{\text{cell}} = (-0.44) - (-0.74) = +0.30\,\text{V}.$$

Its positive value confirms the spontaneous galvanic direction. Balancing electrons gives $2\text{Cr(s)} + 3\text{Fe}^{2+} \longrightarrow 2\text{Cr}^{3+} + 3\text{Fe(s)}$. Multiplying half-reactions to balance electrons does not multiply their electrode potentials.

Step 3: Conclusion Reaction (II) remains reduction and reaction (I) becomes oxidation. This choice gives $E^\circ_{\text{cell}} = +0.30\,\text{V}$.

Quick Tip to Solve: Compare signed potentials: the less negative reduction potential is higher and identifies the cathode.

33(a)(ii). Represent the cell in which the following reaction takes place:
Mg(s) + 2Ag$^+$(0.001 M) → Mg^{2+}(0.100 M) + 2Ag(s)
Calculate E_{cell} if E°_{cell} = 3.17 V. (log 10 = 1) [3 marks]

Solution:

Concept:

- A galvanic cell is written with the oxidation half-cell (anode) on the left and the reduction half-cell (cathode) on the right. A single vertical line denotes a phase boundary; a double line denotes a salt bridge.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrode reactions Magnesium loses electrons and acts as the anode:

$$\text{Mg(s)} \rightarrow \text{Mg}^{2+}\text{(aq)} + 2\text{e}^-.$$

Silver ions gain electrons at the cathode:

$$2\text{Ag}^+\text{(aq)} + 2\text{e}^- \rightarrow 2\text{Ag(s)}.$$

Thus the balanced overall reaction transfers $n = 2$ electrons. The coefficient 2 of silver ions must also appear as a power in the reaction quotient.

Step 2: Represent the cell and form the reaction quotient The cell representation, using the given concentrations, is

$$\text{Mg(s)}\,|\,\text{Mg}^{2+}(0.100\,\text{M})\,\|\,\text{Ag}^+(0.001\,\text{M})\,|\,\text{Ag(s)}.$$

The solid electrodes do not enter the quotient. Using the concentration approximation for the dissolved ions,

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.100}{(0.001)^2} = 10^5.$$

Hence $\log Q = 5\log 10 = 5$.

Quick Tip to Solve: Write the balanced reaction first: two silver ions give a squared concentration in Q, while two electrons give n = 2.

Step 3: Apply the Nernst equation Using the usual room-temperature Nernst coefficient,

$$\begin{aligned} E_{\text{cell}} &= 3.17 - \frac{0.0591}{2} \times 5 \\ &= 3.17 - 0.14775 \\ &= 3.02225\,\text{V}. \end{aligned}$$

The positive reaction quotient logarithm lowers the cell potential below its standard value. Taking the rounded coefficient 0.059 gives the same answer to two decimal places.

Step 4: Conclusion The cell is $\text{Mg(s)}|\text{Mg}^{2+}(0.100\,\text{M})||\text{Ag}^{+}(0.001\,\text{M})|\text{Ag(s)}$, and $\boxed{E_{\text{cell}} \approx 3.02\,\text{V}}$ at $298\,\text{K}$.

Quick Tip to Solve: Write the balanced reaction first: two silver ions give a squared concentration in Q, while two electrons give n = 2.

OR

33(b)(i). State Kohlrausch's law. Give any two applications of it. [2 marks]

Solution:

Concept:

- At infinite dilution, interionic interactions become negligible and each ion makes an independent contribution to the limiting molar conductivity of an electrolyte.
- For an electrolyte producing ν_+ cations and ν_- anions per formula unit, $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$. Here λ_+° and λ_-° are the limiting ionic molar conductivities.

Step 1: State Kohlrausch's law Kohlrausch's law of independent migration of ions states that, at infinite dilution, each ion contributes a definite amount to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. The limiting molar conductivity equals the sum of the individual ionic contributions, with each multiplied by its stoichiometric coefficient.

Step 2: Give two applications **1. Limiting molar conductivity of a weak electrolyte:** It can be calculated from the limiting molar conductivities of suitable strong electrolytes. For example,

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{CH}_3\text{COONa}) + \Lambda_m^\circ(\text{HCl}) - \Lambda_m^\circ(\text{NaCl}).$$

The sodium and chloride contributions cancel.

2. Degree of dissociation of a weak electrolyte: Once its limiting molar conductivity is known, the fraction dissociated at a given concentration follows from $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m is the measured molar conductivity at that concentration.

Step 3: Conclusion Kohlrausch's law gives independent, additive ionic contributions at infinite dilution. Two applications are finding the limiting molar conductivity and the degree of dissociation of weak electrolytes.

Quick Tip to Solve: Choose strong electrolytes so unwanted ions cancel when calculating the limiting conductivity of a weak electrolyte.

33(b)(ii). Λ_m^∞ **NH_4Cl,** Λ_m^∞ **NaOH and** Λ_m^∞ **NaCl are 129.8, 217.4, and 108.9 S cm^2 mol^{-1} respectively. Molar conductivity of 1×10^{-2} M solution of NH_4OH is 9.33 S cm^2 mol^{-1}. Calculate the degree of dissociation (α) of NH_4OH solution at this concentration.** [3 marks]

Solution:

Concept:

- Kohlrausch's law gives $\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$ for a 1:1 electrolyte, where the two terms are the limiting ionic molar conductivities.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$. Both conductivities must be expressed in the same units; their ratio is dimensionless.

Step 1: Combine the limiting conductivities The required ions are NH_4^+ and OH^-. Write

$$\begin{aligned}\Lambda_m^\circ(NH_4Cl) &= \lambda^\circ(NH_4^+) + \lambda^\circ(Cl^-),\\ \Lambda_m^\circ(NaOH) &= \lambda^\circ(Na^+) + \lambda^\circ(OH^-),\\ \Lambda_m^\circ(NaCl) &= \lambda^\circ(Na^+) + \lambda^\circ(Cl^-).\end{aligned}$$

Adding the first two expressions and subtracting the third cancels the sodium and chloride contributions, leaving exactly the ionic sum for ammonium hydroxide.

Step 2: Calculate the limiting molar conductivity Therefore

$$\begin{aligned}\Lambda_m^\circ(NH_4OH) &= \Lambda_m^\circ(NH_4Cl) + \Lambda_m^\circ(NaOH) - \Lambda_m^\circ(NaCl)\\ &= 129.8 + 217.4 - 108.9\\ &= 238.3\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

This is the limiting value corresponding to complete dissociation, unlike the measured value at the stated finite concentration.

Step 3: Find the fraction and percentage dissociated For the 1×10^{-2} M solution, the measured molar conductivity is $9.33\,\text{S cm}^2\,\text{mol}^{-1}$. Thus

$$\alpha = \frac{9.33}{238.3} = 0.039152\ldots.$$

The conductivity units cancel. Expressed as a percentage, $100\alpha = 3.9152\ldots\%$. The stated concentration identifies the solution for which this dissociation fraction applies; it need not be multiplied into the conductivity ratio.

Step 4: Conclusion $\boxed{\alpha \approx 0.0392}$, so approximately $\boxed{3.92\%}$ of the NH_4OH is dissociated at the given concentration.

Quick Tip to Solve: Add NH4Cl and NaOH, then subtract NaCl: cancel the unwanted ions before taking measured conductivity divided by the limiting value.