CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-5-1

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. 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.
- The equilibrium constant and the reaction enthalpy and Gibbs energy depend on the thermodynamic states of reactants and products, not on the reaction pathway.

Step 1: Identify the kinetic effect In the Arrhenius equation, $k = Ae^{-E_a/(RT)}$, k is the rate constant, E_a the activation energy, R the gas constant and T the absolute temperature. Lowering E_a allows more collisions to lead to reaction and increases the rate at the same temperature.

Step 2: Eliminate the thermodynamic quantities A catalyst does not change the energies of the initial and final states, so the enthalpy change and Gibbs energy change remain unchanged. It accelerates both forward and reverse reactions without shifting equilibrium. Thus options (A), (B) and (C) are incorrect; equilibrium is reached sooner but its constant is unchanged.

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

Quick Tip to Solve: Distinguish the energy barrier from the energy difference: a catalyst lowers the barrier but leaves the reactant-to-product energy difference unchanged.

2. 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 alkyl halides, identify a tetrahedral carbon bonded to four different groups.

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

- A carbon bearing two identical groups cannot be a stereogenic centre in these molecules.

Step 1: Examine the four carbon skeletons 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 has a stereogenic centre. In 2-chloropropane, $CH_3CHClCH_3$, the middle carbon has two identical methyl groups, so it is also achiral.

Step 2: Identify four different substituents In 2-chlorobutane, $CH_3CHClCH_2CH_3$, carbon 2 is bonded to H, Cl, CH_3 and CH_2CH_3. All four groups are different. Its mirror-image configurations are non-superimposable and form an enantiomeric pair.

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

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

3. 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:

- Oxidation of a primary alcohol first gives an aldehyde; further oxidation gives a carboxylic acid.
- Pyridinium chlorochromate (PCC) is a mild oxidising reagent used under anhydrous conditions to stop the oxidation of a primary alcohol at the aldehyde stage.

Step 1: Identify the required change Ethanol is a primary alcohol and ethanal is the corresponding aldehyde. The transformation removes two hydrogen atoms without changing the number of carbon atoms:

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

This is controlled oxidation, for which PCC is suitable.

Step 2: Compare the other reagents Catalytic hydrogenation adds hydrogen and is a reduction process. $LiAlH_4$ is also a reducing agent, so neither achieves the required oxidation. $KMnO_4$ is a strong oxidising agent and generally oxidises the primary alcohol further to ethanoic acid under the usual conditions, rather than selectively isolating ethanal.

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

Quick Tip to Solve: When a primary alcohol must stop at an aldehyde, choose PCC; strong aqueous oxidants generally carry oxidation through to the acid.

4. 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:

- A tertiary amine has three carbon-containing groups bonded directly to nitrogen. Choose the longest of these carbon chains as the parent alkanamine.
- Other groups bonded to nitrogen are named with the locant N, and different substituent names are arranged alphabetically.

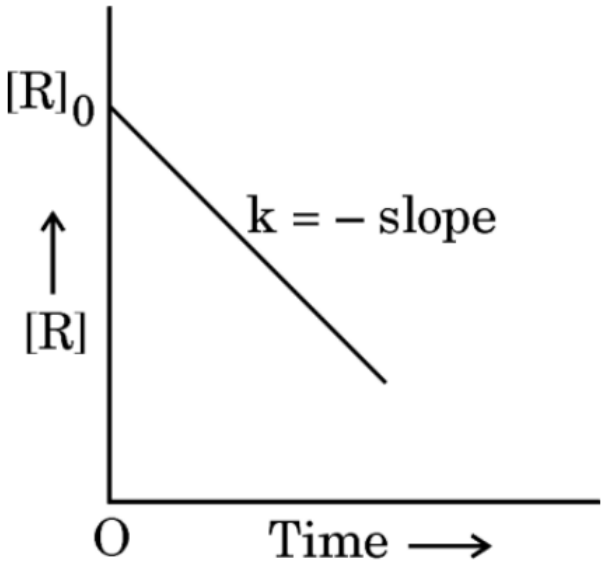
Step 1: Select the parent chain The nitrogen in $CH_3CH_2N(CH_3)CH_2CH_2CH_3$ carries an ethyl group, a methyl group and a propyl group. The longest chain directly attached to it contains three carbon atoms. Nitrogen is attached to an end carbon of this chain, so the parent is propan-1-amine. Carbon chains on opposite sides of nitrogen are not joined into a five-carbon parent chain.

Step 2: Name the nitrogen substituents The remaining substituents are N-ethyl and N-methyl, with ethyl preceding methyl alphabetically. Option (A) incorrectly uses a pentane parent. Option (C) requires two ethyl groups and option (D) requires two methyl groups, whereas the given nitrogen has 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, select the longest carbon chain as the parent, then prefix each remaining group with N.

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



(A) Third order

(B) Second order

(C) First order

(D) Zero order

Correct Answer: (D) Zero order

Solution:

Concept:

- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$, where $[R]$ is concentration, t is time and k is the rate constant.
- Its integrated rate equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration. Thus a concentration-versus-time plot is a straight line of slope $-k$.

Step 1: Read the plotted quantities The vertical axis is the reactant concentration $[R]$, rather than its logarithm or reciprocal. The graph starts at $[R]_0$ and falls linearly with time; the printed relation $k = -$slope identifies a constant rate of concentration decrease.

Step 2: Compare the integrated rate laws This graph agrees directly with $[R] = [R]_0 - kt$. For first order, $\ln[R]$ versus time is linear; for second order, $1/[R]$ versus time is linear; and for third order, $1/[R]^2$ versus time is linear. Their concentration-versus-time plots are not the straight decreasing line shown here.

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

Quick Tip to Solve: Read the vertical-axis label before identifying order: a straight falling $[R]$-versus-time line indicates zero order, while a falling $\ln[R]$ line indicates first order.

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

(A) ethyl nitrite

(B) nitroethane

(C) nitromethane

(D) ethene

Correct Answer: (B) nitroethane

Solution:

Concept:

- Nitrite is an ambident nucleophile: it can form a new bond through nitrogen or oxygen, giving different products.
- Silver nitrite is predominantly covalent and favours bond formation through nitrogen, giving a nitroalkane. Alkali-metal nitrites generally favour alkyl nitrites with a carbon-oxygen bond.

Step 1: Write the substitution product With alcoholic silver nitrite, the bromine of ethyl bromide is replaced by a nitro group attached through nitrogen. The two-carbon skeleton is preserved:

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

The organic product contains a carbon-nitrogen bond and is named nitroethane.

Step 2: Distinguish the alternative products Ethyl nitrite, CH_3CH_2ONO, has a carbon-oxygen bond and is favoured with an ionic nitrite such as KNO_2, so (A) is incorrect here. Nitromethane has only one carbon and cannot result from this substitution. Ethene is an elimination product, typically formed with alcoholic KOH, rather than the product asked for with silver nitrite.

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

Quick Tip to Solve: Pair $AgNO_2$ with nitroalkane formation through nitrogen; pair KNO_2 with alkyl nitrite formation through oxygen.

7. 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 freezing-point depression constant and m is molality.
- More dissolved particles cause a larger depression; the highest freezing point corresponds to the smallest depression.

Quick Tip to Solve: For this comparison, count particles first: highest freezing point means the smallest van't Hoff factor, not the largest.

Step 1: Compare the dissolved particles In the usual comparison of these equally concentrated aqueous solutions, glucose remains molecular and has $i = 1$. The salts dissociate: KCl gives two ions, Na_2SO_4 gives three ions, and $AlCl_3$ gives four ions per formula unit in the ideal limit.

Step 2: Relate particle count to freezing point Since $T_f = T_f^\circ - \Delta T_f$, the solution producing the fewest particles suffers the least decrease in freezing point. Thus all three ionic solutes cause a greater depression than glucose; choosing the solute with the greatest ion count would give the opposite trend.

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

Quick Tip to Solve: For this comparison, count particles first: highest freezing point means the smallest van't Hoff factor, not the largest.

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

(A) CH_3–$CH(CH_3)$–CHO

(B) $(CH_3)_3C$–CHO

(C) CH_3–CH_2–CHO

(D) CH_3–$CH(CH_3)$–$CH(CH_3)$–CHO

Correct Answer: (B) $(CH_3)_3C$–CHO

Solution:

Concept:

- An aldehyde without an α-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali, producing an alcohol and a carboxylate salt.
- The α-carbon is the carbon directly attached to the $-$CHO group; only hydrogens on that carbon determine this test.

Step 1: Inspect the carbon adjacent to the aldehyde group In $(CH_3)_3C-CHO$, the α-carbon is bonded to three methyl groups and the aldehyde carbon. All four bonds are to carbon, so it has no hydrogen. The hydrogens on the three methyl groups are not α-hydrogens.

Step 2: Check the other three structures Option (A) has an adjacent CH group and therefore one α-hydrogen. Option (C) has an adjacent CH_2 group and two α-hydrogens. The carbon next to $-$CHO in option (D) is also CH, so it has one. These three aldehydes can undergo aldol reaction instead of the usual Cannizzaro reaction.

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

Quick Tip to Solve: Circle only the carbon directly beside $-$CHO; hydrogens farther along the chain do not count as α-hydrogens.

9. 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, ligand-field splitting permits absorption of visible light through d-d transitions when suitable partially filled d orbitals are present.
- Ions with d^0 or d^{10} configurations do not show colour from d-d transitions; the four ions can be compared by their electron configurations.

Step 1: Determine the configurations of ions I and II Neutral copper is $[\mathrm{Ar}]3d^{10}4s^{1}$, so Cu^{+} is $[\mathrm{Ar}]3d^{10}$. Titanium loses its two $4s$ and two $3d$ electrons to form Ti^{4+}, which is $[\mathrm{Ar}]3d^{0}$. Both ions I and II are colourless in aqueous solution.

Step 2: Determine the configurations of ions III and IV Removing the two $4s$ electrons gives Co^{2+} the configuration $[\mathrm{Ar}]3d^{7}$ and Fe^{2+} the configuration $[\mathrm{Ar}]3d^{6}$. Both have partially filled d subshells and are coloured in water. Options (A), (B) and (D) each include at least one of the colourless ions.

Step 3: Conclusion Both III, Co^{2+}, and IV, Fe^{2+}, are coloured. Hence, the correct option is (C).

Quick Tip to Solve: Calculate the ionic configuration carefully: Ti^{4+} is d^0, whereas Ti^{3+} would be d^1.

10. 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 aqueous sodium hydrogen carbonate, releasing carbon dioxide with brisk effervescence.
- A useful distinguishing test must give different observations for the two compounds, rather than the same negative result.

Quick Tip to Solve: When a pair contains a carboxylic acid, try $NaHCO_3$: bubbles of CO_2 identify the acid immediately.

Step 1: Apply the bicarbonate test Propanoic acid is sufficiently acidic to liberate CO_2 from $NaHCO_3$:

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

Propanal does not contain a carboxyl group and does not produce this effervescence with sodium hydrogen carbonate.

Step 2: Eliminate the other tests The Hinsberg test distinguishes classes of amines, whereas the Lucas test distinguishes suitable alcohols. Neither applies to these functional groups. Propanal is not ethanal or a methyl ketone, and propanoic acid is also iodoform-negative; the iodoform test therefore does not distinguish this pair.

Step 3: Conclusion Sodium bicarbonate gives brisk effervescence with CH_3CH_2COOH but not with CH_3CH_2CHO. Hence, the correct option is (A).

Quick Tip to Solve: When a pair contains a carboxylic acid, try $NaHCO_3$: bubbles of CO_2 identify the acid immediately.

11. 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:

- Cells are chosen for applications according to their capacity, portability, voltage stability and whether their reactants can be replenished or the cell recharged.
- Lead storage cells are secondary cells, dry and mercury cells are primary cells, and fuel cells use a continuous supply of fuel and oxidant.

Step 1: Match the familiar portable and rechargeable cells A lead storage cell can be recharged and supplies backup power in an inverter, giving i-d. A mercury cell provides a nearly constant potential in a compact form and is associated with a wrist watch, giving ii-c. A dry cell powers devices such as wall clocks, giving iii-a.

Step 2: Match the fuel cell and check the codes Hydrogen-oxygen fuel cells were used in the Apollo Space Programme; they generate electricity and produce water. Thus iv-b. Code (B) contains all four matches. Code (A) incorrectly pairs lead storage with a wall clock; code (C) pairs it with a wrist

Quick Tip to Solve: Anchor the matching with rechargeable lead storage for the inverter and hydrogen-oxygen fuel cells for Apollo.

watch; code (D) pairs it with the Apollo programme.

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

Quick Tip to Solve: Anchor the matching with rechargeable lead storage for the inverter and hydrogen-oxygen fuel cells for Apollo.

12. 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, whereas dichromate ions, $Cr_2O_7^{2-}$, are orange.
- Their interconversion depends on acidity: added H^+ favours dichromate, while added OH^- favours chromate.

Step 1: Write the acid-dependent equilibrium The colour change is explained by

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

An acid supplies H^+, shifting this equilibrium to the right and converting yellow chromate into orange dichromate. Chromium remains in the $+6$ oxidation state, so this is not a reduction reaction.

Step 2: Compare the possible liquids HCl supplies the required hydrogen ions. Sodium hydroxide is alkaline and favours yellow chromate; sodium hydrogen carbonate solution is also mildly alkaline. Methyl orange is an indicator and does not provide the intended acid-driven chromate-to-dichromate conversion.

Step 3: Conclusion The residual liquid was most likely HCl solution. Hence, the correct option is (D).

Quick Tip to Solve: Remember the direction: adding acid changes yellow chromate into orange dichromate; adding alkali reverses it.

13. 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:

- Resistance measurements should probe the ionic solution without changing its composition during measurement.
- Direct current can cause electrolysis and electrode polarisation; an alternating source of suitable frequency limits persistent ion accumulation and net chemical change.

Step 1: Evaluate the assertion An AC source is used to measure the resistance of an ionic solution. Rapid reversal of the field avoids sustained unidirectional movement of ions and reduces electrode polarisation. Therefore, Assertion (A) is true.

Step 2: Evaluate the reason With a DC source, ions continuously migrate towards the oppositely charged electrodes and may be discharged there. Electrolysis and unequal ion transport change ionic concentrations, especially near the electrodes, so the measured resistance may drift. Therefore, Reason (R) is true.

Step 3: Test the explanatory link The concentration change caused by DC would alter the very solution whose resistance is being measured. Using AC limits this change, so the reason directly explains the assertion. The code claiming both statements are true without an explanatory link is therefore unsuitable; the codes declaring either statement false are also excluded.

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

Quick Tip to Solve: Link DC to electrolysis and concentration change; AC is chosen so the resistance measurement does not steadily alter the solution.

14. 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 and x is its mole fraction dissolved in the liquid.
- At fixed gas pressure, $x = p/K_H$; therefore a larger Henry's law constant means lower gas solubility.

Step 1: Evaluate the assertion On increasing temperature, gas solubility in a liquid generally decreases. Since $K_H = p/x$, a decrease in x at fixed p means that K_H increases. The assertion says that it decreases, so the assertion is false.

Step 2: Evaluate the reason Dissolution of a gas in a liquid is generally exothermic. Raising the temperature favours the escape of dissolved gas, reducing its solubility. Thus the reason is true in the usual Henry's law context of this question.

Step 3: Match the truth values to the code A false assertion cannot be correctly explained by the reason. Codes (A) and (B) require a true assertion, and code (C) requires a false reason; none matches the truth values found here.

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

Quick Tip to Solve: Write $x = p/K_H$ first: at fixed pressure, lower gas solubility means a higher K_H.

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

Reason (R): Aldehydes and ketones have dipole-dipole interaction. [1 mark]

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

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

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

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

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

Solution:

Concept:

- The polar carbonyl group, $C{=}O$, allows aldehydes and ketones to accept hydrogen bonds from water molecules.
- An alkyl group is non-polar and hydrophobic. Increasing its size reduces the relative influence of the water-attracting carbonyl group.

Step 1: Evaluate the assertion Lower aldehydes and ketones dissolve readily in water because their carbonyl oxygen forms hydrogen bonds with water. As the alkyl group grows, the non-polar hydrocarbon portion becomes larger while there is still only one carbonyl group. Water solubility therefore decreases, so the assertion is true.

Step 2: Evaluate the reason The carbonyl bond is polar because oxygen is more electronegative than carbon. Aldehyde and ketone molecules consequently possess permanent dipoles and exhibit dipole-dipole attractions. The reason is also true.

Step 3: Check whether the reason explains the trend The presence of dipole-dipole interactions does not explain why solubility falls as the alkyl group becomes larger. That trend results from the increasing hydrophobic portion relative to the carbonyl group. Code (A) wrongly treats the reason as the explanation; codes (C) and (D) wrongly declare 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 solubility trends within a carbonyl homologous series, compare the growing non-polar chain with the unchanged polar group.

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

[1 mark]

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

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

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

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

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

Solution:

Concept:

- For the same alkyl group, the boiling point of an alkyl halide depends on the strength of intermolecular attractions.
- A larger, more polarisable electron cloud produces stronger London dispersion forces, which are part of van der Waals attractions.

Step 1: Evaluate the assertion With the alkyl group held constant, alkyl iodides have the highest boiling points and alkyl fluorides the lowest in this series. The stated order $RI > RBr > RCl > RF$ is therefore correct, so the assertion is true.

Step 2: Evaluate the reason The size and polarisability of the halogen atom decrease from iodine to fluorine. The corresponding dispersion attractions decrease in the order $RI > RBr > RCl > RF$. Thus the stated order of van der Waals forces is correct, and the reason is true.

Step 3: Connect intermolecular attraction with boiling Boiling separates molecules from the liquid into the vapour. Stronger attractions require more thermal energy for this separation, so they cause a higher boiling point. The reason directly explains the assertion. Code (B) denies this explanatory link, while codes (C) and (D) incorrectly make one statement 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: Keep the alkyl group fixed and compare halogen polarisability: iodine gives the strongest dispersion forces and highest boiling point.

Section B (10 marks)

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

Solution:

Concept:

- Elevation of boiling point is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent's ebullioscopic constant and m the solute molality.
- Molality is the number of moles of solute per kilogram of solvent. For complete dissociation, i equals the number of ions formed from one formula unit.

Step 1: Determine the van't Hoff factor Calcium chloride dissociates completely as

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

Each formula unit produces three ions, so $i = 3$. The number of dissolved particles, rather than merely the number of formula units added, determines the colligative effect.

Step 2: Calculate the molality Convert the mass of water to kilograms: $260\,\mathrm{g} = 0.260\,\mathrm{kg}$. The moles of solute and its molality are

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

Use the mass of water, not the combined mass of water and solute, in this denominator.

Step 3: Substitute in the boiling-point formula With $K_b = 0.52\,\mathrm{K\ kg\ mol^{-1}}$,

$$\Delta T_b = 3 \times 0.52 \times 0.10395 = 0.16216\,\mathrm{K}.$$

The result is positive because a non-volatile solute raises the boiling point of the solvent.

Step 4: Conclusion The elevation of boiling point is $\boxed{\Delta T_b \approx 0.162\,\mathrm{K}}$, equivalently a temperature rise of approximately $0.162\,^\circ\mathrm{C}$.

Quick Tip to Solve: For completely dissociated $\mathrm{CaCl_2}$, multiply $K_b m$ by 3 and convert the given water mass to kilograms before finding m.

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 solution obeys Raoult's law: $p_X = x_X p_X^\circ$ and $p_Y = x_Y p_Y^\circ$, where x is the liquid-phase mole fraction and p° is the pure-liquid vapour pressure.
- The total vapour pressure is the sum of the partial pressures: $P = p_X + p_Y$, with $x_X + x_Y = 1$.

Step 1: Find the mole fractions Let the amount of each liquid be n moles. Since the solution contains equal moles, its total amount is $2n$, giving

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

Both liquids contribute to the vapour, so each pure-liquid pressure must be weighted by its own mole fraction.

Step 2: Calculate and add the partial pressures Apply Raoult's law using $p_X^\circ = 120\,\text{mm Hg}$ and $p_Y^\circ = 160\,\text{mm Hg}$:

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

As expected for an ideal mixture, this pressure lies between the vapour pressures of the two pure liquids.

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

Quick Tip to Solve: Equal moles give mole fractions of one-half, so the total pressure of an ideal binary solution is the average of the two pure-liquid pressures.

18.

Concentration of KCl solution in $\mathrm{mol/L}$	Conductivity at 298.15 K in $\mathrm{S\,cm^{-1}}$	Molar conductivity at 298.15 K in $\mathrm{S\,cm^2\,mol^{-1}}$
1.000	0.1113	111.3
0.100	0.0129	129.0
0.010	0.00141	141.0

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

Solution:

Concept:

- Conductivity, κ, depends on the number of charge-carrying ions per unit volume and on their mobility.
- Molar conductivity is the conductance contribution per mole of electrolyte: $\Lambda_m = 1000\kappa/c$, when c is in $\mathrm{mol\,L^{-1}}$ and κ is in $\mathrm{S\,cm^{-1}}$.

Step 1: Explain the decrease in conductivity on dilution When the concentration decreases from 1.000 to $0.010\,\mathrm{mol\,L^{-1}}$, the conductivity decreases from 0.1113 to $0.00141\,\mathrm{S\,cm^{-1}}$. Dilution reduces the number of K^+ and Cl^- ions per unit volume. This reduction outweighs the increase in their mobility, so conductivity falls.

Step 2: Explain the increase in molar conductivity on dilution Over the same dilution, Λ_m increases from 111.3 to $141.0\,\mathrm{S\,cm^2\,mol^{-1}}$. KCl is a strong electrolyte and is already almost completely dissociated. Dilution weakens interionic attractions, allowing the ions to move more freely. Hence the conductance contribution of one mole increases; it is not primarily an increase in ionisation as for a weak electrolyte.

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

Quick Tip to Solve: Distinguish ions per unit volume from conductance per mole: dilution lowers the former but improves ionic mobility in a strong electrolyte.

19(a). **Write the rate law expression for the reaction $2HI \rightarrow H_2 + I_2$, if the order of the reaction is zero.** [1 mark]

Solution:

Concept:

- A rate law expresses the dependence of reaction rate on reactant concentration: $r = k[\mathrm{HI}]^n$, where k is the rate constant and n is the order.
- For a zero-order reaction, $n = 0$; the rate is independent of reactant concentration within the zero-order regime.

Step 1: Insert the specified order For $2\,\mathrm{HI} \longrightarrow \mathrm{H_2} + \mathrm{I_2}$, the given order is zero, so $r = k[\mathrm{HI}]^0$. Since any nonzero concentration raised to the power zero equals unity, changing the concentration does not

Quick Tip to Solve: Put the given order, not the stoichiometric coefficient, in the exponent of the reactant concentration.

change this rate at fixed temperature.

Step 2: Relate the rate to concentration changes Using the stoichiometric coefficients, the reaction rate can be written as

$$r = -\frac{1}{2}\frac{d[\mathrm{HI}]}{dt} = \frac{d[\mathrm{H_2}]}{dt} = \frac{d[\mathrm{I_2}]}{dt}.$$

The coefficient 2 in the balanced equation does not imply second-order kinetics; order is specified experimentally.

Step 3: Conclusion The required rate law is $r = k[\mathrm{HI}]^0 = k$.

Quick Tip to Solve: Put the given order, not the stoichiometric coefficient, in the exponent of the reactant concentration.

19(b). What is the effect of temperature on the rate of reaction? Write a mathematical expression for the same. [1 mark]

Solution:

Concept:

- Increasing temperature generally increases the reaction rate because a larger fraction of molecules has energy equal to or greater than the activation energy.
- The Arrhenius equation relates the rate constant to absolute temperature: $k = Ae^{-E_a/(RT)}$.

Step 1: Explain the temperature effect At higher temperature, more reactant molecules can cross the activation-energy barrier. For an ordinary reaction with positive activation energy, the rate constant increases; at the same reactant concentrations, the reaction therefore becomes faster.

Step 2: Write the mathematical dependence

$$k = Ae^{-E_a/(RT)}, \qquad \ln k = \ln A - \frac{E_a}{RT}.$$

Here A is the frequency or pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature in kelvin. Increasing T makes the negative exponent smaller in magnitude, increasing k.

Step 3: Conclusion Reaction rate generally increases on heating; its temperature dependence is expressed through the Arrhenius equation $k = Ae^{-E_a/(RT)}$.

Quick Tip to Solve: Use temperature in kelvin in the Arrhenius equation; doubling the rate per 10 K is only an approximate rule.

20. Explain the mechanism of acid catalysed hydration of ethene. [2 marks]

Solution:

Concept:

- Acid-catalysed hydration adds the elements of water across an alkene double bond, converting ethene into ethanol.
- The mechanism involves protonation of the double bond, nucleophilic attack by water and loss of a proton; the acid catalyst is regenerated.

Step 1: Protonate the ethene double bond The electron-rich π bond accepts a proton from hydronium ion. The bonding electron pair forms a carbon–hydrogen bond, leaving a carbocation on the other carbon:

$$CH_2{=}CH_2 + H_3O^+ \longrightarrow CH_3CH_2{}^+ + H_2O.$$

The two carbon atoms in ethene are equivalent, so either direction of proton addition gives the same intermediate.

Step 2: Add water to the carbocation Water acts as a nucleophile. A lone pair on its oxygen attacks the positively charged carbon, forming protonated ethanol, an oxonium ion:

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

Step 3: Remove a proton and regenerate the catalyst Another water molecule removes a proton from the oxonium ion. The electrons of that oxygen–hydrogen bond remain on oxygen, giving neutral ethanol:

$$CH_3CH_2OH_2{}^+ + H_2O \longrightarrow CH_3CH_2OH + H_3O^+.$$

Hydronium ion is restored, so acid accelerates the reaction without being consumed overall.

Step 4: Conclusion Ethene gives ethanol by protonation, water attack and deprotonation. The overall reaction is $CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$.

Quick Tip to Solve: Follow the charge through the three stages: carbocation, oxonium ion, then neutral alcohol with acid regenerated.

21(a). How can acetaldehyde be prepared from acetyl chloride? [1 mark]

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into the corresponding aldehyde using hydrogen and a poisoned palladium catalyst.
- Palladium supported on barium sulphate has controlled activity, allowing reduction to stop at the aldehyde stage.

Step 1: Select the reagent for partial reduction Treat acetyl chloride, CH_3COCl, with hydrogen gas in the presence of palladium on barium sulphate, $Pd/BaSO_4$. The catalyst may be further poisoned with

Quick Tip to Solve: For the conversion acyl chloride to aldehyde, recall hydrogen with poisoned palladium: Rosenmund reduction.

sulphur or quinoline to suppress further reduction of the aldehyde.

Step 2: Write the balanced conversion

$$CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl.$$

The acyl chloride group becomes an aldehyde group without changing the carbon skeleton. A strong reducing agent such as $LiAlH_4$ would ordinarily continue reduction to the primary alcohol and is unsuitable for obtaining acetaldehyde directly.

Step 3: Conclusion Prepare acetaldehyde from acetyl chloride by Rosenmund reduction using H_2 and poisoned $Pd/BaSO_4$.

Quick Tip to Solve: For the conversion acyl chloride to aldehyde, recall hydrogen with poisoned palladium: Rosenmund reduction.

21(b). Propanal is more reactive than propanone towards nucleophilic addition reaction. Give reason.

[1 mark]

Solution:

Concept:

- A nucleophile attacks the partially positive carbon of a carbonyl group. Greater electrophilicity favours this attack.
- Alkyl groups donate electron density by the positive inductive effect and also hinder approach of the nucleophile.

Step 1: Compare the electronic effects Propanal, CH_3CH_2CHO, has one alkyl group and one hydrogen attached to the carbonyl carbon. Propanone, CH_3COCH_3, has two alkyl groups. The greater electron donation in the ketone reduces the positive character of its carbonyl carbon, making it less susceptible to nucleophilic attack.

Step 2: Compare steric hindrance The two methyl groups of propanone hinder the incoming nucleophile more than the alkyl group and small hydrogen atom of propanal. Attack and formation of the tetrahedral addition product are therefore easier for the aldehyde.

Step 3: Conclusion Propanal is more reactive because its carbonyl carbon is more electrophilic and less sterically hindered than that of propanone.

Quick Tip to Solve: Compare the groups directly attached to the carbonyl carbon: fewer alkyl groups generally means easier nucleophilic addition.

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:

- On mixing liquids, the volume depends on the relative strengths of unlike (A–B) and like (A–A and B–B) intermolecular attractions.
- Expansion on mixing means $\Delta V_{\text{mix}} = V_{\text{solution}} - (V_A + V_B) > 0$, where V_A and V_B are the initial liquid volumes.

Step 1: Calculate the volume change The initial total volume is $10 + 10 = 20\,\text{mL}$. The observed volume is $20.2\,\text{mL}$, so $\Delta V_{\text{mix}} = 20.2 - 20 = +0.2\,\text{mL}$. Thus the mixture expands.

Step 2: Relate expansion to molecular attractions The A–B attractions formed on mixing are weaker than the original A–A and B–B attractions. The molecules are held less closely together, increasing their average separation and the total volume.

Step 3: Conclusion The volume increases because weaker A–B intermolecular attractions cause expansion on mixing; $\Delta V_{\text{mix}} = +0.2\,\text{mL}$.

Quick Tip to Solve: Compare the final volume with the sum of the initial volumes: expansion points to weaker unlike interactions in this solution.

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 with weaker A–B attractions than A–A and B–B attractions shows positive deviation from Raoult's law in the standard model of non-ideal solutions.
- Such mixing is endothermic: $\Delta H_{\text{mix}} > 0$, where ΔH_{mix} is the enthalpy change on mixing.

Step 1: Identify the interaction change The final volume, $20.2\,\text{mL}$, exceeds the initial total $20\,\text{mL}$. This expansion indicates weaker unlike attractions in the mixture. Separating molecules originally held by stronger like attractions requires energy.

Step 2: Compare absorbed and released energy Forming weaker A–B attractions releases less energy than is absorbed in overcoming A–A and B–B attractions. The net mixing process absorbs heat; if heat is not supplied from outside to hold the temperature fixed, the mixture cools.

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

Quick Tip to Solve: For this expanding, positively deviating mixture, link weaker A–B attractions to heat absorption and 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:

- Expansion on mixing in this question is associated with weaker unlike intermolecular attractions and positive deviation from Raoult's law.
- Disrupting the hydrogen-bonded association of an alcohol by adding another liquid can weaken the average intermolecular attraction in the solution.

Step 1: Identify the required type of mixture The volume rises from $20\,\text{mL}$ to $20.2\,\text{mL}$, indicating expansion. An appropriate example is a pair of liquids whose mixing weakens the attractions compared with those in the pure components.

Step 2: Explain the chosen example In an ethanol–acetone mixture, acetone molecules disrupt some hydrogen bonds between ethanol molecules. The resulting interactions are weaker overall than the original attractions, so the mixture shows positive deviation from Raoult's law. Ethanol is C_2H_5OH and acetone is CH_3COCH_3.

Step 3: Conclusion A suitable example is a mixture of ethanol and acetone, which shows positive deviation from Raoult's law.

Quick Tip to Solve: Remember ethanol with acetone as a positive-deviation pair: added acetone disrupts ethanol's hydrogen-bonded association.

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 depression in freezing point.
- 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 on the snow Sprinkled salt dissolves in the thin film of liquid water on the snow. Sodium chloride dissociates into Na^+ and Cl^-, increasing the number of dissolved particles and lowering the freezing point below $0\,^\circ\text{C}$.

Step 2: Compare the road temperature with the new freezing point When the surroundings are warmer than the freezing point of the resulting salt solution, ice melts into this solution. Water can then remain liquid at temperatures at which pure water would freeze, helping remove the snow from the road.

Step 3: Conclusion Salt helps clear snow by lowering water's freezing point, so snow melts to form

Quick Tip to Solve: In road-deicing questions, name freezing-point depression and explain that dissolved salt permits liquid water below $0\,^\circ\text{C}$.

brine at suitable sub-zero temperatures.

Quick Tip to Solve: In road-deicing questions, name freezing-point depression and explain that dissolved salt permits liquid water below $0\,^{\circ}\text{C}$.

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 flow of water through a semipermeable membrane from a solution of lower solute concentration to one of higher solute concentration.
- A 0.9% (mass/vol) NaCl solution is approximately isotonic with red blood cells; a more dilute salt solution is hypotonic to them.

Step 1: Compare the solution with isotonic saline The given 0.5% (mass/vol) NaCl solution is more dilute than 0.9% saline. Its osmotic pressure is lower than that of the fluid inside the red blood cells, so it is a hypotonic medium.

Step 2: Determine the direction of water flow Water enters the cells across their semipermeable membranes by endosmosis. The inflow increases cell volume. Because red blood cells have no rigid cell wall, excessive swelling can rupture their membranes, releasing haemoglobin; this is haemolysis.

Step 3: Conclusion Red blood cells swell and may burst (haemolyse) in 0.5% NaCl solution because water enters them by osmosis from the hypotonic medium.

Quick Tip to Solve: Compare the salt concentration with 0.9%: below it, water enters red blood cells; above it, water leaves them.

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

Solution:

Concept:

- Reverse osmosis forces solvent from a solution through a semipermeable membrane by applying pressure greater than its osmotic pressure on the solution side.
- The membrane allows water to pass while retaining dissolved salts, so the collected water has a much lower salt content.

Step 1: Apply the process to seawater Seawater contains dissolved salts. It is placed on one side of a suitable semipermeable membrane and subjected to pressure greater than the osmotic pressure difference across that membrane.

Step 2: Separate water from the dissolved salts The imposed pressure drives water through the membrane towards the fresh-water side, opposite to the direction of ordinary osmosis. The salts remain mainly on the seawater side, and the water passing through is collected separately.

Quick Tip to Solve: For a reverse-osmosis application, state desalination and remember that pressure above the osmotic pressure is applied to the saline side.

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

Quick Tip to Solve: For a reverse-osmosis application, state desalination and remember that pressure above the osmotic pressure is applied to the saline side.

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

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

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

[3 marks]

Solution:

Concept:

- The experimental rate law is $r = k[A]^m[B]^n$, where r is the initial rate, k is the rate constant, and m, 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 $m + n$; it is determined experimentally, not from the coefficients in the reaction equation.

Step 1: Compare experiments 1 and 2 to determine the order in A In these experiments, $[B] = 0.1\,\text{mol L}^{-1}$ is constant. Doubling $[A]$ from 0.1 to $0.2\,\text{mol L}^{-1}$ doubles the rate from 0.05 to $0.10\,\text{mol L}^{-1}\text{s}^{-1}$. Dividing their rate laws cancels k and the B factor:

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

Thus $2 = 2^m$, giving $m = 1$.

Step 2: Compare experiments 1 and 3 to determine the order in B Here $[A] = 0.1\,\text{mol L}^{-1}$ is constant. Doubling $[B]$ from 0.1 to $0.2\,\text{mol L}^{-1}$ leaves the initial rate unchanged at $0.05\,\text{mol L}^{-1}\text{s}^{-1}$. Therefore,

$$\frac{r_3}{r_1} = \left(\frac{[B]_3}{[B]_1}\right)^n, \qquad 1 = 2^n,$$

so $n = 0$. B is a reactant, but its concentration does not affect the measured rate under these conditions.

Step 3: Add the individual orders Substituting the experimental exponents gives $r = k[A]^1[B]^0 = k[A]$. The sum of the exponents is $1 + 0 = 1$, consistent with the observed proportionality between rate and the concentration of A.

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 rows 1 and 2 for A and rows 1 and 3 for B: doubling concentration with no rate change indicates zero order.

24. (a) What is meant by crystal field splitting energy? For a d^4 ion, write the configuration if (i) $\Delta_o < P$, and (ii) $\Delta_o > P$.

(b) Explain why in tetrahedral coordination entities, low spin configurations are rarely observed.

[3 marks]

Solution:

Concept:

- Crystal field splitting energy is the energy separation between the sets of metal d orbitals formed when ligands remove their degeneracy. In an octahedral field, $\Delta_o = E(e_g) - E(t_{2g})$.
- Electrons occupy orbitals according to the relative sizes of the splitting energy and pairing energy P, the energy required to pair electrons in an orbital.
- For comparable metal ions and ligands, tetrahedral splitting is much smaller than octahedral splitting: $\Delta_t \approx \frac{4}{9}\Delta_o$.

Step 1: Define the octahedral splitting In a free metal ion, the five d orbitals have the same energy. In an octahedral ligand field, the three t_{2g} orbitals lie at lower energy and the two e_g orbitals lie at higher energy. The energy gap between these sets is the octahedral crystal field splitting energy, Δ_o.

Step 2: Place four electrons when the splitting is smaller than pairing energy For part (a)(i), $\Delta_o < P$. The first three electrons occupy the three lower t_{2g} orbitals singly. Putting the fourth electron into an upper e_g orbital costs less energy than pairing it in a lower orbital. Hence the high-spin configuration is $t_{2g}^3 e_g^1$, with four unpaired electrons.

Step 3: Place four electrons when the splitting is greater than pairing energy For part (a)(ii), $\Delta_o > P$. After the first three electrons singly occupy the t_{2g} orbitals, the fourth pairs in one of them because pairing costs less energy than promotion to e_g. The low-spin configuration is $t_{2g}^4 e_g^0$, with two unpaired electrons.

Step 4: Compare tetrahedral splitting with pairing energy For part (b), tetrahedral complexes have only four ligands, and none approaches directly along the d-orbital axes. Their splitting Δ_t is consequently small and is usually less than P. Electrons therefore occupy the higher-energy orbitals singly before pairing in the lower set. The energy condition needed for a low-spin arrangement is rarely satisfied.

Step 5: Conclusion Crystal field splitting energy is the gap between the split d-orbital sets. For a d^4 octahedral ion, the configurations are $t_{2g}^3 e_g^1$ if $\Delta_o < P$, and $t_{2g}^4 e_g^0$ if $\Delta_o > P$. Tetrahedral entities are generally high spin because $\Delta_t < P$.

Quick Tip to Solve: For the fourth d electron, compare promotion with pairing: a small splitting favours promotion; a large splitting favours pairing.

25(a). Account for the following:

The C – Cl bond length in chlorobenzene is shorter than that in methyl chloride. [1 mark]

Solution:

Concept:

- Resonance delocalisation of a chlorine lone pair into an aromatic ring gives the carbon–chlorine bond partial double-bond character.
- A bond with partial double-bond character is shorter than an otherwise comparable single bond; an sp^2 carbon also holds bonding electrons closer than an sp^3 carbon.

Step 1: Examine the bond in chlorobenzene In chlorobenzene, C_6H_5Cl, a lone pair on chlorine overlaps with the conjugated ring orbitals. Resonance therefore gives the carbon–chlorine bond partial double-bond character. Chlorine is also bonded to an sp^2-hybridised carbon.

Step 2: Compare the bond in methyl chloride In methyl chloride, CH_3Cl, chlorine is attached to an sp^3-hybridised carbon, and no aromatic conjugated system is available for this delocalisation. Its carbon–chlorine bond remains an ordinary single bond.

Step 3: Conclusion The carbon–chlorine bond in chlorobenzene is shorter primarily because resonance gives it partial double-bond character; the sp^2 carbon further favours a shorter bond.

Quick Tip to Solve: When comparing an aryl halide with an alkyl halide, first check whether halogen lone-pair resonance adds partial double-bond character.

25(b). Account for the following:

Grignard reagents should be prepared under anhydrous conditions. [1 mark]

Solution:

Concept:

- A Grignard reagent, RMgX, has a strongly polar carbon–magnesium bond, making the carbon end strongly basic and reactive towards proton donors.
- Water supplies a proton and destroys the reagent by converting its organic group into a hydrocarbon, RH.

Step 1: Identify the reaction with moisture Even traces of water react with the Grignard reagent. The carbon bonded to magnesium acquires a proton from water, giving:

$$\mathrm{RMgX} + \mathrm{H_2O} \longrightarrow \mathrm{RH} + \mathrm{Mg(OH)X}.$$

Here R denotes the organic group and X the halogen.

Step 2: Relate the reaction to the preparation conditions Moisture would consume the reagent as it forms and reduce its yield. Preparation therefore uses dry ether, dry apparatus and exclusion of moisture so that the newly formed RMgX survives for its intended reaction.

Step 3: Conclusion Grignard reagents must be prepared under anhydrous conditions because water decomposes them to hydrocarbons.

Quick Tip to Solve: To predict the effect of water on a Grignard reagent, replace its carbon–magnesium linkage by a carbon–hydrogen bond.

25(c). Account for the following:

In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation. [1 mark]

Solution:

Concept:

- An S_N1 substitution proceeds through a carbocation formed by loss of the leaving group in the slow ionisation step.
- The carbocation centre is sp^2-hybridised and trigonal planar, so a nucleophile can attack either face of its plane.

Step 1: Form the planar intermediate When the halide ion leaves the chiral carbon of an optically active alkyl halide, a planar carbocation forms. The original tetrahedral arrangement at this reacting centre is lost, and the empty p orbital is accessible from both sides.

Step 2: Allow nucleophilic attack from both faces Attack from one face gives a product with retention of configuration, while attack from the opposite face gives inversion. Both enantiomeric products therefore form, reducing optical activity. Equal attack gives a racemic mixture; in practice, ion-pair effects can favour inversion and make racemisation incomplete.

Step 3: Conclusion S_N1 reactions are accompanied by racemisation because nucleophilic attack on the planar carbocation can occur from either face, producing both configurations.

Quick Tip to Solve: Link racemisation to the shape of the intermediate: a planar carbocation permits both retention and inversion.

26(a). Arrange the following compounds in the increasing order of their acidic strength:

3,5-dinitrophenol, 4-methylphenol, phenol, 2,4,6-trinitrophenol [1 mark]

Solution:

Concept:

- A phenol is more acidic when its conjugate base, the phenoxide ion, is more stable after loss of H^+.
- Electron-withdrawing nitro groups stabilise phenoxide, whereas an electron-donating methyl group reduces its stability.

Step 1: Compare methylphenol with phenol The methyl group in 4-methylphenol donates electron density through its positive inductive effect and hyperconjugation. It destabilises the negatively charged conjugate base relative to phenoxide, so 4-methylphenol is less acidic than phenol.

Step 2: Compare the nitro-substituted phenols The two meta nitro groups in 3,5-dinitrophenol withdraw electron density mainly through their negative inductive effect, increasing acidity above phenol. In 2,4,6-trinitrophenol, three nitro groups exert strong electron withdrawal, with the ortho and para groups also stabilising the conjugate base by resonance. It is therefore the strongest acid in this set.

Quick Tip to Solve: First place the methyl-substituted phenol below phenol; then place the nitro-substituted phenols above it, with picric acid strongest.

Step 3: Conclusion The increasing order of acidic strength is

$$\text{4-methylphenol} < \text{phenol} < \text{3,5-dinitrophenol} < \text{2,4,6-trinitrophenol.}$$

Quick Tip to Solve: First place the methyl-substituted phenol below phenol; then place the nitro-substituted phenols above it, with picric acid strongest.

26(b). What happens when: (write equations)

(i) Phenol is distilled with Zn dust?

(ii) Anisole is treated with HBr? [2 marks]

Solution:

Concept:

- Heated zinc dust removes oxygen from phenol, reducing it to benzene; zinc is oxidised to zinc oxide.
- Hydrogen bromide cleaves an aryl alkyl ether at its alkyl–oxygen bond after protonation of the ether oxygen.

Step 1: Distil phenol with zinc dust Phenol undergoes deoxygenation on heating with zinc dust. The oxygen atom is accepted by zinc, while the aromatic ring is retained. The balanced equation is

$$C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO.$$

Thus the organic product is benzene and the inorganic product is zinc oxide.

Step 2: Cleave anisole with hydrogen bromide Anisole is methyl phenyl ether, $C_6H_5OCH_3$. Its oxygen is first protonated; the bromide ion then attacks the methyl carbon by an S_N2 process. The methyl–oxygen bond breaks, giving

$$C_6H_5OCH_3 + HBr \longrightarrow C_6H_5OH + CH_3Br.$$

The aryl–oxygen bond has partial double-bond character through resonance and does not undergo this substitution. Consequently, bromobenzene and methanol are not the products.

Step 3: Conclusion (i) Phenol with zinc dust gives benzene and zinc oxide. (ii) Anisole with HBr gives phenol and methyl bromide (bromomethane).

Quick Tip to Solve: In anisole cleavage, attach bromine to the methyl group and retain the phenyl–oxygen bond to obtain phenol.

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27. An organic compound 'A' (molecular formula C_8H_8O) gives 2,4-DNP test. It does not give Tollen's test, but gives a yellow precipitate 'B' with NaOH and I_2. On drastic oxidation, it gives a carboxylic acid 'C' with formula $C_7H_6O_2$. Identify 'A', 'B', 'C' and write the reactions involved. [3 marks]

Solution:

Concept:

- Aldehydes and ketones give a 2,4-dinitrophenylhydrazine (2,4-DNP) test by forming a hydrazone derivative of their carbonyl group.
- A negative Tollens' test suggests a ketone. A positive iodoform test identifies a methyl ketone, whose methyl group is directly bonded to the carbonyl carbon, and yields yellow CHI_3.
- Vigorous oxidation can cleave a ketone next to its carbonyl group; the carbonyl-containing aromatic fragment gives a carboxylic acid.

Step 1: Identify the carbonyl compound The positive 2,4-DNP test shows that A contains a carbonyl group. Since it does not reduce Tollens' reagent, A is a ketone rather than an aldehyde. The yellow precipitate with iodine and sodium hydroxide shows that it contains a methyl ketone group. The compound satisfying these tests and the formula C_8H_8O is acetophenone, $C_6H_5COCH_3$. Its aromatic fragment also accounts for formation of an acid containing seven carbon atoms on oxidation.

Step 2: Write the carbonyl-test reaction Let R denote the 2,4-dinitrophenyl group, $C_6H_3(NO_2)_2$. Reaction with 2,4-DNP forms the corresponding hydrazone with elimination of water:

$$C_6H_5COCH_3 + H_2NNHR \longrightarrow C_6H_5C(CH_3){=}NNHR + H_2O.$$

The hydrazone is the precipitated derivative in this test. With Tollens' reagent, acetophenone gives no silver mirror.

Step 3: Write the iodoform reaction Iodine in aqueous sodium hydroxide converts the methyl ketone into sodium benzoate and yellow iodoform. The balanced equation is

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow + 3\,NaI + 3\,H_2O.$$

Thus the isolated yellow precipitate B is iodoform, also called triiodomethane, rather than the dissolved sodium benzoate.

Step 4: Write the drastic oxidation reaction Hot, strong oxidising conditions, such as acidified permanganate, cleave the ketone side chain. The aromatic acid is benzoic acid, whose formula $C_7H_6O_2$ agrees with C. The overall oxidation may be represented as

$$C_6H_5COCH_3 + 4\,[O] \xrightarrow{\text{vigorous oxidation}} C_6H_5COOH + CO_2 + H_2O.$$

The additional carbon from the methyl group is completely oxidised to carbon dioxide under these drastic conditions.

Step 5: Conclusion A is acetophenone, $C_6H_5COCH_3$; B is yellow iodoform, CHI_3; and C is benzoic acid, C_6H_5COOH.

Quick Tip to Solve: Combine the negative Tollens' test with the positive iodoform test to identify a methyl ketone; then use the molecular formula to identify its other group.

28(a). Name the type of linkage responsible for the formation of proteins from α-amino acids.

[1 mark]

Solution:

Concept:

- Each α-amino acid contains an amino group and a carboxyl group attached to the same α-carbon.
- A condensation reaction between a carboxyl group and an amino group forms an amide bond with elimination of water.

Step 1: Identify the groups that react The carboxyl group, $-\mathrm{COOH}$, of one amino acid reacts with the amino group, $-\mathrm{NH_2}$, of another. The carboxyl group loses OH and the amino group loses H; together these form a water molecule.

Step 2: Identify the bond in the chain The carbonyl carbon of the first amino acid becomes bonded to the nitrogen of the second, producing the $-\mathrm{CO}-\mathrm{NH}-$ unit. Repetition of this condensation joins many amino acid residues into a polypeptide chain, which forms the backbone of a protein.

Step 3: Conclusion The linkage is a **peptide linkage** (peptide bond), $-\mathrm{CO}-\mathrm{NH}-$, an amide linkage.

Quick Tip to Solve: Look for the carbonyl carbon bonded directly to nitrogen: the repeating $-\mathrm{CO}-\mathrm{NH}-$ unit identifies a peptide linkage.

28(b). Write any two differences between DNA and RNA. [2 marks]

Solution:

Concept:

- DNA and RNA are nucleic acids made from nucleotides. A nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- Comparing the sugar and the set of nitrogenous bases gives two direct chemical differences between DNA and RNA.

Step 1: Compare the pentose sugars **DNA contains 2-deoxyribose, whereas RNA contains ribose.** At the $2'$-carbon of the sugar, DNA has a hydrogen atom where RNA has a hydroxyl group. Thus deoxyribose has one fewer oxygen atom than ribose. This sugar difference is reflected in the names deoxyribonucleic acid (DNA) and ribonucleic acid (RNA).

Step 2: Compare the nitrogenous bases **DNA contains thymine, whereas RNA contains uracil in its place.** DNA's four main bases are adenine, guanine, cytosine and thymine; RNA's four main bases are adenine, guanine, cytosine and uracil. Adenine, guanine and cytosine are therefore common to both, so they do not constitute a difference.

Step 3: Conclusion The two differences are: (i) DNA has 2-deoxyribose sugar, while RNA has ribose sugar; (ii) DNA has thymine, while RNA has uracil.

Quick Tip to Solve: Remember the paired contrasts: DNA = deoxyribose and thymine; RNA = ribose and uracil. State both sides of each comparison.

Section D (8 marks)

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

29(a). 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:

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

[2 marks]

Solution:

Concept:

- Mild oxidation changes an aldehyde group, $-\text{CHO}$, into a carboxylic acid group, $-\text{COOH}$, without changing the carbon skeleton.
- Prolonged heating with hydriodic acid reduces the oxygen-containing groups of glucose; the hydrocarbon formed reveals its carbon skeleton.

Step 1: Establish the aldehyde group Bromine water oxidises glucose to gluconic acid. In the open-chain formula, the terminal $-\text{CHO}$ group changes to $-\text{COOH}$, while the primary alcohol group remains unchanged:

$$\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH} + \text{Br}_2 + \text{H}_2\text{O} \longrightarrow \text{COOH}-(\text{CHOH})_4-\text{CH}_2\text{OH} + 2\,\text{HBr}.$$

This mild oxidation supports the presence of an aldehydic group in glucose rather than a ketonic group.

Step 2: Establish the unbranched carbon chain On prolonged heating with excess HI, glucose gives normal hexane:

$$\text{C}_6\text{H}_{12}\text{O}_6 + 14\,\text{HI} \xrightarrow{\text{heat}} \text{CH}_3-(\text{CH}_2)_4-\text{CH}_3 + 6\,\text{H}_2\text{O} + 7\,\text{I}_2.$$

The six carbon atoms are retained in one unbranched hydrocarbon chain. Formation of n-hexane therefore shows that the six carbon atoms of glucose are connected in a straight chain.

Step 3: Conclusion Oxidation with bromine water to gluconic acid shows the aldehydic group; reduction with HI to n-hexane establishes the straight six-carbon chain.

Quick Tip to Solve: Pair bromine water with gluconic acid for the aldehyde test, and HI with normal hexane for the carbon-chain test.

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

Solution:

Concept:

- Cyclisation of a monosaccharide forms a new stereocentre at the carbon that originally belonged to its carbonyl group.
- This centre is called the anomeric carbon; it is C-1 in glucose, an aldose.

Step 1: Identify the differing centre Compare two cyclic forms of the same sugar. If their configurations differ only at the anomeric carbon while all other stereocentres are unchanged, they form a pair of anomers.

Step 2: Relate the definition to glucose In α-D-glucopyranose and β-D-glucopyranose, only the configuration of C-1 differs. The orientation of the hydroxyl group at C-1 distinguishes these two cyclic forms.

Step 3: Conclusion Anomers are cyclic stereoisomers of a sugar that differ in configuration only at the anomeric carbon.

Quick Tip to Solve: For glucose, check C-1 alone: a change only at this carbon distinguishes the alpha and beta anomers.

OR

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

Solution:

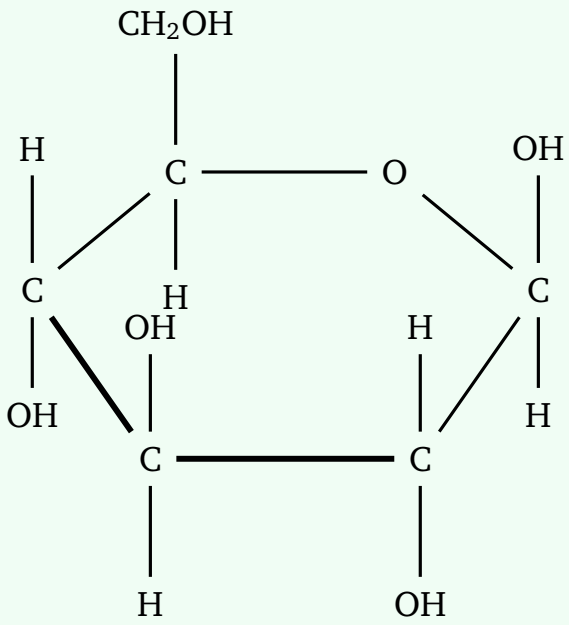
Concept:

- Glucopyranose has a six-membered ring containing five carbon atoms and one oxygen atom, formed by reaction of the C-1 aldehyde with the C-5 hydroxyl group.
- In a standard Haworth projection of a D-sugar, the C-5 CH_2OH group points up; the beta anomer has its C-1 OH on the same side.

Step 1: Draw the pyranose ring Place the ring oxygen at the upper right and number clockwise from the rightmost carbon, C-1, to C-5 at the upper left. The external CH_2OH group is attached to C-5.

Step 2: Set the hydroxyl orientations Draw the C-1 hydroxyl up for the beta anomer. The hydroxyl groups at C-2, C-3 and C-4 point down, up and down, respectively. Each hydrogen points opposite to the other substituent on its carbon.

Quick Tip to Solve: For beta-D-glucopyranose, place both the C-1 hydroxyl and the C-5 hydroxymethyl group up, then use down-up-down at C-2 to C-4.



Haworth projection of β-D-glucopyranose

Step 3: Conclusion The Haworth structure shown is β-D-glucopyranose: its anomeric OH and CH_2OH groups are both above the ring.

Quick Tip to Solve: For beta-D-glucopyranose, place both the C-1 hydroxyl and the C-5 hydroxymethyl group up, then use down-up-down at C-2 to C-4.

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

Solution:

Concept:

- Hydrolysis of sucrose produces an equimolar mixture of D-glucose and D-fructose, called invert sugar.
- Optical inversion means that the sign of rotation changes from positive to negative during this hydrolysis.

Step 1: Hydrolyse sucrose Sucrose is dextrorotatory. Dilute acid or the enzyme invertase hydrolyses its glycosidic linkage:

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

Step 2: Explain the change in rotation D-glucose rotates plane-polarised light to the right, while D-fructose rotates it more strongly to the left. The equimolar product mixture is therefore laevorotatory, whereas the original sucrose solution was dextrorotatory.

Step 3: Conclusion The reversal in optical rotation is called inversion, and the hydrolysed glucose-fructose mixture is called invert sugar. Strictly, the name refers to this mixture formed from sucrose.

Quick Tip to Solve: Remember that fructose's negative rotation outweighs glucose's positive rotation, so sucrose hydrolysis changes the sign of rotation.

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

Answer the following questions:

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

Solution:

Concept:

- Excess aqueous $AgNO_3$ precipitates ionisable chloride ions outside the coordination sphere as AgCl; coordinated chlorido ligands remain within the complex ion.
- Werner's secondary valency is the coordination number: the number of donor atoms directly bonded to the central metal ion.

Step 1: Locate the chloride ions One mole of the compound gives one mole of AgCl, so exactly one of its three chloride ions is present outside the coordination sphere:

$$Ag^+ + Cl^- \longrightarrow AgCl\downarrow.$$

The remaining two chlorides are bonded directly to chromium. The four water molecules also act as monodentate ligands within the coordination sphere.

Step 2: Write the complex and count donor atoms Chromium has oxidation state $+3$. Four neutral water ligands and two chlorido ligands give the complex ion a charge of $+1$, balanced by one external chloride ion:

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

Four oxygen donor atoms from water and two chloride donor atoms are attached to chromium. Thus the coordination number is $4 + 2 = 6$, corresponding to an octahedral coordination sphere. The precipitation data do not distinguish the possible geometrical isomers.

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

Quick Tip to Solve: Count precipitated AgCl to find chloride outside the brackets; then count all donor atoms inside the brackets for secondary valency.

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

Solution:

Concept:

- A double salt dissociates into all its constituent simple ions when dissolved in water.
- A coordination compound retains its complex entity in solution; ligands remain attached to the central metal ion.

Step 1: Describe a double salt in water A double salt loses its individual identity in solution. For example, Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6\,H_2O$, gives NH_4^+, Fe^{2+} and SO_4^{2-} ions, which show their usual ionic tests.

Step 2: Describe a complex in water A complex retains its coordination sphere. For example, $K_4[Fe(CN)_6]$ gives K^+ and $[Fe(CN)_6]^{4-}$ ions; it does not simply furnish free Fe^{2+} and CN^- ions.

Step 3: Conclusion A double salt dissociates completely into its constituent simple ions in water, whereas a complex retains its complex entity in solution.

Quick Tip to Solve: Ask whether the metal-ligand unit survives dissolution: it survives for a complex, but a double salt gives simple ions.

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

Solution:

Concept:

- Electrical conduction in an aqueous solution depends on mobile ions. For comparable concentrations, the expected order here follows the number of ions released per formula unit.
- Chloride ligands inside the coordination sphere remain bound; chloride counterions outside the brackets dissociate in water.

Step 1: Count the ions supplied by each compound The neutral complex $[Cr(NH_3)_3Cl_3]$ has no counterions and gives no ions by ordinary dissociation. The other compounds dissociate as follows:

$$[Cr(NH_3)_5Cl]Cl_2 \longrightarrow [Cr(NH_3)_5Cl]^{2+} + 2\,Cl^-$$

$$[Cr(NH_3)_6]Cl_3 \longrightarrow [Cr(NH_3)_6]^{3+} + 3\,Cl^-$$

Their formula units therefore yield three and four ions, respectively.

Step 2: Compare the mobile charge carriers Under the same solution conditions, the neutral complex conducts least. The salt producing three ions conducts less than the salt producing four ions. Coordinated chloride is not counted as a separate mobile chloride ion.

Step 3: Conclusion The increasing conductivity order is

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

Quick Tip to Solve: Count the complex ion once, then add only the chloride ions outside the square brackets.

OR

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

[1 mark]

Solution:

Concept:

- In Werner's theory, primary valence corresponds to the oxidation state of the central metal, while secondary valence corresponds to its coordination number.
- The coordination number counts the donor atoms directly bonded to the metal in its coordination sphere.

Step 1: Compare their ionisation behaviour Primary valences are normally ionisable and are satisfied by negative ions. Secondary valences are non-ionisable and are satisfied by negative ions or neutral molecules that act as ligands.

Step 2: Compare their spatial character Primary valences are non-directional, whereas secondary valences are directed towards definite positions in space. The arrangement of secondary valences determines the geometry of the coordination entity, such as an octahedral arrangement for six suitably placed donor atoms.

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

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

Section E (15 marks)

31(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:

- A galvanic cell operates spontaneously: its cathode undergoes reduction and its anode undergoes oxidation.
- The half-cell with the higher standard reduction potential has the greater tendency to accept electrons. Using reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

Step 1: Compare the standard reduction potentials The given potentials satisfy $-0.44\,\text{V} > -0.74\,\text{V}$. Thus the Fe^{2+}/Fe half-cell has the higher reduction potential and a greater tendency to undergo reduction than the Cr^{3+}/Cr half-cell. A negative reduction potential does not prevent reduction when it is paired with an even more negative one.

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

Step 2: Write the electrode reactions and check spontaneity Reaction (II) remains the cathodic reduction:

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

Reaction (I) is reversed to give the anodic oxidation:

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

The standard cell potential is

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

Its positive sign confirms that these directions give spontaneous galvanic-cell operation under standard conditions. Balancing electrons multiplies reaction coefficients, but does not multiply electrode potentials.

Step 3: Conclusion Reaction (II) remains a reduction reaction; reaction (I) is reversed to become oxidation because the iron half-cell has the higher standard reduction potential.

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

31(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:

- Cell notation places oxidation at the left anode and reduction at the right cathode. A single vertical line is a phase boundary and a double line denotes the salt bridge.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solids have unit activity and are omitted from Q; for these dilute solutions, ionic activities are approximated by concentrations relative to 1 M.

Step 1: Identify the electrode reactions Magnesium loses electrons at the anode and silver ions gain them at the cathode:

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

Adding these reactions gives the printed overall reaction. Hence $n = 2$, despite the presence of only one magnesium atom.

Step 2: Represent the cell Write the magnesium electrode on the left and the silver electrode on the

Quick Tip to Solve: Use two electrons and square the silver-ion concentration; omit both solid metals from the reaction quotient.

right, including the given ionic concentrations:

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

The salt bridge completes the ionic circuit between the two half-cells.

Step 3: Form the reaction quotient and apply Nernst's equation For the reaction as written, the product ion is in the numerator and the silver-ion concentration is squared because its coefficient is two:

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

Thus $\log Q = 5 \log 10 = 5$. Using the usual 298 K form of the equation,

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

The correction is subtracted because $Q > 1$; the low silver-ion concentration reduces the cell potential relative to its standard value.

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

Quick Tip to Solve: Use two electrons and square the silver-ion concentration; omit both solid metals from the reaction quotient.

OR

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

Solution:

Concept:

- At infinite dilution, interionic interactions become negligible and each ion contributes independently to the limiting molar conductivity.
- Kohlrausch's law is $\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$, where ν_+ and ν_- are the numbers of cations and anions per formula unit, and λ_+^∞, λ_-^∞ are their limiting ionic molar conductivities.

Step 1: State the law of independent migration of ions 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. Thus the limiting molar conductivity is the sum of the ionic contributions, with each contribution multiplied by its stoichiometric number.

Step 2: Give two applications First, the law calculates the limiting molar conductivity of weak electrolytes from those of suitable strong electrolytes. For example,

$$\begin{aligned} \Lambda_m^\infty(\mathrm{CH_3COOH}) = \Lambda_m^\infty(\mathrm{CH_3COONa}) \\ + \Lambda_m^\infty(\mathrm{HCl}) - \Lambda_m^\infty(\mathrm{NaCl}). \end{aligned}$$

Quick Tip to Solve: Combine strong electrolytes so the unwanted ions cancel, then use the remaining limiting conductivity in $\alpha = \Lambda_m/\Lambda_m^\infty$.

The sodium and chloride ion contributions cancel. Second, the resulting limiting value gives the degree of dissociation of a weak electrolyte at a specified concentration: $\alpha = \Lambda_m/\Lambda_m^\infty$, where Λ_m is its measured molar conductivity at that concentration.

Step 3: Conclusion Kohlrausch's law states that ionic contributions to limiting molar conductivity are independent and additive. Two applications are finding the limiting molar conductivity and the degree of dissociation of weak electrolytes.

Quick Tip to Solve: Combine strong electrolytes so the unwanted ions cancel, then use the remaining limiting conductivity in $\alpha = \Lambda_m/\Lambda_m^\infty$.

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

Solution:

Concept:

- Kohlrausch's law gives the limiting molar conductivity as the sum of the limiting ionic conductivities, independent of the counterions present.
- For a weak electrolyte, $\alpha = \Lambda_m/\Lambda_m^\infty$, where α is its degree of dissociation, Λ_m is the molar conductivity at the specified concentration and Λ_m^∞ is its limiting value.

Step 1: Combine the limiting conductivities The ions required for ammonium hydroxide are NH_4^+ and OH^-. Write the ionic sums:

$$\Lambda_m^\infty(NH_4Cl) = \lambda^\infty(NH_4^+) + \lambda^\infty(Cl^-),$$
$$\Lambda_m^\infty(NaOH) = \lambda^\infty(Na^+) + \lambda^\infty(OH^-),$$
$$\Lambda_m^\infty(NaCl) = \lambda^\infty(Na^+) + \lambda^\infty(Cl^-).$$

Add the first two expressions and subtract the third. The unwanted Na^+ and Cl^- contributions cancel, leaving those of NH_4^+ and OH^-.

Step 2: Calculate the limiting value Therefore,

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

Step 3: Find the fraction dissociated At 1×10^{-2} mol L^{-1}, the measured molar conductivity is 9.33 S cm^2 mol^{-1}. The weak electrolyte produces only a fraction of the ions corresponding to complete dissociation, so

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

The conductivity units cancel. The percentage dissociation is $100\alpha = 3.915\%$. The concentration

Quick Tip to Solve: Add NH_4Cl and NaOH, subtract NaCl, and divide the measured conductivity by the resulting limiting value.

identifies the solution for which this ratio applies; no additional concentration factor is needed because the measured quantity is already molar conductivity.

Step 4: Conclusion The degree of dissociation of NH_4OH is $\boxed{\alpha = 0.0392}$, or approximately $\boxed{3.92\%}$, at the given concentration.

Quick Tip to Solve: Add NH_4Cl and NaOH, subtract NaCl, and divide the measured conductivity by the resulting limiting value.

32(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, benzenesulphonyl chloride ($C_6H_5SO_2Cl$), distinguishes primary, secondary and tertiary amines by their reaction and the product's solubility in alkali.
- A primary amine gives a sulphonamide containing an acidic N–H bond; its salt forms in NaOH and is soluble.

Step 1: Identify the type of amine Since X reacts with the Hinsberg reagent and the product dissolves in NaOH, X is a primary amine. A secondary amine gives a sulphonamide without an N–H bond, which is insoluble in alkali; a tertiary amine does not give this sulphonamide.

Step 2: Apply the molecular formula For the formula C_2H_7N, the primary amine has an ethyl group attached to NH_2. Its formula is $CH_3CH_2NH_2$. The other amine isomer, $(CH_3)_2NH$, is secondary and would not give the observed alkali-soluble product.

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

Quick Tip to Solve: An alkali-soluble Hinsberg product identifies a primary amine; then use the molecular formula to identify its alkyl group.

32(a)(ii). Arrange the following in the increasing order of their pK_b value in aqueous phase:
$C_6H_5NH_2$, $(CH_3)_2NH$, NH_3, CH_3NH_2, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- $pK_b = -\log K_b$: a stronger base has a larger base dissociation constant K_b, and hence a smaller pK_b.
- Basic strength in water depends on the availability of nitrogen's lone pair and the hydration of the protonated amine.

Step 1: Compare basic strengths in water For methylamines in aqueous solution, the combined

Quick Tip to Solve: For aqueous methylamines use secondary, primary, tertiary in decreasing basicity, and remember that stronger bases have smaller pK_b.

effects of electron donation and hydration give the order $(CH_3)_2NH$ greater than CH_3NH_2 greater than $(CH_3)_3N$ in basic strength. All three are stronger bases than NH_3. Aniline, $C_6H_5NH_2$, is the weakest here because nitrogen's lone pair is delocalised into the benzene ring and is less available for protonation.

Step 2: Reverse the order for the logarithmic scale Increasing pK_b means decreasing basic strength. Therefore place the strongest base, dimethylamine, first and the weakest base, aniline, last. The tertiary methylamine does not come first in water because its conjugate acid is less effectively hydrated than those of the primary and secondary methylamines.

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

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

Quick Tip to Solve: For aqueous methylamines use secondary, primary, tertiary in decreasing basicity, and remember that stronger bases have smaller pK_b.

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

Solution:

Concept:

- Aniline is a base and is protonated in the strongly acidic mixture used for nitration.
- The amino group $-NH_2$ is ortho/para directing, whereas the protonated group $-NH_3{}^+$ is electron withdrawing and meta directing.

Step 1: Account for protonation in the nitrating mixture The mixture of concentrated nitric and sulphuric acids converts a considerable proportion of aniline into anilinium ions:

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

After protonation, nitrogen's lone pair is no longer available for donation into the aromatic ring.

Step 2: Explain the positions of substitution The positively charged $-NH_3{}^+$ group deactivates the ring and directs incoming electrophiles mainly to the meta position. Consequently, nitration of anilinium ions produces a considerable amount of the meta product. The unprotonated aniline present is ortho/para directing and gives the ortho and para products.

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

Quick Tip to Solve: Before assigning a directing effect, check the medium: strong acid changes aniline's $-NH_2$ group into meta-directing $-NH_3{}^+$.

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

(I) p-bromoaniline

(II) phenol [2 marks]

Solution:

Concept:

- The strongly activating amino group of aniline is protected by acetylation before controlled monobromination. The acetamido group remains ortho/para directing.
- Diazotisation changes an aromatic primary amino group into a diazonium group; warming its aqueous solution replaces this group by a hydroxyl group.

Step 1: (I) Protect the amino group and brominate Treat aniline with acetic anhydride to form acetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

Brominate acetanilide using Br_2 in glacial acetic acid. The para isomer is the major product because substitution at the para position is less sterically hindered:

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

Hydrolyse the separated para product by heating with aqueous acid, then neutralise to regenerate the free amino group. The net hydrolysis is

$$\text{p-}BrC_6H_4NHCOCH_3 + H_2O \longrightarrow \text{p-}BrC_6H_4NH_2 + CH_3COOH.$$

Direct treatment of aniline with bromine water would instead give 2,4,6-tribromoaniline.

Step 2: (II) Diazotise and hydrolyse Treat aniline with $NaNO_2$ and dilute HCl at 273–278 K to form benzenediazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2\,H_2O.$$

Warm the diazonium salt with water. Nitrogen is evolved and phenol is formed:

$$C_6H_5N_2Cl + H_2O \xrightarrow{\text{warm}} C_6H_5OH + N_2 + HCl.$$

Step 3: Conclusion Obtain p-bromoaniline by acetylation, para bromination and hydrolysis; obtain phenol by cold diazotisation followed by warming with water.

Quick Tip to Solve: Protect $-NH_2$ before ring monobromination; replace it through a diazonium salt when making phenol.

OR

32(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 the reaction of a primary amine with chloroform and alcoholic potassium hydroxide on heating.
- It produces an isocyanide, R–NC, with a characteristic offensive smell; the alkyl group remains attached to nitrogen.

Step 1: Identify the reacting functional group Ethylamine, $C_2H_5NH_2$, is a primary amine and therefore gives the carbylamine test. Its ethyl group is retained, while the chloroform carbon supplies the carbon of the isocyanide group.

Step 2: Write the balanced reaction on heating Using ethanolic KOH, the equation is

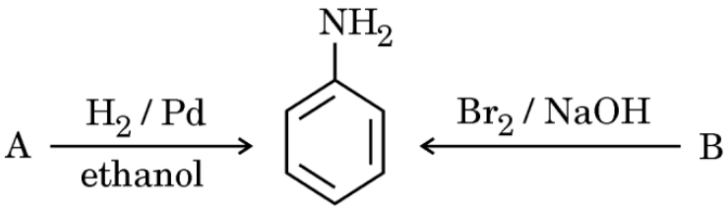
$$C_2H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} C_2H_5NC + 3\,KCl + 3\,H_2O.$$

Three molecules of KOH account for the three chlorine atoms as KCl. The product has the connectivity C_2H_5-NC, rather than that of a nitrile, C_2H_5-CN.

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

Quick Tip to Solve: With $CHCl_3$ and alcoholic KOH, replace the primary amine's $-NH_2$ by $-NC$ and use three KOH in the equation.

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



Solution:

Concept:

- Catalytic hydrogenation with H_2/Pd reduces the nitro group of nitrobenzene to the amino group of aniline.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into a primary amine, RNH_2, with one fewer carbon atom, using Br_2/NaOH.

Step 1: Identify A from the hydrogenation arrow The central product in the printed scheme is aniline, $C_6H_5NH_2$. Hydrogenation of nitrobenzene in ethanol over palladium supplies this product, so A is

Quick Tip to Solve: Follow both arrows towards aniline: H_2/Pd suggests a nitro precursor, while Br_2/NaOH requires an amide with one additional carbon.

nitrobenzene, $C_6H_5NO_2$:

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

The benzene ring is retained while the nitro group is reduced to an amino group.

Step 2: Identify B from the bromine and alkali arrow In the second reaction, the arrow also points towards aniline. Hofmann degradation removes the carbonyl carbon from the starting amide. To retain a phenyl group bonded directly to nitrogen, B must be benzamide, $C_6H_5CONH_2$:

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

Benzamide has seven carbon atoms, whereas aniline has six; the removed carbon is accounted for in sodium carbonate.

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

Quick Tip to Solve: Follow both arrows towards aniline: H_2/Pd suggests a nitro precursor, while Br_2/NaOH requires an amide with one additional carbon.

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

(I) benzene

(II) sulphanilic acid [2 marks]

Solution:

Concept:

- Aniline undergoes diazotisation with nitrous acid generated from $NaNO_2$ and HCl at 273–278 K. The diazonium group can then be replaced by hydrogen.
- Sulphonation of aniline with concentrated sulphuric acid proceeds through anilinium hydrogensulphate and gives sulphanilic acid on strong heating.

Step 1: (I) Prepare the diazonium salt and reduce it First convert aniline into benzenediazonium chloride under cold conditions:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2\,H_2O.$$

Treat this salt with hypophosphorous acid, H_3PO_2, and water. The diazonium group is replaced by hydrogen, with liberation of nitrogen:

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

Thus the amino group is removed without changing the benzene ring.

Step 2: (II) Sulphonate aniline on heating Concentrated H_2SO_4 first protonates aniline to give

Quick Tip to Solve: To replace $-NH_2$ by hydrogen, use a diazonium salt and H_3PO_2; for sulphanilic acid, remember concentrated acid followed by strong heating.

anilinium hydrogensulphate:

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

Heat this salt at 453–473 K. Sulphonation yields sulphanilic acid, with the amino and sulphonic acid groups at para positions:

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

Sulphanilic acid is 4-aminobenzenesulphonic acid and exists predominantly in the zwitterionic form p-$H_3N^+C_6H_4SO_3^-$.

Step 3: Conclusion Aniline gives benzene by diazotisation followed by reduction with H_3PO_2; it gives sulphanilic acid by heating with concentrated H_2SO_4 at 453–473 K.

Quick Tip to Solve: To replace $-NH_2$ by hydrogen, use a diazonium salt and H_3PO_2; for sulphanilic acid, remember concentrated acid followed by strong heating.

33(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:

- Fusion of pyrolusite, MnO_2, with KOH in air oxidises manganese from $+4$ to $+6$, giving green potassium manganate.
- Manganate disproportionates in acidic medium to permanganate and MnO_2. In acid, permanganate is reduced to Mn^{2+} by accepting five electrons.

Step 1: (I) Identify the green and purple compounds Oxygen from air oxidises pyrolusite during alkaline fusion:

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

Thus A is potassium manganate, K_2MnO_4, which is dark green. On acidification, manganate ions disproportionate:

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

The purple compound B is potassium permanganate, $KMnO_4$; its colour comes from the permanganate ion.

Step 2: (II) Balance the reaction with ferrous ions In acidic medium the reduction half-reaction is

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

Each ferrous ion loses one electron: $Fe^{2+} \longrightarrow Fe^{3+} + e^-$. Multiply the iron half-reaction by five and

Quick Tip to Solve: Green manganate has Mn(VI); purple permanganate has Mn(VII). Its reduction to Mn(II) in acid fixes the $1:5$ permanganate-to-ferrous ratio.

add, cancelling the electrons:

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

Both sides have total charge $+17$, and the oxygen and hydrogen atoms are balanced by water and hydrogen ions.

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

Quick Tip to Solve: Green manganate has Mn(VI); purple permanganate has Mn(VII). Its reduction to Mn(II) in acid fixes the $1:5$ permanganate-to-ferrous ratio.

33(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 positive standard reduction potential favours reduction under standard conditions.
- Across an inner-transition series, poor shielding by the added f electrons increases effective nuclear charge and contracts atomic and ionic radii.
- The potential of a metal-ion/metal couple reflects the combined effects of atomisation, ionisation and hydration; electronic stability also influences these energy changes.

Step 1: (I) Explain the reduction of cerium(IV) In aqueous solution, the $+3$ oxidation state of cerium is more stable than its $+4$ state. Thus Ce^{4+} readily accepts an electron:

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

The large positive standard reduction potential for this couple indicates a strong tendency to undergo reduction. In accepting an electron, Ce^{4+} oxidises the other reactant, explaining its good oxidising action.

Step 2: (II) Compare the shielding by f electrons Successive actinoids gain electrons in the 5f subshell, whereas successive lanthanoids gain electrons in the 4f subshell. The 5f electrons shield the increasing nuclear charge less effectively than the 4f electrons. Hence the effective nuclear attraction increases more strongly from element to element among actinoids, causing a greater contraction of their sizes.

Step 3: (III) Compare the zinc and copper electrode potentials The aqueous Zn^{2+} ion has the particularly stable, completely filled $3d^{10}$ configuration. Formation of this stable ion, together with zinc's relatively low enthalpy of atomisation, favours oxidation of the metal. The reverse reduction $Zn^{2+} + 2\,e^- \longrightarrow Zn$ is therefore less favourable, making its standard reduction potential unusually negative. For copper, the energy required to atomise the metal and ionise its atoms to Cu^{2+} is high.

Quick Tip to Solve: For metal potentials, compare atomisation plus ionisation with hydration; then remember that easier oxidation means a more negative reduction potential.

Hydration of Cu^{2+} does not compensate sufficiently for this energy requirement. Oxidation of copper to the aqueous ion is consequently unfavourable relative to the standard hydrogen electrode, so the reverse Cu^{2+}/Cu reduction potential is positive.

Step 4: Conclusion Ce^{4+} oxidises readily because it is reduced to the more stable aqueous +3 state; poorer 5f shielding causes the greater actinoid contraction. Stabilisation of Zn^{2+} favours zinc oxidation, whereas copper's high atomisation and ionisation requirements give a positive reduction potential.

Quick Tip to Solve: For metal potentials, compare atomisation plus ionisation with hydration; then remember that easier oxidation means a more negative reduction potential.

OR

33(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 across the lanthanoid series with increasing atomic number; comparison of ionic radii uses ions in the same oxidation state.
- The 4f electrons shield the increasing nuclear charge poorly, so the effective nuclear attraction on the outer electrons increases across the series.

Step 1: (I) Identify and apply lanthanoid contraction The phenomenon is lanthanoid contraction: the progressive decrease in the sizes of lanthanoid atoms and their corresponding ions as atomic number increases. The lanthanoid series lies before hafnium in the sixth period. Poor shielding by the added 4f electrons leads to increased effective nuclear attraction and contracts the size of hafnium. This contraction almost offsets the usual increase in size on moving down a group from zirconium to hafnium; hence Zr and Hf have nearly equal atomic sizes.

Step 2: (II) State another consequence The basic strength of lanthanoid hydroxides decreases across the series, from $La(OH)_3$ to $Lu(OH)_3$. As the radius of the trivalent ion decreases while its charge remains +3, its polarising power increases. The metal–oxygen bond develops greater covalent character and the hydroxide becomes less basic.

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

Quick Tip to Solve: When a 5d element has almost the same size as its 4d partner, look for the intervening 4f series and lanthanoid contraction.

33(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 of lower activation energy and is regenerated during the reaction.
- Enthalpy of atomisation measures the energy required to form gaseous atoms from an element; stronger metallic bonding gives a higher value.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.

Step 1: (I) Explain catalytic activity Transition metals show variable oxidation states and can form intermediate compounds or complexes with reactants. They can therefore participate in successive oxidation and reduction steps, providing a lower-activation-energy route while being regenerated at the end. In heterogeneous catalysis, their surfaces also adsorb reactant molecules, bring them close together and weaken bonds before reaction. For example, iron provides the catalytic surface in the Haber process for making ammonia, NH_3.

Step 2: (II) Relate atomisation to metallic bonding In transition metals, both the outer ns electrons and the $(n-1)d$ electrons can contribute to metallic bonding. The availability of several unpaired d electrons generally strengthens the bonding between metal atoms. A large energy input is therefore required to overcome these interatomic attractions and separate the solid into gaseous atoms, giving high enthalpies of atomisation. This is a general trend; the strength varies with the electronic configuration across the series.

Step 3: (III) Compare scandium and zinc configurations The ground-state configuration of Sc is $[Ar]\,3d^1 4s^2$. Its atom has an incompletely filled 3d subshell, so scandium satisfies the definition of a transition element even though Sc^{3+} is $3d^0$. Zinc has configuration $[Ar]\,3d^{10}4s^2$, and its common ion, Zn^{2+}, is $[Ar]\,3d^{10}$. Both have a completely filled d subshell. Thus zinc belongs to the d block but does not satisfy the definition of a transition element.

Step 4: Conclusion Transition-metal catalysis follows from intermediate formation, variable oxidation states and surface adsorption. Strong metallic bonding explains high atomisation enthalpies. Sc is a transition element because its atom is $3d^1$, whereas Zn and Zn^{2+} both have filled $3d^{10}$ subshells.

Quick Tip to Solve: To classify a transition element, inspect both its neutral atom and its common ions: scandium qualifies through the atom, while zinc has no incomplete d subshell in either.