CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-5-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper contains **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. 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 hydrogen carbonate to liberate carbon dioxide, whereas aldehydes do not give this acid-base reaction.
- A distinguishing test must produce different visible observations for the two compounds.

Step 1: Compare the bicarbonate reactions Propanoic acid contains the acidic carboxyl group and gives brisk effervescence with aqueous sodium bicarbonate:

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

Propanal, CH_3CH_2CHO, has no carboxyl group and does not liberate CO_2 with this reagent.

Step 2: Eliminate the other tests Hinsberg reagent distinguishes classes of amines and Lucas reagent distinguishes suitable alcohols; neither targets this aldehyde-acid pair. The iodoform test detects the methyl ketone group or compounds oxidised to it (and ethanal). Propanal and propanoic acid both give a negative iodoform test, so it cannot distinguish them.

Step 3: Conclusion Sodium bicarbonate gives effervescence with propanoic acid but not with propanal. Hence, the correct option is (A).

Quick Tip to Solve: When one compound is a carboxylic acid, look for bicarbonate: escaping CO_2 gives an immediate distinguishing observation.

2. 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.
- Their interconversion is an acid-base equilibrium: adding acid favours dichromate, while adding alkali favours chromate.

Step 1: Identify the effect of acid The relevant equilibrium is

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

A rise in the hydrogen-ion concentration shifts it to the right. Thus a few drops of hydrochloric acid explain the observed change from yellow to orange. Chromium remains in oxidation state $+6$; the change is not a reduction.

Step 2: Check the remaining choices Sodium hydroxide is alkaline, so it favours yellow chromate instead. Sodium hydrogen carbonate solution is mildly alkaline and likewise cannot explain acid-driven dichromate formation. Methyl orange is an indicator; adding the indicator itself is not the characteristic reagent for converting chromate into dichromate. Among the choices, hydrochloric acid supplies the required H^+ directly.

Step 3: Conclusion The liquid was most likely HCl solution, which converts yellow chromate to orange dichromate. Hence, the correct option is (D).

Quick Tip to Solve: Remember the direction: acid changes yellow chromate to orange dichromate; alkali reverses this colour change.

3. 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, the energy barrier that reactants must overcome.
- A catalyst changes reaction rates but does not change the thermodynamic properties of the initial and final states.

Step 1: Relate activation energy to reaction rate The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature. The catalysed pathway has a lower barrier, allowing the reaction to proceed faster at the same temperature.

Step 2: Distinguish kinetics from thermodynamics The catalyst leaves reactant and product energies unchanged, so the enthalpy change and Gibbs energy change of reaction do not change. Since $\Delta G^\circ = -RT \ln K$, the equilibrium constant K also remains unchanged at fixed temperature. Both forward and reverse reactions are accelerated, so equilibrium is reached sooner without shifting its position. This excludes options (A), (B) and (C).

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

Quick Tip to Solve: Separate the energy barrier from the energy difference: catalysts lower the barrier but leave reactant-to-product energy changes unchanged.

4. 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 chiral molecule is not superimposable on its mirror image. For these simple haloalkanes, a tetrahedral carbon attached to four different groups provides the stereogenic centre.
- Repeated substituents on a candidate carbon prevent that carbon from being a stereogenic centre.

Quick Tip to Solve: At the chlorine-bearing carbon, compare the entire groups: methyl and ethyl are different, even though both begin with carbon.

Step 1: Inspect the substituted carbon in each molecule In 1-chloropropane, $CH_3CH_2CH_2Cl$, and 1-chlorobutane, $CH_3CH_2CH_2CH_2Cl$, the chlorine-bearing carbon has two identical hydrogen atoms. Neither molecule contains a carbon with four different substituents. In 2-chloropropane, $CH_3CHClCH_3$, the central carbon has two identical methyl groups, so it also fails the test.

Step 2: Identify the four groups in 2-chlorobutane Write 2-chlorobutane as $CH_3CHClCH_2CH_3$. Carbon 2 is bonded to a hydrogen atom, a chlorine atom, a methyl group and an ethyl group. All four are different. This carbon is stereogenic, and the two possible spatial arrangements form a pair of non-superimposable mirror images.

Step 3: Conclusion 2-Chlorobutane is chiral because its second carbon has four different substituents. Hence, the correct option is (D).

Quick Tip to Solve: At the chlorine-bearing carbon, compare the entire groups: methyl and ethyl are different, even though both begin with carbon.

5. 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:

- A primary alcohol undergoes controlled oxidation to an aldehyde; stronger oxidation can continue to the corresponding carboxylic acid.
- Pyridinium chlorochromate (PCC) is a mild oxidising reagent that converts a primary alcohol into an aldehyde under anhydrous conditions.

Step 1: Identify the required transformation Ethanol, CH_3CH_2OH, must be oxidised to ethanal, CH_3CHO, while preserving the two-carbon skeleton. With PCC, oxidation stops at the aldehyde stage:

$$CH_3CH_2OH + [O] \xrightarrow{PCC} CH_3CHO + H_2O.$$

The symbol $[O]$ represents the oxidising equivalent supplied by the reagent.

Step 2: Compare the other reagents Catalytic hydrogenation is a reduction process, and $LiAlH_4$ is also a reducing agent; neither accomplishes the required oxidation of ethanol. $KMnO_4$ is a strong oxidising agent and ordinarily oxidises a primary alcohol further to the carboxylic acid (or carboxylate in alkaline medium). It is therefore unsuitable for selectively obtaining ethanal in this choice of reagents.

Step 3: Conclusion Treatment with PCC converts ethanol to ethanal without further oxidation to the acid. Hence, the correct option is (C).

Quick Tip to Solve: For the selective conversion of a primary alcohol to an aldehyde, choose PCC over strong aqueous oxidants such as permanganate.

6. 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.
- Name the remaining alkyl groups as nitrogen substituents using the locant N, and arrange their names alphabetically.

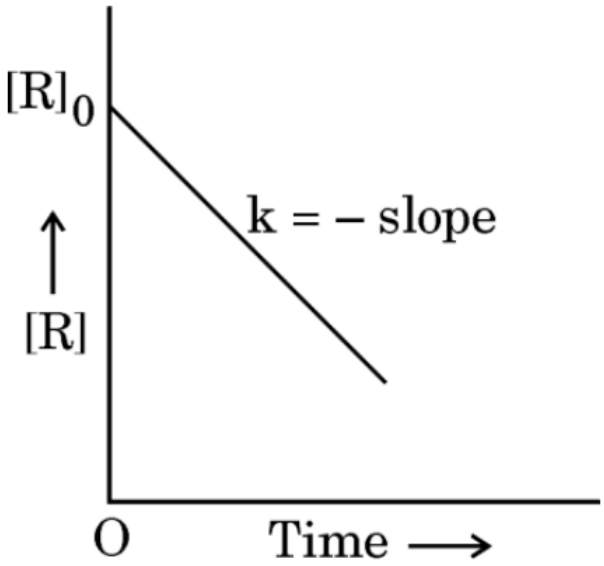
Step 1: Identify the groups bonded to nitrogen The nitrogen is bonded to an ethyl group, CH_3CH_2, a methyl group, CH_3, and a straight-chain propyl group, $CH_2CH_2CH_3$. The longest chain is the three-carbon propyl chain. Nitrogen is attached at its terminal carbon, so the parent is propan-1-amine. A carbon chain is not extended through the nitrogen atom to form a five-carbon parent.

Step 2: Add the nitrogen substituents The ethyl and methyl groups are substituents on nitrogen, giving the prefixes N-ethyl and N-methyl in alphabetical order. The proposed pentan-2-amine parent in (A) does not match the connectivity. Option (C) would require two ethyl substituents on nitrogen, whereas (D) would require two methyl substituents. The printed structure contains one of each.

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

Quick Tip to Solve: Split the structure at nitrogen first: propyl gives the parent, while ethyl and methyl become the alphabetically ordered N-substituents.

7. 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:

- The reaction order is the power of reactant concentration in the rate law. A zero-order rate is independent of concentration: $-d[R]/dt = k$.
- Its integrated law is $[R] = [R]_0 - kt$, where $[R]_0$ is initial concentration, $[R]$ is concentration at time t, and k is the rate constant.

Step 1: Compare the plot with a straight-line equation The printed graph is a straight line with concentration itself on the vertical axis. 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.

Step 2: Eliminate the other orders A first-order reaction gives a straight line for $\ln[R]$ against t, a second-order reaction for $1/[R]$ against t, and a third-order reaction for $1/[R]^2$ against t. Their concentration-versus-time plots are curved, so options (A), (B) and (C) do not match this plot.

Step 3: Conclusion The graph represents a zero-order reaction. Hence, the correct option is (D).

Quick Tip to Solve: Identify the vertical-axis quantity first: a straight falling line of $[R]$, rather than $\ln[R]$, identifies zero order.

8. 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 attach through oxygen to form an alkyl nitrite, or through nitrogen to form a nitroalkane.
- Silver nitrite, $AgNO_2$, is predominantly covalent; its oxygen is bonded to silver, so nitrogen attacks the alkyl halide.

Step 1: Identify the bond formed Ethyl bromide reacts with alcoholic silver nitrite by replacement of bromine. Attack through nitrogen forms a carbon–nitrogen bond, giving $CH_3CH_2NO_2$:

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

Step 2: Check the alternatives Ethyl nitrite, CH_3CH_2ONO, is favoured with ionic potassium nitrite, not silver nitrite. Nitromethane has only one carbon, whereas substitution preserves the two-carbon ethyl group. Ethene would arise from elimination, typically with alcoholic potassium hydroxide; this reagent instead gives the nitro substitution product.

Step 3: Conclusion The product is nitroethane, $CH_3CH_2NO_2$. Hence, the correct option is (B).

Quick Tip to Solve: Pair $AgNO_2$ with a carbon–nitrogen bond (nitroalkane), and KNO_2 with a carbon–oxygen bond (alkyl nitrite).

9. 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 a colligative property: $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f is the solvent's cryoscopic constant and m is molality.
- The solution freezes at $T_f = T_f^0 - \Delta T_f$. Thus the highest freezing point corresponds to the smallest depression, or the fewest effective solute particles for comparable concentrations.

Quick Tip to Solve: For this equal-concentration comparison, choose the non-electrolyte for the highest freezing point: fewer particles cause less depression.

Step 1: Compare the numbers of solute particles In the usual ideal comparison of the given equal-concentration aqueous solutions, glucose remains as molecules and has $i = 1$. The salts dissociate:

$$\begin{aligned} \mathrm{KCl} &\longrightarrow \mathrm{K^+ + Cl^-} && i = 2, \\ \mathrm{Na_2SO_4} &\longrightarrow 2\,\mathrm{Na^+ + SO_4{}^{2-}} && i = 3, \\ \mathrm{AlCl_3} &\longrightarrow \mathrm{Al^{3+}} + 3\,\mathrm{Cl^-} && i = 4. \end{aligned}$$

Step 2: Relate particle count to freezing point Glucose produces the fewest particles and therefore gives the least freezing-point depression in this comparison. Each electrolyte produces more particles and lowers the freezing point further, excluding (A), (B) and (D). The greatest depression would mean the lowest, rather than the highest, freezing point.

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

Quick Tip to Solve: For this equal-concentration comparison, choose the non-electrolyte for the highest freezing point: fewer particles cause less depression.

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

(A) CH_3–$CH(CH_3)$–CHO

(B) $(CH_3)_3$C–CHO

(C) CH_3–CH_2–CHO

(D) CH_3–$CH(CH_3)$–$CH(CH_3)$–CHO

Correct Answer: (B) $(CH_3)_3$C–CHO

Solution:

Concept:

- Aldehydes without any α-hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one aldehyde molecule is reduced to an alcohol while another is oxidised to a carboxylate.
- An α-hydrogen is attached to the carbon adjacent to the carbonyl carbon. The hydrogen directly attached to the aldehyde carbon is not an α-hydrogen.

Step 1: Inspect the carbon next to the aldehyde group In option (B), $(CH_3)_3C{-}CHO$, the adjacent carbon has four carbon–carbon bonds: three to methyl groups and one to the aldehyde carbon. It bears no hydrogen, satisfying the Cannizzaro condition. Hydrogens on its methyl groups are not α-hydrogens.

Step 2: Exclude the other aldehydes Option (A), $CH_3{-}CH(CH_3){-}CHO$, has one α-hydrogen. Option (C), $CH_3{-}CH_2{-}CHO$, has two. Option (D), $CH_3{-}CH(CH_3){-}CH(CH_3){-}CHO$, has one on the $CH(CH_3)$ carbon next to $-CHO$. These aldehydes can undergo aldol reaction and do not satisfy the standard Cannizzaro criterion.

Step 3: Conclusion $(CH_3)_3C{-}CHO$, 2,2-dimethylpropanal, undergoes Cannizzaro reaction. Hence, the correct option is (B).

Quick Tip to Solve: Circle the carbon immediately next to $-CHO$ and count only its attached hydrogens; zero indicates the Cannizzaro candidate.

11. 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, water ligands split the energies of the d orbitals. Absorption of visible light can promote an electron between these levels, giving colour.
- For the ions listed, partially filled d subshells allow such transitions, whereas d^0 and d^{10} configurations do not. Remove $4s$ electrons before $3d$ electrons when forming these ions.

Step 1: Determine the ionic electronic configurations Copper has configuration $[\mathrm{Ar}]3d^{10}4s^{1}$, so Cu^{+} is $3d^{10}$. Titanium loses two $4s$ and two $3d$ electrons, giving Ti^{4+} a $3d^{0}$ configuration. Cobalt and iron lose their two $4s$ electrons, giving Co^{2+} as $3d^{7}$ and Fe^{2+} as $3d^{6}$.

Step 2: Identify the coloured pair Ions I and II are colourless because their d subshells are respectively full and empty. Ions III and IV have partially filled d orbitals; aqueous Co^{2+} is pink and Fe^{2+} is pale green. Each of options (A), (B) and (D) includes at least one of the colourless ions.

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

Quick Tip to Solve: For these ions, calculate the d-electron count after removing $4s$ electrons first; discard pairs containing d^0 or d^{10}.

12. 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:

- Cell applications depend on their output, rechargeability and ability to provide steady current. A secondary cell is rechargeable, while a primary cell is normally used until its reactants are exhausted.
- A fuel cell generates electrical energy while its fuel and oxidant are supplied continuously; the hydrogen–oxygen cell also produces water.

Step 1: Match the storage and compact cells A lead storage cell is rechargeable and can supply substantial current, making it suitable for an inverter: i–d. A mercury cell provides nearly constant voltage and is used for low-current compact devices such as a wrist watch: ii–c.

Step 2: Match the remaining applications A dry cell is a common primary cell used in a wall clock: iii–a. Hydrogen–oxygen fuel cells were used in the Apollo Space Programme to supply electricity, with water as a useful product: iv–b. Thus every entry agrees with option (B); the other options assign the cells to different applications and fail these standard matches.

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

Quick Tip to Solve: Start with the distinctive pair fuel cell–Apollo, then match rechargeable lead storage cells with inverters and dry cells with wall clocks.

13. 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 oxygen atom of a carbonyl group can accept hydrogen bonds from water, helping lower aldehydes and ketones dissolve.
- An alkyl group is nonpolar and hydrophobic; its increasing size reduces the relative influence of the polar carbonyl group.

Step 1: Evaluate the assertion Assertion (A) is true. As the alkyl group becomes larger, the nonpolar hydrocarbon portion of the molecule increases. Its unfavourable interaction with water increasingly outweighs the hydration of the carbonyl group, so water solubility decreases.

Step 2: Evaluate the reason Reason (R) is also true. The polar carbonyl group gives aldehyde and ketone molecules permanent dipoles, so dipole-dipole attractions act between their molecules.

Step 3: Test the explanatory link The existence of dipole-dipole attraction does not explain the decrease in solubility as the alkyl group grows. The relevant cause is the increasing hydrophobic portion relative to the water-attracting carbonyl group. Thus option (A) wrongly asserts a causal link, while (C) and (D) incorrectly call one statement 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 a solubility trend within one functional-group family, compare the growing nonpolar chain with the unchanged polar group.

14. 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 a fixed alkyl group, the size and polarizability of the halogen increase from fluorine to iodine.
- Stronger intermolecular attractions require more thermal energy to separate molecules into the vapour phase and therefore raise the boiling point.

Step 1: Evaluate the assertion Assertion (A) is true. For the same alkyl group, the boiling-point order is $\mathrm{RI} > \mathrm{RBr} > \mathrm{RCl} > \mathrm{RF}$. The large, easily distorted electron cloud of iodine contributes much stronger dispersion attraction than that of fluorine.

Step 2: Evaluate the reason Reason (R) is true. The van der Waals attractions decrease in the stated order because the electron cloud becomes smaller and less polarizable on going from iodide to fluoride.

Step 3: Connect attraction with boiling Boiling separates neighbouring molecules. The stronger attractions in the iodide need more energy to overcome, giving its higher boiling point. Thus the reason directly explains the assertion; option (B) misses this causal link, while (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: Keep the alkyl group fixed and compare halogen polarizability: iodine gives the strongest dispersion forces and highest boiling point.

15. 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:

- The resistance of an electrolyte depends on the concentration and mobility of the ions present in solution.
- Direct current can cause sustained electrode reactions and polarization; alternating current reverses direction rapidly and minimizes these changes during measurement.

Step 1: Evaluate the assertion Assertion (A) is true. An alternating-current source is used to measure the resistance of an ionic solution so that the measured value represents the solution without a sustained change in its ionic composition.

Step 2: Evaluate the reason Reason (R) is true in the conductance measurement described. A direct-current source drives electrolysis and ion migration continuously in one direction. Ions can be consumed or produced at the electrodes, changing concentrations, especially near the electrode surfaces.

Step 3: Relate the reason to the measurement Such concentration changes and electrode polarization disturb the resistance reading. Rapid reversal with a suitable AC source minimizes their build-up, which explains its use. Option (B) overlooks this direct explanation; (C) and (D) incorrectly treat a true statement as false.

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

Quick Tip to Solve: In conductance measurements, remember that DC changes the electrolyte at the electrodes, whereas suitable AC minimizes sustained electrolysis.

16. 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 the gas partial pressure, x its mole fraction in solution and K_H Henry's law constant.
- At a fixed gas pressure, $x = p/K_H$; therefore a higher Henry's law constant corresponds to lower gas solubility.

Step 1: Evaluate the assertion Assertion (A) is false. In the usual temperature dependence considered for gases dissolved in liquids, K_H increases when temperature rises. It does not decrease as the assertion states.

Step 2: Evaluate the reason Reason (R) is true. Increasing temperature generally reduces the solubility of a gas in a liquid. Dissolution of a gas is usually exothermic, so heating favours the escape of dissolved gas into the gas phase.

Step 3: Check the relation between the statements At the same gas pressure, decreased solubility means a smaller x. Henry's law gives $K_H = p/x$, so K_H must rise. Thus the true reason actually contradicts the direction of change claimed in the assertion. Options (A), (B) and (C) all wrongly call the assertion true.

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

Quick Tip to Solve: Start with $K_H = p/x$ at fixed pressure: if heating lowers the dissolved mole fraction, Henry's law constant must increase.

Section B (10 marks)

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

Solution:

Concept:

- Elevation of boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b is the ebullioscopic constant of the solvent and m is the molality of the solute before dissociation.

Quick Tip to Solve: For completely dissociated $CaCl_2$, multiply $K_b m$ by three and convert the 260 g of water to 0.260 kg before calculating molality.

- Molality is the number of moles of solute per kilogram of solvent. Complete dissociation of one formula unit of $CaCl_2$ gives three ions, so $i = 3$.

Step 1: Count the particles formed on dissociation Calcium chloride dissociates according to

$$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + 2\,Cl^-(aq).$$

One mole of the salt therefore produces one mole of calcium ions and two moles of chloride ions. Since dissociation is complete, the effective number of dissolved particles is three times that for an undissociated solute: $i = 3$.

Step 2: Calculate the molality and boiling-point elevation The solvent mass is $260\,g = 0.260\,kg$. Thus,

$$\begin{aligned} n(CaCl_2) &= \frac{3}{111}\,mol, \\ m &= \frac{3/111}{0.260} = 0.10395\,mol\,kg^{-1}, \\ \Delta T_b &= 3 \times 0.52 \times 0.10395\,K \\ &= 0.16216\,K. \end{aligned}$$

Use the mass of water in the denominator, because molality refers to the solvent mass, and include the dissociation factor only once.

Step 3: Conclusion The elevation of boiling point is $\boxed{\Delta T_b \approx 0.162\,K}$. This is the increase in boiling point, rather than the absolute boiling temperature.

Quick Tip to Solve: For completely dissociated $CaCl_2$, multiply $K_b m$ by three and convert the 260 g of water to 0.260 kg before calculating molality.

OR

17(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:

- An ideal liquid solution obeys Raoult's law: $p_X = x_X p_X^0$ and $p_Y = x_Y p_Y^0$, where x is the liquid-phase mole fraction and p^0 is the vapour pressure of the corresponding pure liquid at the same temperature.
- The total vapour pressure is the sum of the partial pressures: $p = p_X + p_Y$. Equal numbers of moles of the two liquids imply $x_X = x_Y = 1/2$.

Step 1: Determine the mole fractions Let the solution contain n moles of each liquid. The total

Quick Tip to Solve: For an equimolar ideal binary solution, take half of each pure-liquid vapour pressure and add: $(120 + 160)/2$.

number of moles in the liquid mixture is $2n$, so

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

These fractions refer to the liquid mixture specified in the question, and their sum is unity.

Step 2: Apply Raoult's law to both volatile components Both liquids contribute to the vapour pressure. Using their respective pure-liquid vapour pressures,

$$p_X = \frac{1}{2} \times 120 = 60\,\text{mm Hg},$$
$$p_Y = \frac{1}{2} \times 160 = 80\,\text{mm Hg},$$
$$p = p_X + p_Y = 60 + 80 = 140\,\text{mm Hg}.$$

Equal liquid mole fractions do not make the partial pressures equal: the more volatile liquid Y, with the larger pure vapour pressure, contributes more.

Step 3: Conclusion The vapour pressure of the ideal solution is $\boxed{140\,\text{mm Hg}}$, the arithmetic mean of the two pure-liquid vapour pressures for this equimolar mixture.

Quick Tip to Solve: For an equimolar ideal binary solution, take half of each pure-liquid vapour pressure and add: $(120 + 160)/2$.

18.

Concentration of KCl solution in mol/L	**Conductivity at** $298.15\ \text{K}$ **in** S cm^{-1}	**Molar Conductivity at** $298.15\ \text{K}$ **in** $\text{S cm}^2\,\text{mol}^{-1}$
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 depends on the number of charge-carrying ions per unit volume and their mobility. Dilution reduces the number of ions per unit volume.
- Molar conductivity Λ_m measures the conducting contribution per mole of electrolyte: $\Lambda_m = 1000\kappa/c$, when κ is in S cm^{-1} and concentration c is in mol L^{-1}.

Step 1: Explain the decrease in conductivity on dilution As the concentration of KCl decreases from 1.000 to $0.010\,\text{mol L}^{-1}$, the conductivity decreases from 0.1113 to $0.00141\,\text{S cm}^{-1}$. Dilution increases the volume occupied by a given amount of electrolyte, so there are fewer K^+ and Cl^- ions per unit volume to carry current. This reduction in the density of charge carriers causes the observed decrease in κ.

Quick Tip to Solve: For strong KCl, distinguish ions per unit volume, which control the fall in κ, from greater ionic mobility per mole, which raises Λ_m on dilution.

Step 2: Explain the increase in molar conductivity on dilution Over the same dilution, Λ_m increases from 111.3 to $141.0\,\text{S cm}^2\,\text{mol}^{-1}$. KCl is a strong electrolyte and is already almost completely dissociated. Dilution reduces interionic attractions and the associated hindrance to ionic motion, increasing ionic mobility. Thus the conducting contribution per mole increases. For example, the last row gives

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

The rise is mainly due to increased ionic mobility, rather than a large increase in the degree of dissociation.

Step 3: Conclusion On dilution, conductivity decreases because the number of ions per unit volume decreases, while molar conductivity increases because reduced interionic interactions allow the ions to move more freely. Increasing concentration reverses these trends.

Quick Tip to Solve: For strong KCl, distinguish ions per unit volume, which control the fall in κ, from greater ionic mobility per mole, which raises Λ_m on dilution.

19(a). Give any two differences between order and molecularity of a reaction. [1 mark]

Solution:

Concept:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- Molecularity is the number of reacting species taking part in one elementary reaction step.

Step 1: Compare how they are determined Order is determined experimentally from the rate law; it cannot generally be obtained from the balanced overall equation. Molecularity is obtained by counting the reacting species in the equation of an elementary step, so it describes that step's mechanism.

Step 2: Compare their possible values Order may be zero, a positive integer or a fraction. Molecularity must be a positive integer, commonly one, two or three; it cannot be zero or fractional because it counts actual reacting species.

Step 3: Conclusion Order is an experimental rate-law quantity and may be zero or fractional; molecularity counts species in an elementary step and is always a positive integer.

Quick Tip to Solve: For two differences, compare the method of determination and the allowed numerical values. Apply molecularity to an elementary step only.

19(b). For a reaction X + Y $\rightarrow$ Z, in which both X and Y follow first order kinetics; if the concentration of X is increased 2 times and concentration of Y is increased 3 times, how does it affect the rate of reaction? [1 mark]

Solution:

Concept:

- First order with respect to each reactant means the rate law is $r = k[X][Y]$, where k is the rate constant and brackets denote molar concentration.
- At unchanged temperature, k remains the same, so the individual concentration factors multiply to give the rate factor.

Step 1: Write the original and changed rates Let the original concentrations be $[X]$ and $[Y]$. The original rate is $r = k[X][Y]$. After the specified changes, $[X]' = 2[X]$ and $[Y]' = 3[Y]$, hence

$$r' = k\big(2[X]\big)\big(3[Y]\big).$$

Step 2: Calculate the rate ratio Divide by the original rate to cancel the unchanged rate constant and original concentrations:

$$\frac{r'}{r} = \frac{k(2[X])(3[Y])}{k[X][Y]} = 2 \times 3 = 6.$$

Each reactant contributes independently through its first power; their effects are multiplied, not added.

Step 3: Conclusion The rate becomes six times its original value, assuming the temperature is unchanged.

Quick Tip to Solve: Raise each concentration multiplier to that reactant's order, then multiply: here $2^1 \times 3^1 = 6$.

20. Write the mechanism of dehydration of ethyl alcohol with conc. H_2SO_4 at 443 K. [2 marks]

Solution:

Concept:

- Concentrated H_2SO_4 supplies H^+ and promotes dehydration of ethanol at $443\,K$, forming ethene by elimination of water.
- Protonation converts the poor leaving group $-OH$ into a water leaving group. The acid catalyst is regenerated at the end of the mechanism.

Step 1: Protonate the alcohol oxygen A lone pair on the oxygen atom accepts a proton from the acid, forming protonated ethanol, an ethyloxonium ion:

$$CH_3CH_2OH + H^+ \rightleftharpoons CH_3CH_2OH_2{}^+.$$

This activates the carbon–oxygen bond for cleavage because neutral water can now leave.

Step 2: Remove water In the standard stepwise representation, protonated ethanol loses a water

Quick Tip to Solve: Remember the sequence: protonate oxygen, remove water, then remove a neighbouring proton. At $443\,K$, the product is ethene.

molecule to give an ethyl carbocation. This is the slow, rate-determining step:

$$CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2^+ + H_2O.$$

The positive charge is on the carbon from which water departed.

Step 3: Eliminate a proton to form the double bond Loss of a proton from the adjacent carbon allows the electrons of its carbon–hydrogen bond to form the carbon–carbon double bond:

$$CH_3CH_2^+ \longrightarrow CH_2{=}CH_2 + H^+.$$

The regenerated proton can catalyse dehydration of another ethanol molecule.

Step 4: Conclusion Ethanol undergoes acid-catalysed dehydration to ethene at $443\,K$:

$$CH_3CH_2OH \xrightarrow[443\ K]{\text{conc}\cdot\ H_2SO_4} CH_2{=}CH_2 + H_2O.$$

Quick Tip to Solve: Remember the sequence: protonate oxygen, remove water, then remove a neighbouring proton. At $443\,K$, the product is ethene.

21(a). Carboxylic acid is more acidic than phenol. Give reason. [1 mark]

Solution:

Concept:

- The more stable the conjugate base formed on loss of H^+, the stronger the acid.
- Carboxylic acids form carboxylate ions, $RCOO^-$; phenol forms the phenoxide ion, $C_6H_5O^-$.

Step 1: Examine the carboxylate ion The carboxylate ion has two equivalent major resonance structures. Its negative charge is delocalised equally over two electronegative oxygen atoms, giving strong resonance stabilisation.

Step 2: Compare the phenoxide ion In phenoxide, the resonance structures are not equivalent. Some place negative charge on ring carbon atoms, which are less electronegative than oxygen. Phenoxide therefore receives less effective stabilisation than the carboxylate ion.

Step 3: Conclusion Carboxylic acid is more acidic than phenol because its conjugate base, the carboxylate ion, is more strongly resonance-stabilised than phenoxide.

Quick Tip to Solve: Compare the stability of the conjugate bases: equivalent resonance forms with charge on oxygen favour the carboxylate ion.

21(b). Give a chemical test to distinguish between benzaldehyde and acetophenone. [1 mark]

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate, containing the complex ion $[Ag(NH_3)_2]^+$. Aldehydes reduce it to metallic silver.
- Benzaldehyde, C_6H_5CHO, is an aldehyde; acetophenone, $C_6H_5COCH_3$, is a ketone and does not give this test.

Step 1: Perform Tollens' test Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Benzaldehyde produces a silver mirror on the inner wall of the test tube as silver(I) is reduced to metallic silver; the aldehyde is oxidised to benzoate in the alkaline medium.

Step 2: Compare the observation for acetophenone Acetophenone gives no silver mirror under the same conditions because its ketone group is not oxidised by this mild reagent. The contrasting observations identify the samples without relying on their similar appearance.

Step 3: Conclusion Tollens' test distinguishes them: benzaldehyde gives a silver mirror, whereas acetophenone does not.

Quick Tip to Solve: Choose Tollens' reagent for this aromatic aldehyde–ketone pair; benzaldehyde gives the positive silver-mirror test.

Section C (21 marks)

22(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:

- Mixing changes intermolecular attractions: compare the unlike $A-B$ attractions with the like $A-A$ and $B-B$ attractions.
- The volume change on mixing is $\Delta V_{\text{mix}} = V_{\text{solution}} - (V_A + V_B)$, where the volumes refer to the mixture and its initial components.

Step 1: Calculate the volume change The separate liquids occupy $10 + 10 = 20\,\text{mL}$, whereas their solution occupies $20.2\,\text{mL}$.

$$\Delta V_{\text{mix}} = 20.2 - 20 = +0.2\,\text{mL}.$$

Thus, mixing causes an expansion rather than a contraction.

Step 2: Relate expansion to molecular attractions In this non-ideal mixture, the attractions between unlike molecules A and B are weaker than the attractions in the pure liquids. The molecules are consequently held less closely together after mixing, so the mixture occupies a larger volume.

Step 3: Conclusion The volume increases because the $A-B$ intermolecular attractions are weaker than the $A-A$ and $B-B$ attractions, giving $\Delta V_{\text{mix}} = +0.2\,\text{mL}$.

Quick Tip to Solve: First subtract the sum of the initial volumes; a positive change identifies expansion and weaker unlike attractions in this mixture.

22(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:

- A mixture showing positive deviation from Raoult's law has weaker unlike $A - B$ attractions than the like attractions in its components.
- Such mixing is endothermic: $\Delta H_{\text{mix}} > 0$, where ΔH_{mix} is the enthalpy change on mixing.

Step 1: Identify the nature of the mixture The final volume, $20.2\,\text{mL}$, exceeds the initial total of $20\,\text{mL}$. For the mixture described, this expansion indicates weaker attractions between unlike molecules and positive deviation from Raoult's law.

Step 2: Compare the energy changes Separating molecules against the stronger $A - A$ and $B - B$ attractions requires more energy than is released when weaker $A - B$ attractions form. Mixing therefore absorbs heat. Without compensating heat supplied from outside, the mixture cools during mixing.

Step 3: Conclusion The temperature decreases because mixing is endothermic, with $\Delta H_{\text{mix}} > 0$.

Quick Tip to Solve: For this positive-deviation mixture, connect weaker unlike attractions to heat absorption and hence a fall in temperature.

22(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 intermolecular attractions can show positive deviation from Raoult's law and expansion on mixing.
- Pure ethanol molecules form intermolecular hydrogen bonds; adding acetone disrupts this association.

Step 1: Identify the required type of solution The initial total volume is $20\,\text{mL}$, while the solution occupies $20.2\,\text{mL}$. This is the expanding, positive-deviation type of non-ideal solution for which an example is required.

Step 2: Choose a mixture with weaker effective attractions Consider ethanol, C_2H_5OH, mixed with acetone, CH_3COCH_3. Acetone molecules disturb the hydrogen-bonded association between ethanol molecules. The resulting effective attractions are weaker than those in the separate liquids, so molecules escape into the vapour more readily and the mixture shows positive deviation from Raoult's law.

Quick Tip to Solve: Remember ethanol with acetone as a positive-deviation example: acetone disrupts the hydrogen-bonded association of ethanol.

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

Quick Tip to Solve: Remember ethanol with acetone as a positive-deviation example: acetone disrupts the hydrogen-bonded association of ethanol.

OR

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

Solution:

Concept:

- Dissolving a non-volatile solute in water lowers its freezing point, a colligative property called freezing-point depression.
- The depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant of water and m the solute molality.

Step 1: Form a salt solution at the snow surface Sprinkled salt dissolves in the thin layer of liquid water present on the snow. Sodium chloride dissociates into Na^+ and Cl^-, increasing the number of dissolved particles in this surface water.

Step 2: Apply freezing-point depression The resulting salt solution freezes below the freezing point of pure water, $0\,^\circ$C. When the surrounding temperature lies above this lowered freezing point, snow melts into the solution and the water does not immediately refreeze, helping clear the road.

Step 3: Conclusion Salt helps clear snow by lowering the freezing point of water, causing snow to melt under suitable ambient conditions.

Quick Tip to Solve: Link road de-icing with depression of freezing point; the dissolved salt changes the freezing temperature rather than supplying heat.

22(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 selectively permeable membrane from the more dilute solution towards the more concentrated solution.
- About 0.9% (mass/volume) NaCl solution is isotonic with red blood cells; a more dilute salt solution is hypotonic to them.

Step 1: Compare the external solution with the cell contents The given 0.5% (mass/volume) NaCl solution is more dilute than the isotonic 0.9% solution. Its osmotic pressure is therefore lower than that of the fluid inside the red blood cells.

Step 2: Determine the direction of water movement The cell membrane allows water to pass, so water

Quick Tip to Solve: Compare the given salt concentration with 0.9%: a lower value makes water enter red blood cells and causes swelling.

enters the cells by osmosis, also called endosmosis in this situation. The increase in their internal water volume makes the cells swell; with sufficient water entry their membranes can rupture, causing haemolysis.

Step 3: Conclusion Red blood cells swell and may burst in 0.5% NaCl solution because this hypotonic solution drives water into them by endosmosis.

Quick Tip to Solve: Compare the given salt concentration with 0.9%: a lower value makes water enter red blood cells and causes swelling.

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

Solution:

Concept:

- Reverse osmosis drives solvent through a semipermeable membrane from the solution side to the pure-solvent side, opposite to spontaneous osmosis.
- The pressure applied on the solution must exceed its osmotic pressure, π; the membrane allows water through while retaining dissolved salts.

Step 1: Apply the principle to seawater Seawater contains dissolved salts and has an appreciable osmotic pressure. Place it on one side of a suitable semipermeable membrane and apply a pressure greater than its osmotic pressure on that side.

Step 2: Separate water from dissolved salts The applied pressure forces water molecules across the membrane while most dissolved salts remain on the seawater side. Collecting the water that passes through gives fresh water, while the retained solution becomes more concentrated.

Step 3: Conclusion Reverse osmosis is used for the desalination of seawater to obtain fresh water.

Quick Tip to Solve: For an application of reverse osmosis, state seawater desalination and remember that pressure greater than the osmotic pressure is applied to the salty side.

23. For the reaction A + B $\rightarrow$ 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 experimental rate law is $r = k[A]^m[B]^n$, where r is the initial rate, k is the rate constant, and m and n are the orders with respect to A and B.
- Compare two experiments in which only one reactant concentration changes. The overall order is the sum $m + n$, not necessarily the sum of the coefficients in the reaction equation.

Step 1: Determine the order with respect to A Compare experiments 1 and 2. The concentration of B stays at 0.1 mol L^{-1}, while that of A doubles from 0.1 to 0.2 mol L^{-1}. Taking the ratio cancels k and the unchanged B term:

$$\frac{r_2}{r_1} = \left(\frac{[A]_2}{[A]_1}\right)^m, \qquad \frac{0.10}{0.05} = \left(\frac{0.2}{0.1}\right)^m.$$

Thus $2 = 2^m$, so $m = 1$: doubling A doubles the rate.

Step 2: Determine the order with respect to B Compare experiments 1 and 3. A remains at 0.1 mol L^{-1}, while B doubles. The measured rate remains 0.05 mol $L^{-1}s^{-1}$. Therefore,

$$\frac{r_3}{r_1} = \left(\frac{[B]_3}{[B]_1}\right)^n, \qquad \frac{0.05}{0.05} = \left(\frac{0.2}{0.1}\right)^n.$$

Hence $1 = 2^n$, which gives $n = 0$. A zero order means that changing B does not affect the rate under the experimental conditions; it does not mean that B is absent from the reaction.

Step 3: Add the individual orders Substitution in the rate law gives $r = k[A]^1[B]^0 = k[A]$. Since the overall order is the sum of the experimentally determined exponents, it is $m + n = 1 + 0 = 1$.

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: Use experiments 1 and 2 for A, and 1 and 3 for B: a doubled concentration with unchanged rate immediately gives zero order.

24(a). Write the name and structure of a hexadentate ligand. [1 mark]

Solution:

Concept:

- A hexadentate ligand can coordinate to one metal ion through six donor atoms, each donating an electron pair.
- Ethylenediaminetetraacetate, $EDTA^{4-}$, contains two amine nitrogen donors and four carboxylate oxygen donors.

Step 1: Name the ligand A standard example is the ethylenediaminetetraacetate ion, abbreviated as $EDTA^{4-}$. It is the tetra-anion obtained by removing the four acidic carboxyl hydrogen atoms from ethylenediaminetetraacetic acid.

Step 2: Write its structure and identify the donors Its condensed structural formula is

$$(^{-}OOC-CH_2)_2N-CH_2-CH_2-N(CH_2-COO^{-})_2.$$

Each nitrogen bears two $-CH_2-COO^{-}$ arms. Both nitrogen atoms and one oxygen atom from each of the four carboxylate groups can bond to the same metal ion, giving $2 + 4 = 6$ donor atoms.

Step 3: Conclusion Ethylenediaminetetraacetate, $EDTA^{4-}$, is a hexadentate ligand; its structure contains two nitrogen and four carboxylate oxygen donor sites.

Quick Tip to Solve: Count donor atoms, not total oxygen atoms: EDTA binds through two N atoms and only one O from each of its four carboxylate groups.

24(b). Why is $[Ni(CN)_4]^{2-}$ square planar while $[Ni(CO)_4]$ is tetrahedral? [Atomic number: Ni = 28] [2 marks]

Solution:

Concept:

- The geometry of a four-coordinate complex depends on the metal's oxidation state, its electronic configuration and the orbitals available for hybridisation.
- In valence bond theory, dsp^2 hybridisation gives a square planar arrangement, whereas sp^3 hybridisation gives a tetrahedral arrangement.

Step 1: Examine the cyanide complex In $[Ni(CN)_4]^{2-}$, each CN^{-} ligand carries charge -1. If the oxidation state of nickel is x, then $x - 4 = -2$, so $x = +2$. Thus Ni^{2+} has configuration $[Ar]3d^8$. The strong-field CN^{-} ligands cause the $3d$ electrons to pair, leaving one $3d$ orbital vacant. This orbital combines with one $4s$ and two $4p$ orbitals to form four dsp^2 hybrid orbitals directed towards the corners of a square.

Step 2: Examine the carbonyl complex In $[Ni(CO)_4]$, CO is a neutral ligand, so nickel has oxidation state zero. On complex formation, the valence electrons rearrange from the free-atom configuration $3d^8 4s^2$ to $3d^{10}$, with an empty $4s$ orbital. All five $3d$ orbitals are occupied; therefore, a vacant inner $3d$ orbital is unavailable for dsp^2 hybridisation. One $4s$ and three $4p$ orbitals form four sp^3 hybrid

Quick Tip to Solve: Calculate the nickel oxidation state first: the cyanide complex contains a d-eight ion, while the carbonyl complex has a filled d-ten configuration.

orbitals with tetrahedral directions. Both complexes have paired electrons and are diamagnetic.

Step 3: Conclusion $[Ni(CN)_4]^{2-}$ is square planar with dsp^2 hybridisation, whereas $[Ni(CO)_4]$ is tetrahedral with sp^3 hybridisation because the metal has a different oxidation state and d-electron configuration.

Quick Tip to Solve: Calculate the nickel oxidation state first: the cyanide complex contains a d-eight ion, while the carbonyl complex has a filled d-ten configuration.

25(a). Account for the following:

Haloarenes are less reactive towards nucleophilic substitution reactions. [1 mark]

Solution:

Concept:

- Nucleophilic substitution involves cleavage of the carbon-halogen bond; a stronger bond is more difficult to break.
- In haloarenes, a halogen lone pair overlaps with the aromatic ring's π system, producing resonance.

Step 1: Identify the effect of resonance Delocalisation of a halogen lone pair into the benzene ring gives the carbon-halogen bond partial double-bond character. This makes the bond shorter and stronger than the corresponding single bond in a haloalkane, so its cleavage is difficult.

Step 2: Examine the carbon bonded to halogen The halogen is attached to an sp^2-hybridised carbon in a haloarene. Its greater s-character, compared with an sp^3 carbon in a haloalkane, further strengthens the carbon-halogen bond. Thus nucleophilic replacement of the halogen requires much harsher conditions.

Step 3: Conclusion Haloarenes are less reactive towards nucleophilic substitution mainly because resonance and the sp^2 carbon make the carbon-halogen bond shorter, stronger and harder to cleave.

Quick Tip to Solve: Link resonance to partial double-bond character, then to a stronger carbon-halogen bond: this chain directly explains the reduced reactivity.

25(b). Account for the following:

p-dichlorobenzene has higher melting point than ortho and meta isomers. [1 mark]

Solution:

Concept:

- Melting involves overcoming the interactions that hold molecules in a crystal lattice.
- Molecular symmetry can improve packing in the solid state, producing a more stable crystal lattice and a higher melting point.

Step 1: Compare the arrangements of the substituents In para-dichlorobenzene, the two chlorine atoms occupy opposite positions, 1 and 4, on the benzene ring. This arrangement makes the molecule more symmetrical than the ortho (1,2) and meta (1,3) isomers.

Quick Tip to Solve: For melting points of these positional isomers, compare molecular symmetry and solid-state packing rather than using polarity alone.

Step 2: Relate symmetry to crystal packing The more symmetrical para isomer fits into an ordered crystal lattice more efficiently. Its closer and more regular packing makes the lattice more stable, so more thermal energy is required to overcome the intermolecular attractions during melting.

Step 3: Conclusion Para-dichlorobenzene has a higher melting point because its greater symmetry allows more efficient crystal packing than the ortho and meta isomers.

Quick Tip to Solve: For melting points of these positional isomers, compare molecular symmetry and solid-state packing rather than using polarity alone.

25(c). Account for the following:

Tertiary alkyl halides are least reactive towards S_N2 reaction. [1 mark]

Solution:

Concept:

- An S_N2 substitution occurs in one concerted step: the nucleophile attacks from the side opposite the leaving group while the carbon–halogen bond breaks.
- Steric hindrance means that bulky groups obstruct access to the reaction centre and raise the activation barrier.

Step 1: Examine access to the carbon A tertiary alkyl halide has three alkyl groups attached to the carbon bearing the halogen. These groups crowd the carbon and obstruct the required backside approach of the nucleophile.

Step 2: Relate crowding to substitution rate Formation of the crowded S_N2 transition state is therefore strongly hindered. The usual reactivity order is methyl halide greater than primary greater than secondary greater than tertiary; tertiary substrates show negligible S_N2 reaction.

Step 3: Conclusion Tertiary alkyl halides are least reactive towards S_N2 because their three alkyl groups cause maximum steric hindrance to backside attack.

Quick Tip to Solve: For an S_N2 comparison, count the alkyl groups on the carbon bearing the halogen: more crowding means slower attack.

26(a). Write the chemical equation for the following: [2 marks]

26(a)(i). Preparation of phenol from cumene

Solution:

Concept:

- Cumene is isopropylbenzene, $C_6H_5CH(CH_3)_2$. Oxidation by air first forms cumene hydroperoxide.
- Acidic cleavage of the hydroperoxide produces phenol and acetone without changing the total number of carbon atoms.

Step 1: Oxidise cumene with air Pass air through cumene to form its hydroperoxide at the benzylic

Quick Tip to Solve: Remember the two stages: oxygen forms the hydroperoxide, then dilute acid gives phenol plus acetone.

carbon:

$$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2OOH.$$

Step 2: Carry out acidic cleavage Treat the hydroperoxide with dilute acid:

$$C_6H_5C(CH_3)_2OOH \xrightarrow{H^+} C_6H_5OH + CH_3COCH_3.$$

The aromatic fragment becomes phenol, and the three-carbon fragment becomes acetone. Both products must be included in the equation.

Step 3: Conclusion Cumene gives phenol through air oxidation followed by acid cleavage of cumene hydroperoxide; acetone is the coproduct.

Quick Tip to Solve: Remember the two stages: oxygen forms the hydroperoxide, then dilute acid gives phenol plus acetone.

26(a)(ii). Nitration of anisole

Solution:

Concept:

- The methoxy group in anisole, $C_6H_5OCH_3$, donates electron density to the benzene ring by resonance.
- It activates electrophilic substitution and directs the incoming nitro group mainly to the ortho and para positions.

Step 1: Identify the nitrating conditions Anisole undergoes nitration with concentrated nitric acid in the presence of concentrated sulphuric acid. The mixture generates the electrophile $NO_2{}^+$, which substitutes a ring hydrogen.

Step 2: Write the substitution equations The two substitution products are represented separately:

$$C_6H_5OCH_3 + HNO_3 \xrightarrow{H_2SO_4} \text{o-}NO_2C_6H_4OCH_3 + H_2O,$$
$$C_6H_5OCH_3 + HNO_3 \xrightarrow{H_2SO_4} \text{p-}NO_2C_6H_4OCH_3 + H_2O.$$

The para product predominates because substitution there has less steric hindrance than at the ortho position.

Step 3: Conclusion Nitration of anisole gives ortho-nitroanisole and para-nitroanisole, with para-nitroanisole as the major product.

Quick Tip to Solve: Use the methoxy group to locate the nitro group: ortho and para are favoured, with para predominant.

26(b). Complete the following:

$(CH_3)_3C - O - CH_3 + HI \rightarrow$ [1 mark]

Solution:

Concept:

- Hydrogen iodide cleaves an ether after protonation of its oxygen, converting the ether oxygen into a better leaving group.
- When one ether group is tertiary, cleavage can proceed through the stable tertiary carbocation, followed by attack by iodide.

Step 1: Identify the preferred bond cleavage The ether contains a tert-butyl group and a methyl group. After oxygen protonation, the bond between oxygen and the tertiary carbon breaks to form the tert-butyl carbocation and methanol. A methyl carbocation is not formed.

Step 2: Combine the tertiary carbon with iodide Iodide captures the tertiary carbocation. The overall balanced equation is

$$(CH_3)_3C{-}O{-}CH_3 + HI \longrightarrow (CH_3)_3C{-}I + CH_3OH.$$

Thus, the oxygen-containing fragment remains methanol during the stated ether cleavage.

Step 3: Conclusion The products are tert-butyl iodide (2-iodo-2-methylpropane), $(CH_3)_3CI$, and methanol, CH_3OH.

Quick Tip to Solve: Check for a tertiary group before applying the usual less-hindered-carbon rule for cleavage of unsymmetrical ethers by HI.

27(a). Write the products formed in the following reactions:

$CH_3CHO + NH_2CONHNH_2 \rightarrow$ [1 mark]

Solution:

Concept:

- Aldehydes react with semicarbazide, $NH_2NHCONH_2$, by addition followed by loss of water to give semicarbazones.
- The terminal hydrazino $-NH_2$ group reacts with the carbonyl group; the amide $-CONH_2$ group remains intact.

Step 1: Identify the reacting functional groups Ethanal has the carbonyl group $CH_3CH{=}O$. The terminal nitrogen of $NH_2{-}NH{-}CO{-}NH_2$ attacks its carbonyl carbon. This is the same semicarbazide molecule as the formula written in reverse order in the question.

Step 2: Remove water and form the carbon–nitrogen double bond Condensation replaces the carbonyl oxygen by the $=N{-}NH{-}CO{-}NH_2$ group:

$$CH_3CHO + NH_2NHCONH_2 \longrightarrow CH_3CH{=}NNHCONH_2 + H_2O.$$

The methyl group and the hydrogen originally attached to the carbonyl carbon are retained.

Quick Tip to Solve: To write a semicarbazone, replace the carbonyl $C{=}O$ by $C{=}N{-}NH{-}CO{-}NH_2$, keeping the original carbon substituents.

Step 3: Conclusion Ethanal semicarbazone, $CH_3CH{=}NNHCONH_2$, is formed along with water.

Quick Tip to Solve: To write a semicarbazone, replace the carbonyl $C{=}O$ by $C{=}N{-}NH{-}CO{-}NH_2$, keeping the original carbon substituents.

27(b). Write the products formed in the following reactions:

$CH_3CHO \xrightarrow{\text{dil. NaOH}}$ [1 mark]

Solution:

Concept:

- An aldehyde with an α-hydrogen undergoes aldol addition in dilute alkali, giving a β-hydroxy aldehyde.
- Ethanal contains α-hydrogens on its methyl group, so two ethanal molecules can combine to form a four-carbon product.

Step 1: Form the new carbon–carbon bond Dilute $NaOH$ removes an α-hydrogen from one ethanal molecule. The resulting enolate attacks the carbonyl carbon of a second molecule, joining their carbon chains.

Step 2: Protonate the addition product Protonation of the alkoxide gives the aldol:

$$2\,CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3CH(OH)CH_2CHO.$$

Numbering from the aldehyde carbon puts the hydroxyl group at carbon 3. Heating would cause dehydration to but-2-enal, but no heating is specified here.

Step 3: Conclusion The product is 3-hydroxybutanal (aldol), $CH_3CH(OH)CH_2CHO$.

Quick Tip to Solve: With dilute alkali alone, stop at the β-hydroxy aldehyde; use the unsaturated aldehyde only when dehydration conditions are given.

27(c). Write the products formed in the following reactions:

$CH_3COOH \xrightarrow[H_2O]{Cl_2/\text{red P}}$ [1 mark]

Solution:

Concept:

- The Hell–Volhard–Zelinsky reaction replaces an α-hydrogen of a carboxylic acid by chlorine or bromine in the presence of red phosphorus.
- The α-carbon is the carbon directly adjacent to $-COOH$; hydrolysis gives the corresponding α-halocarboxylic acid.

Step 1: Identify the position of substitution In ethanoic acid, CH_3COOH, the methyl carbon is the α-carbon and has replaceable hydrogen atoms. Chlorination with red phosphorus therefore introduces chlorine at that carbon, rather than replacing the hydroxyl group in the final acid.

Quick Tip to Solve: For Cl_2/red phosphorus followed by water, place chlorine on the carbon next to $-COOH$ and retain the acid group.

Step 2: Write the product after hydrolysis Water hydrolyses the intermediate acyl halide. The net reaction is

$$CH_3COOH + Cl_2 \xrightarrow[H_2O]{\text{red P}} ClCH_2COOH + HCl.$$

One hydrogen on the methyl group has been replaced by chlorine, while the carboxyl group is retained in the isolated product.

Step 3: Conclusion The organic product is chloroethanoic acid (chloroacetic acid), $ClCH_2COOH$.

Quick Tip to Solve: For Cl_2/red phosphorus followed by water, place chlorine on the carbon next to $-COOH$ and retain the acid group.

28(a). Name the vitamin which is responsible for coagulation of blood. [1 mark]

Solution:

Concept:

- Vitamins are organic nutrients required in small amounts for normal physiological functions.
- Vitamin K is a fat-soluble vitamin associated with the normal clotting of blood.

Step 1: Identify the function asked Coagulation is the formation of a blood clot that helps stop bleeding after an injury. The question asks for the vitamin required for this process.

Step 2: Associate the function with its vitamin Vitamin K is needed for the normal production of functional blood-clotting proteins. Its deficiency can therefore cause delayed blood clotting and excessive bleeding.

Step 3: Conclusion The vitamin responsible for coagulation of blood is **vitamin K**.

Quick Tip to Solve: Link vitamin K with blood clotting; vitamin C is associated with collagen formation and vitamin D with calcium metabolism.

28(b). What is meant by denaturation of protein? Give an example. [2 marks]

Solution:

Concept:

- A protein has a characteristic three-dimensional shape that is essential for its biological activity.
- Its secondary and tertiary structures are maintained by interactions such as hydrogen bonds; its primary structure is the sequence of amino acids joined by peptide bonds.

Step 1: Explain denaturation Denaturation is the loss of a protein's native three-dimensional structure and biological activity under the influence of a physical or chemical change, such as heating or a change in pH. These conditions disrupt the interactions that maintain the folded structure. The protein unfolds, with its secondary and tertiary structures disturbed, while its primary structure remains intact: the peptide bonds are not broken by denaturation itself.

Step 2: Give an everyday example When an egg is boiled, the albumin proteins in the egg white

Quick Tip to Solve: In a denaturation answer, pair loss of biological activity with unchanged primary structure, and use boiled egg white as the example.

become denatured by heat. The unfolded proteins aggregate and coagulate, changing the transparent egg white into an opaque solid. This illustrates a change in protein structure rather than hydrolysis of the protein into its constituent amino acids.

Step 3: Conclusion Denaturation is the loss of the native structure and biological activity of a protein without changing its primary structure. Coagulation of egg white on boiling is an example.

Quick Tip to Solve: In a denaturation answer, pair loss of biological activity with unchanged primary structure, and use boiled egg white as the example.

Section D (8 marks)

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

29. 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 2n, 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: [4 marks]

29(a). Give chemical reactions to show the presence of an aldehydic group and straight chain in glucose. [2 marks]

Solution:

Concept:

- Mild oxidation converts an aldehyde group, $-\mathrm{CHO}$, into a carboxyl group, $-\mathrm{COOH}$. Bromine water supplies a mild oxidising agent.
- Prolonged heating with hydrogen iodide reduces glucose to a hydrocarbon while preserving its carbon skeleton; the hydrocarbon reveals the carbon-chain arrangement.

Step 1: Show the aldehydic group by oxidation Glucose is oxidised by bromine water to gluconic acid:

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O \longrightarrow COOH(CHOH)_4CH_2OH + 2\,HBr.}$$

Only the terminal aldehydic group is converted into a carboxyl group under these mild conditions. Thus formation of the six-carbon monocarboxylic gluconic acid supports the presence of an aldehydic group in glucose.

Step 2: Show the straight carbon chain by reduction On prolonged heating with excess hydrogen iodide, glucose gives normal hexane:

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

Quick Tip to Solve: Pair each inference with its product: gluconic acid shows the aldehyde, whereas n-hexane shows the unbranched chain.

The product is an unbranched six-carbon hydrocarbon. Since this reduction preserves the carbon skeleton, it establishes that the six carbon atoms of glucose lie in a straight, unbranched chain.

Step 3: Conclusion Bromine-water oxidation to gluconic acid demonstrates the aldehydic group; prolonged HI reduction to n-hexane establishes the straight chain of six carbon atoms.

Quick Tip to Solve: Pair each inference with its product: gluconic acid shows the aldehyde, whereas n-hexane shows the unbranched chain.

29(b)(i). Define anomers. [1 mark]

Solution:

Concept:

- Cyclisation of a sugar creates a new stereocentre at its former carbonyl carbon, called the anomeric carbon.
- Anomers are cyclic sugar stereoisomers that differ only in configuration at the anomeric carbon.

Step 1: Identify the distinguishing carbon In glucose the aldehydic carbon, C1, becomes the anomeric carbon when the cyclic hemiacetal forms. The other stereocentres retain their configurations.

Step 2: Distinguish the two anomers The α and β forms of D-glucopyranose differ only in the orientation of the hydroxyl group at C1. In the conventional Haworth representation, this hydroxyl group is opposite to the CH_2OH group in the α form and on the same side in the β form.

Step 3: Conclusion Anomers are cyclic stereoisomers of a carbohydrate differing only in configuration at the anomeric carbon, for example α- and β-D-glucopyranose.

Quick Tip to Solve: For glucose, inspect C1 only: changing its hydroxyl orientation interconverts the alpha and beta anomers.

OR

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

Solution:

Concept:

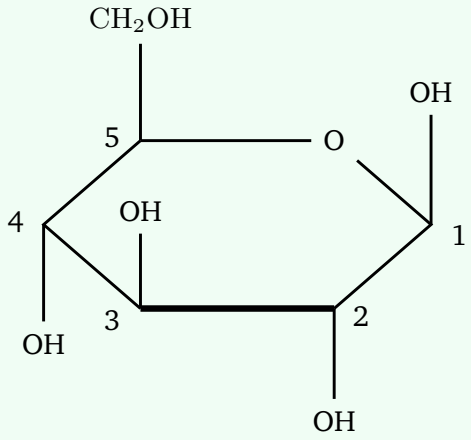
- Glucopyranose has a six-membered ring containing five carbon atoms and one oxygen atom.
- In the conventional Haworth form of a D-sugar, the C5 CH_2OH group points up; the β anomer has its C1 hydroxyl group on the same side.

Step 1: Construct the pyranose ring Close the open-chain glucose structure by reaction of the C5 hydroxyl group with the C1 aldehyde. The resulting ring contains C1 to C5 and an oxygen between C5 and C1.

Step 2: Set the hydroxyl orientations For D-glucose, the hydroxyl groups at C2, C3 and C4 point down, up and down, respectively, in the standard Haworth projection. Place the C1 hydroxyl group up

Quick Tip to Solve: Check beta by comparing C1-OH with C5-CH2OH: both must point up in beta-D-glucopyranose.

to obtain the β anomer. The skeletal Haworth structure below omits carbon-bound hydrogen atoms.



Haworth projection of β-D-glucopyranose; carbon-bound hydrogens are omitted.

Step 3: Conclusion The structure is β-D-glucopyranose: the C1 hydroxyl and C5 CH_2OH groups are both above the ring.

Quick Tip to Solve: Check beta by comparing C1-OH with C5-CH2OH: both must point up in beta-D-glucopyranose.

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

Solution:

Concept:

- Hydrolysis of sucrose gives equimolar D-glucose and D-fructose; optical rotation of a mixture depends on the contributions of both sugars.
- Inversion is the change in optical rotation from dextrorotatory to laevorotatory during sucrose hydrolysis.

Step 1: Identify the hydrolysis products Sucrose is dextrorotatory. In the presence of acid or the enzyme invertase, its glycosidic bond hydrolyses to give glucose and fructose:

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

Step 2: Explain the reversal of optical rotation Glucose is dextrorotatory, whereas fructose is laevorotatory. The magnitude of fructose's negative rotation is greater than glucose's positive rotation, so their equimolar mixture is laevorotatory. Thus the initially positive rotation of sucrose becomes negative after hydrolysis.

Step 3: Conclusion The reversal in sign of optical rotation is called inversion. Strictly, the glucose-fructose mixture obtained on hydrolysing sucrose is called invert sugar; this inversion explains the terminology used in the question.

Quick Tip to Solve: Remember that fructose's negative rotation outweighs glucose's positive rotation in hydrolysed sucrose.

30. 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: [4 marks]

30(a). 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:

- Werner's primary valency is the oxidation state; secondary valency is the number of donor atoms directly attached to the metal.
- Only chloride ions outside the coordination sphere are readily ionised and precipitated by aqueous $AgNO_3$; coordinated chloride remains inside the brackets.

Step 1: Locate the ionisable chloride One mole of the compound gives one mole of AgCl. Thus one of its three chloride ions is outside the coordination sphere. The other two chlorides are ligands directly coordinated to chromium. The four water molecules occupy the remaining coordination positions. The precipitating reaction is

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

Step 2: Write the coordination sphere and count donors The complex ion contains four neutral water ligands and two monodentate chloride ligands. Chromium is in the $+3$ oxidation state, so its complex ion has charge $3 - 2 = +1$. Therefore the formula is $[Cr(H_2O)_4Cl_2]Cl$. Its aqueous ionisation is

$$[Cr(H_2O)_4Cl_2]Cl \longrightarrow [Cr(H_2O)_4Cl_2]^+ + Cl^-.$$

The six directly attached donor atoms give secondary valency $4 + 2 = 6$.

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

Quick Tip to Solve: Use the moles of AgCl to count chlorides outside brackets, then count ligands inside the brackets.

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

Solution:

Concept:

- Double salts and coordination compounds differ in whether the constituent complex entity retains its identity in aqueous solution.

Quick Tip to Solve: Compare the species present after dissolving: all simple ions indicate a double salt; a retained complex ion indicates a complex.

- A complex ion behaves as one ion in solution; the ions constituting a double salt separate completely.

Step 1: Describe the double salt A double salt dissociates completely into all of its constituent simple ions in water and loses its separate identity. For example, Mohr's salt gives Fe^{2+}, $NH_4{}^+$ and $SO_4{}^{2-}$ ions, which show their usual tests.

Step 2: Describe the complex A coordination compound retains its complex entity in solution. For example, $K_4[Fe(CN)_6]$ gives K^+ and $[Fe(CN)_6]^{4-}$ ions, rather than releasing all the coordinated cyanide and iron as their simple ions.

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

Quick Tip to Solve: Compare the species present after dissolving: all simple ions indicate a double salt; a retained complex ion indicates a complex.

30(c)(i). 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:

- Electrical conduction in a solution requires mobile ions.
- For the usual comparison at comparable concentration, complexes producing more ions on dissociation have higher conductivity; coordinated ligands remain within the complex.

Step 1: Count the ions released $[Cr(NH_3)_3Cl_3]$ has no counterions outside its coordination sphere and is a non-electrolyte. $[Cr(NH_3)_5Cl]Cl_2$ gives one complex cation and two chloride ions, i.e. three ions per formula unit.

Step 2: Compare with the hexaammine complex $[Cr(NH_3)_6]Cl_3$ dissociates into $[Cr(NH_3)_6]^{3+}$ and three Cl^- ions, making four ions per formula unit. Thus the neutral complex conducts least, and the salt with three outer-sphere chloride ions conducts most.

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 chloride ions outside the square brackets when predicting the number of mobile ions.

OR

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

[1 mark]

Solution:

Concept:

- In Werner's theory, the metal exhibits primary as well as secondary valency.
- Primary valency corresponds to oxidation state; secondary valency corresponds to coordination number.

Step 1: Compare ionisation Primary valences are normally ionisable and are satisfied by negative ions. Secondary valences are non-ionisable and are satisfied by neutral molecules or negative ions directly coordinated to the metal.

Step 2: Compare spatial character Primary valences are non-directional. Secondary valences are directional: ligands occupy definite positions about the metal and therefore determine the geometry of the coordination entity. For example, six secondary valences commonly produce an octahedral arrangement.

Step 3: Conclusion Two differences: primary valences are ionisable and non-directional, whereas secondary valences are non-ionisable and directional.

Quick Tip to Solve: Link primary valency with oxidation state and ionisation, and secondary valency with coordination number and geometry.

Section E (15 marks)

31(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:

- Pyrolusite is MnO_2. Oxidative fusion with KOH converts manganese from oxidation state $+4$ to $+6$, giving green manganate.
- In acidic solution, manganate disproportionates to permanganate and manganese dioxide. Acidified permanganate oxidises Fe^{2+} to Fe^{3+} while being reduced to Mn^{2+}.

Step 1: Identify the green and purple compounds Fusion in air produces potassium manganate, K_2MnO_4, the dark green compound A:

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

Quick Tip to Solve: Green manganate contains Mn(VI); purple permanganate contains Mn(VII) and accepts five electrons in acidic medium.

Acidification converts manganate into purple permanganate, corresponding to potassium permanganate, $KMnO_4$, compound B:

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

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

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

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

Multiply the iron half-reaction by five and add the two equations, cancelling the electrons. The resulting equation conserves oxygen, hydrogen and charge; the total charge is $+17$ on either side.

Step 3: Conclusion (I) A is K_2MnO_4 and B is $KMnO_4$. (II) The required ionic equation is

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

Quick Tip to Solve: Green manganate contains Mn(VI); purple permanganate contains Mn(VII) and accepts five electrons in acidic medium.

31(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 large positive standard reduction potential favours this process.
- Poor shielding by inner f-electrons causes increasing effective nuclear charge and decreasing size across an f-block series.
- The standard potential of the M^{2+}/M couple depends on the overall energetics of atomisation, ionisation and hydration, not on electronic configuration alone.

Step 1: Explain the oxidising action of cerium(IV) (I) The +3 oxidation state is the usual stable state of lanthanoids in aqueous solution. The Ce^{4+}/Ce^{3+} couple has a large positive standard reduction potential, so Ce^{4+} readily accepts an electron:

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

In accepting this electron, it oxidises the other reactant. Thus the tendency of Ce^{4+} to change to the more stable aqueous +3 state accounts for its strong oxidising action.

Step 2: Compare shielding in the two f-block series (II) The added 5f-electrons in the actinoid series

Quick Tip to Solve: For an electrode-potential anomaly, compare atomisation, ionisation and hydration together; a filled d-subshell alone is not a complete explanation.

shield the increasing nuclear charge less effectively than the added 4f-electrons in the lanthanoid series. Consequently, the effective nuclear attraction experienced by the outer electrons increases more strongly from one actinoid to the next. The resulting element-to-element contraction is therefore greater for actinoids.

Step 3: Compare the energetics of zinc and copper (III) For zinc, its relatively low enthalpy of atomisation and the considerable hydration enthalpy of Zn^{2+} favour formation of the aqueous ion. The ion also has a stable, completely filled $3d^{10}$ configuration. These factors make oxidation of Zn favourable and its reduction potential more negative than expected from a smooth trend.

For copper, the energy required for atomisation and ionisation to Cu^{2+} is high and is not compensated by the energy released on hydration. In particular, the second ionisation removes an electron from the filled $3d^{10}$ configuration of Cu^{+}. Copper therefore has a positive standard reduction potential.

Step 4: Conclusion Ce^{4+} readily reduces to Ce^{3+}; poorer 5f shielding causes the greater actinoid contraction. The balance of atomisation, ionisation and hydration energies favours aqueous Zn^{2+} formation but opposes aqueous Cu^{2+} formation, explaining their respective negative and positive reduction potentials.

Quick Tip to Solve: For an electrode-potential anomaly, compare atomisation, ionisation and hydration together; a filled d-subshell alone is not a complete explanation.

OR

31(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 4f-electrons shield nuclear charge poorly, so the effective nuclear attraction increases across the series and draws the electron cloud inward.

Step 1: Identify and explain the contraction (I) The phenomenon is lanthanoid contraction. It is the gradual decrease in atomic and ionic radii from lanthanum to lutetium as atomic number increases. The 4f-electrons added across this series do not fully screen the increase in nuclear charge. Hafnium follows the lanthanoids, so this contraction largely offsets the normal increase in size expected on moving down from zirconium to hafnium. Their atomic sizes are therefore almost equal despite hafnium having an additional principal shell.

Step 2: State another consequence (II) The basic strength of lanthanoid hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. The Ln^{3+} ion becomes smaller while its charge remains the same, increasing

Quick Tip to Solve: When two 4d and 5d congeners have nearly equal radii, check whether the 4f series lies between them; then cite lanthanoid contraction.

its polarising power. Its bonding to hydroxide becomes less ionic and more covalent, so the hydroxide becomes less basic.

Step 3: Conclusion Lanthanoid contraction explains the nearly equal sizes of zirconium and hafnium. Another consequence is the decreasing basicity of lanthanoid hydroxides from $La(OH)_3$ to $Lu(OH)_3$.

Quick Tip to Solve: When two 4d and 5d congeners have nearly equal radii, check whether the 4f series lies between them; then cite lanthanoid contraction.

31(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:

- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated in the overall process.
- Enthalpy of atomisation measures the energy needed to separate a solid into gaseous atoms; strong metallic bonding gives a high value.
- A transition element has a partially filled d-subshell in its atom or in at least one of its usual ions.

Step 1: Explain catalytic activity (I) Transition metals show variable oxidation states and can form intermediate compounds with reactants. They can therefore participate in successive electron-transfer steps and be regenerated, offering a reaction route of lower activation energy. Transition-metal surfaces can also adsorb reactants using available d-orbitals. Adsorption brings reactants together and weakens their bonds, facilitating reaction. These features explain the catalytic activity of many transition metals and their compounds.

Step 2: Relate atomisation to metallic bonding (II) Transition metals generally have several electrons from the $(n-1)d$ and ns subshells available for metallic bonding. The participation of these electrons produces strong interatomic attraction in the metal lattice. A large amount of energy is therefore needed to separate the lattice into individual gaseous atoms, giving a high enthalpy of atomisation. The strength varies across a series with the number of electrons participating in bonding.

Step 3: Apply the definition to scandium and zinc (III) A scandium atom has electronic configuration $[Ar]\,3d^1 4s^2$, so its d-subshell is incomplete. It is a transition element even though its common ion, Sc^{3+}, has no d-electrons. A zinc atom has configuration $[Ar]\,3d^{10}4s^2$, and its common ion Zn^{2+} has $[Ar]\,3d^{10}$. The d-subshell is completely filled in both, so zinc does not meet the definition of a transition element.

Step 4: Conclusion Variable oxidation states, intermediate formation and adsorption explain catalysis; strong metallic bonding explains high atomisation enthalpy. Scandium qualifies through its atomic $3d^1$ configuration, whereas zinc and Zn^{2+} both have filled $3d^{10}$ subshells.

Quick Tip to Solve: Test the d-subshell of both the neutral atom and its usual ions: an incomplete d-subshell in either is sufficient, so scandium still qualifies.

32(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) $Cr^{3+} + 3e^- \rightarrow Cr(s)$; $E^\circ = -0.74$ V

(II) $Fe^{2+} + 2e^- \rightarrow Fe(s)$; $E^\circ = -0.44$ 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.
- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, where both tabulated values are reduction potentials. A positive value makes the standard cell reaction spontaneous.

Step 1: Compare the two reduction potentials Since $-0.44\,\text{V} > -0.74\,\text{V}$, the iron half-cell has the greater tendency to accept electrons. Thus reaction (II) remains a reduction at the cathode:

$$\text{Fe}^{2+}(\text{aq}) + 2\,\text{e}^- \longrightarrow \text{Fe}\,(\text{s}).$$

Reaction (I) must reverse to supply the electrons at the anode:

$$\text{Cr}\,(\text{s}) \longrightarrow \text{Cr}^{3+}(\text{aq}) + 3\,\text{e}^-.$$

Step 2: Check the spontaneous direction Using the supplied reduction potentials,

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

The positive cell potential confirms this direction. Balancing six electrons by multiplying the chromium oxidation by two and the iron reduction by three gives

$$2\,\text{Cr}\,(\text{s}) + 3\,\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\,\text{Cr}^{3+}(\text{aq}) + 3\,\text{Fe}\,(\text{s}).$$

Electrode potentials are not multiplied when half-reactions are scaled, because potential is an intensive quantity.

Step 3: Conclusion Reaction (II) remains a reduction, while reaction (I) is reversed to become oxidation. This gives $E^\circ_{\text{cell}} = +0.30\,\text{V}$, as required for a spontaneous galvanic cell under standard conditions.

Quick Tip to Solve: Among two negative reduction potentials, the less negative value is the cathode value; subtract the anode value without multiplying either potential.

32(a)(ii). Represent the cell in which the following reaction takes place:

$Mg(s) + 2Ag^+(0.001\ M) \rightarrow Mg^{2+}(0.100\ M) + 2Ag(s)$

Calculate E_{cell} if E°_{cell} = 3.17 V. (log 10 = 1) [3 marks]

Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction at the cathode. Cell notation places the anode on the left and the cathode on the right; a double vertical line represents the salt bridge.
- The Nernst equation at the usual temperature of 298 K is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrodes and electron transfer Magnesium loses two electrons, while two silver ions together gain those electrons:

$$\text{Anode: } \mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$\text{Cathode: } 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag(s)}.$$

Therefore $n = 2$. The magnesium electrode is the negative terminal and the silver electrode is the positive terminal.

Step 2: Write the cell representation The single vertical lines denote the boundaries between each solid electrode and its electrolyte. Using the printed ion concentrations gives

$$\mathrm{Mg(s)} \mid \mathrm{Mg^{2+}(0.100\,M)} \parallel \mathrm{Ag^+(0.001\,M)} \mid \mathrm{Ag(s)}.$$

Electrons flow through the external circuit from magnesium to silver.

Step 3: Evaluate the reaction quotient and apply the Nernst equation The silver-ion concentration is squared because its coefficient in the balanced reaction is two. Neither solid enters the reaction quotient:

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

Thus $\log Q = 5\log 10 = 5$, and

$$E_{\text{cell}} = 3.17 - \frac{0.0591}{2}(5) = 3.17 - 0.14775 = 3.02225\,\text{V}.$$

Since $Q > 1$, the potential is lower than the standard potential, as expected from the sign in the Nernst equation.

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

Quick Tip to Solve: Use the balanced reaction to get both $n = 2$ and the square on $[\mathrm{Ag^+}]$; omit both solid metals from Q.

OR

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

Solution:

Concept:

- Limiting molar conductivity, Λ_m°, is the molar conductivity at infinite dilution, where interactions between ions become negligible.
- For an electrolyte yielding ν_+ cations and ν_- anions per formula unit, Kohlrausch's law gives $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$. Here λ_+° and λ_-° are the limiting ionic molar conductivities at a fixed temperature.

Step 1: State Kohlrausch's law At infinite dilution, each ion makes a definite contribution to the molar conductivity of an electrolyte, independent of the nature of the other ion present. The limiting molar conductivity is the sum of these individual ionic contributions, multiplied by the number of each kind of ion produced per formula unit.

Step 2: Give two applications First, the law determines the limiting molar conductivity of a weak electrolyte from the limiting molar conductivities of suitable strong electrolytes. For example, cancellation of the contributions from Na^+ and Cl^- gives

$$\Lambda_m^\circ(\mathrm{CH_3COOH}) = \Lambda_m^\circ(\mathrm{CH_3COONa}) + \Lambda_m^\circ(\mathrm{HCl}) - \Lambda_m^\circ(\mathrm{NaCl}).$$

Second, it permits determination of the degree of dissociation of a weak electrolyte. Once its Λ_m° is known, the measured molar conductivity Λ_m at the required concentration gives

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}.$$

Step 3: Conclusion Kohlrausch's law states the independent migration of ions at infinite dilution. Two applications are finding the limiting molar conductivity of a weak electrolyte and determining its degree of dissociation.

Quick Tip to Solve: To obtain a weak electrolyte's limiting conductivity, add strong electrolytes containing its desired ions and subtract the salt containing the unwanted ions.

32(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 states that limiting molar conductivity is the sum of the limiting ionic contributions. Suitable combinations of strong electrolytes therefore give the limiting molar conductivity of a weak electrolyte.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m is its molar conductivity at the stated concentration and Λ_m° is its limiting molar conductivity. The ratio is dimensionless.

Step 1: Combine the ionic contributions The required ions are NH_4^+ and OH^-. Write the supplied limiting conductivities in terms of ionic contributions:

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

Adding the first two expressions and subtracting the third cancels the unwanted sodium and chloride contributions.

Step 2: Calculate the limiting molar conductivity Hence, using all conductivities in S cm^2 mol^{-1},

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

This corresponds to the limiting value when the weak electrolyte is completely dissociated.

Step 3: Obtain the fraction dissociated at the given concentration The measured molar conductivity at 1×10^{-2} M is already given, so no conversion from conductivity or further concentration factor is needed:

$$\alpha = \frac{9.33}{238.3} = 0.03915\ldots.$$

The conductivity units cancel. Multiplication by 100 gives a percentage dissociation of $3.915\ldots\%$, consistent with a weak base having only a small fraction dissociated at this concentration.

Step 4: Conclusion The degree of dissociation of NH_4OH at 1×10^{-2} M is $\boxed{\alpha \approx 0.0392}$, or approximately 3.92%.

Quick Tip to Solve: Add the NH_4Cl and NaOH values, subtract NaCl, then divide 9.33 by the result; do not multiply the ratio by concentration.

33(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'? [1 mark]

Solution:

Concept:

- The Hinsberg reagent, $C_6H_5SO_2Cl$, distinguishes primary and secondary amines by the alkali solubility of their sulphonamide products.
- A primary amine produces a sulphonamide with an acidic N–H proton; its salt dissolves in aqueous alkali.

Step 1: Interpret the soluble product The product dissolves in NaOH, so it has a removable N–H proton. Hence X is a primary amine. A secondary amine would form a sulphonamide without an N–H bond, which is insoluble in alkali.

Step 2: Match the molecular formula The primary amine with formula C_2H_7N is ethylamine, $CH_3CH_2NH_2$. It gives $C_6H_5SO_2NHC_2H_5$, whose N–H proton is removed by NaOH to form a soluble sodium salt. Dimethylamine has the same molecular formula but is secondary, so it does not satisfy the observed solubility.

Step 3: Conclusion Compound X is $\boxed{CH_3CH_2NH_2}$, ethylamine (ethanamine), a primary amine.

Quick Tip to Solve: For a Hinsberg product soluble in NaOH, look for a remaining N–H bond and select a primary amine.

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

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

[1 mark]

Solution:

Concept:

- $pK_b = -\log K_b$, so a stronger base has a lower pK_b.
- In aqueous solution, methylamine basicity depends on both the electron-releasing effect of methyl groups and solvation of the conjugate ammonium ions.

Step 1: Compare basic strengths in water The aqueous basicity order of the methylamines is $(CH_3)_2NH$ greater than CH_3NH_2 greater than $(CH_3)_3N$; all three are stronger bases than NH_3. Solvation makes the tertiary methylamine less basic than the primary methylamine in water.

Step 2: Place aniline and reverse the order Aniline is weaker than ammonia because its nitrogen lone pair is delocalised into the benzene ring and is less available to accept a proton. Since increasing basicity means decreasing pK_b, the strongest base must come first in the requested increasing pK_b order.

Quick Tip to Solve: For aqueous methylamines remember secondary, primary, tertiary basicity, then reverse basic strength to order pKb.

Step 3: Conclusion Increasing pK_b:

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

Quick Tip to Solve: For aqueous methylamines remember secondary, primary, tertiary basicity, then reverse basic strength to order pKb.

33(a)(iii). Aniline on nitration gives considerable amount of meta product along with ortho and para products. Why? [1 mark]

Solution:

Concept:

- The amino group in neutral aniline donates electron density by resonance and directs electrophilic substitution to ortho and para positions.
- The strongly acidic nitrating mixture protonates the amino group and changes its directing effect.

Step 1: Identify the species in the acidic medium In the mixture of concentrated nitric and sulphuric acids, aniline is substantially protonated:

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

This forms the anilinium ion.

Step 2: Explain the meta substitution The $-NH_3{}^+$ group has no available nitrogen lone pair to donate into the ring. It withdraws electron density and is meta-directing, giving a considerable amount of the meta nitro product. The neutral aniline present retains the ortho/para-directing $-NH_2$ group and accounts for the ortho and para products.

Step 3: Conclusion The acidic nitrating medium converts aniline into the meta-directing anilinium ion, causing considerable meta product alongside the ortho and para products.

Quick Tip to Solve: Before assigning the directing effect in an acidic reaction, check whether the amino group has been protonated.

33(a)(iv). Convert aniline to:

(I) p-bromoaniline

(II) phenol [2 marks]

Solution:

Concept:

- Acetylating aniline protects the amino group and reduces its activating effect, allowing controlled para bromination.
- Aniline forms a diazonium salt with nitrous acid at 273–278 K; warming the salt with water replaces

Quick Tip to Solve: Protect the amino group before para bromination; for phenol, diazotise cold and then warm the diazonium salt with water.

the diazonium group by hydroxyl.

Step 1: Prepare p-bromoaniline through protection First treat aniline with acetic anhydride to give acetanilide:

$$C_6H_5NH_2 \xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3.$$

Brominate with Br_2 in glacial acetic acid, then isolate the major para product and hydrolyse the acetyl group with aqueous acid and heat:

$$C_6H_5NHCOCH_3 \xrightarrow{Br_2/CH_3COOH} p\text{-}BrC_6H_4NHCOCH_3.$$

$$p\text{-}BrC_6H_4NHCOCH_3 \xrightarrow{H_3O^+,\,heat} p\text{-}BrC_6H_4NH_3{}^+ \xrightarrow{OH^-} p\text{-}BrC_6H_4NH_2.$$

The final basic work-up gives free p-bromoaniline. Direct bromination of aniline with bromine water instead produces 2,4,6-tribromoaniline.

Step 2: Prepare phenol through diazotisation Treat a separate portion of aniline with $NaNO_2$/HCl at 273–278 K:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O.$$

Warm the benzene diazonium chloride with water to release nitrogen and form phenol:

$$C_6H_5N_2{}^+Cl^- + H_2O \xrightarrow{warm} C_6H_5OH + N_2 + HCl.$$

Low temperature during diazotisation prevents premature decomposition of the diazonium salt.

Step 3: Conclusion (I) Aniline → acetanilide → p-bromoacetanilide → p-bromoaniline. (II) Aniline → benzene diazonium chloride → phenol.

Quick Tip to Solve: Protect the amino group before para bromination; for phenol, diazotise cold and then warm the diazonium salt with water.

OR

33(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:

- The carbylamine reaction is given by primary amines on heating with chloroform and alcoholic potassium hydroxide.
- A primary amine RNH_2 gives the foul-smelling isocyanide RNC; the alkyl group remains attached to nitrogen.

Step 1: Identify the reacting amine and product Ethylamine, $C_2H_5NH_2$, is a primary amine. With chloroform and ethanolic potassium hydroxide on heating, its amino group is converted into an isocyanide group. The foul-smelling substance is ethyl isocyanide, C_2H_5NC, not ethyl cyanide, whose carbon-nitrogen connectivity is different.

Quick Tip to Solve: Keep the ethyl group bonded to nitrogen: the carbylamine product is C_2H_5NC, not the nitrile C_2H_5CN.

Step 2: Write the balanced carbylamine equation Three molecules of potassium hydroxide supply the alkali needed to remove the three chlorine atoms of chloroform as potassium chloride:

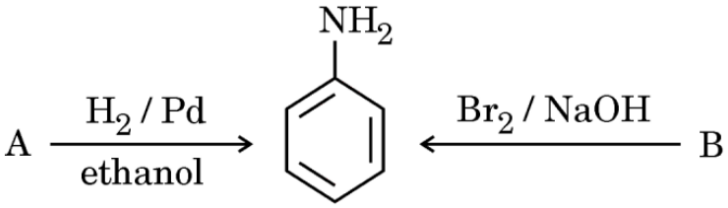
$$C_2H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\text{ethanol, heat}} C_2H_5NC + 3\,KCl + 3\,H_2O.$$

The equation conserves carbon, hydrogen, nitrogen, chlorine, potassium and oxygen; it is the characteristic carbylamine test for primary amines.

Step 3: Conclusion Ethylamine gives foul-smelling ethyl isocyanide, C_2H_5NC, by the carbylamine reaction shown above.

Quick Tip to Solve: Keep the ethyl group bonded to nitrogen: the carbylamine product is C_2H_5NC, not the nitrile C_2H_5CN.

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



Solution:

Concept:

- Catalytic hydrogenation with H_2/Pd reduces an aromatic nitro group, $-NO_2$, to an amino group, $-NH_2$.
- The Hofmann bromamide reaction converts a primary amide $RCONH_2$ into a primary amine RNH_2, removing the carbonyl carbon from the organic product.

Step 1: Identify A from catalytic reduction The product shown is aniline, $C_6H_5NH_2$, and the arrow from A uses hydrogen with palladium in ethanol. Nitrobenzene undergoes reduction of its nitro group under these conditions, retaining the benzene ring:

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

Therefore A is nitrobenzene, $C_6H_5NO_2$. The oxygen atoms leave as water while the nitrogen remains attached to the phenyl group.

Step 2: Identify B from Hofmann degradation Bromine with aqueous sodium hydroxide converts a primary amide into an amine with one carbon fewer. To produce aniline, the starting amide must have the phenyl group directly attached to its carbonyl carbon: benzamide, $C_6H_5CONH_2$.

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

The carbonyl carbon enters carbonate rather than the amine; hence benzamide with seven carbon

Quick Tip to Solve: Work backwards from aniline: replace $-NH_2$ by $-NO_2$ for hydrogenation, and by $-CONH_2$ for Hofmann degradation.

atoms gives aniline with six.

Step 3: Conclusion A is nitrobenzene, $C_6H_5NO_2$, and B is benzamide, $C_6H_5CONH_2$.

Quick Tip to Solve: Work backwards from aniline: replace $-NH_2$ by $-NO_2$ for hydrogenation, and by $-CONH_2$ for Hofmann degradation.

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

(I) benzene

(II) sulphanilic acid [2 marks]

Solution:

Concept:

- Diazotisation converts aniline into benzenediazonium chloride using nitrous acid generated from $NaNO_2$ and HCl at 273–278 K. Reduction of the diazonium group with hypophosphorous acid replaces it by hydrogen.
- Aniline reacts with concentrated sulphuric acid to form anilinium hydrogensulphate. Heating this salt at 453–473 K gives sulphanilic acid, with the sulphonic acid group para to the amino group.

Step 1: (I) Diazotise aniline and reduce the diazonium salt First prepare benzenediazonium chloride in the cold; keeping the temperature low prevents decomposition of this intermediate:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \xrightarrow{273-278\,K} C_6H_5N_2Cl + NaCl + 2\,H_2O.$$

Then treat the diazonium salt with hypophosphorous acid, H_3PO_2, in water. Nitrogen is evolved and the diazonium group is replaced by hydrogen:

$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl.$$

Step 2: (II) Sulphonate aniline on heating Treat aniline with concentrated sulphuric acid to obtain the anilinium hydrogensulphate salt, then heat at 453–473 K. The net conversion is

$$C_6H_5NH_2 + H_2SO_4 \xrightarrow{453-473\,K} p\text{-}H_2NC_6H_4SO_3H + H_2O.$$

The product is sulphanilic acid (4-aminobenzenesulphonic acid). The prefix p specifies that NH_2 and SO_3H occupy opposite positions on the benzene ring.

Step 3: Conclusion (I) Aniline gives benzene by cold diazotisation followed by reduction with H_3PO_2. (II) Concentrated H_2SO_4, followed by heating at 453–473 K, converts aniline into sulphanilic acid.

Quick Tip to Solve: To replace an aromatic amino group by hydrogen, use a diazonium salt and H_3PO_2; to retain the amino group and introduce para-SO_3H, heat with concentrated sulphuric acid.