

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-5-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **35** questions. **All** questions are compulsory.
- (ii) Question paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.
- (iii) **In section – A** : Question Numbers **1** to **18** are Multiple Choice (MCQ) type Questions carrying **1** mark each.
- (iv) **In section – B** : Question Numbers **19** to **25** are Very Short Answer (VSA) type questions carrying **2** marks each.
- (v) **In section – C** : Question Numbers **26** to **30** are Short Answer (SA) type questions carrying **3** marks each.
- (vi) **In section – D** : Question Numbers **31** and **32** are case based questions carrying **4** marks each.
- (vii) **In section – E** : Question Numbers **33** to **35** are Long Answer (LA) type questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section – B, 2 questions in Section – C, 2 questions in Section – D and 2 questions in Section – E.
- (ix) Use of calculators is NOT allowed.

Section A (18 marks)

1. The magnetic moment of $[\text{NiCl}_4]^{2-}$ is

[Atomic number : Ni = 28]

[1 mark]

- (A) 1.82 BM
- (B) 2.82 BM
- (C) 4.42 BM
- (D) 5.46 BM

Correct Answer: (B) 2.82 BM

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \text{ BM}$, where n is the number of unpaired electrons.
- Chloride is a weak-field ligand; tetrahedral nickel(II) retains two unpaired electrons.

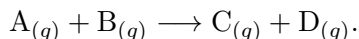
Step 1: Determine the metal configuration Four chloride ligands contribute charge -4 . Since the complex has charge -2 , nickel has oxidation state $+2$. Neutral nickel has configuration $[\text{Ar}]3d^84s^2$; removing the two outer electrons gives $\text{Ni}^{2+} : 3d^8$.

Step 2: Calculate and check the options The weak-field tetrahedral complex has two unpaired electrons. Thus $\mu = \sqrt{2(2+2)} = \sqrt{8} \approx 2.82 \text{ BM}$. The values 1.82, 4.42 and 5.46 BM do not match the spin-only moment for two unpaired electrons.

Step 3: Conclusion The magnetic moment is 2.82 BM. Hence, the correct option is (B).

Quick Tip to Solve: Find the oxidation state before counting unpaired electrons; chloride gives a tetrahedral nickel(II) complex.

2. The following experimental rate data were obtained for a reaction carried out at 25 °C:



Initial $[A_{(g)}]/\text{mol dm}^{-3}$	Initial $[B_{(g)}]/\text{mol dm}^{-3}$	Initial rate/ $\text{mol dm}^{-3}\text{s}^{-1}$
3.0×10^{-2}	2.0×10^{-2}	1.89×10^{-4}
3.0×10^{-2}	4.0×10^{-2}	1.89×10^{-4}
6.0×10^{-2}	4.0×10^{-2}	7.56×10^{-4}

What are the orders with respect to $A_{(g)}$ and $B_{(g)}$?

[1 mark]

- (A) Order w.r.t. A: Zero; Order w.r.t. B: Second
(B) Order w.r.t. A: First; Order w.r.t. B: Zero
(C) Order w.r.t. A: Second; Order w.r.t. B: Zero
(D) Order w.r.t. A: Second; Order w.r.t. B: First

Correct Answer: (C) Order w.r.t. A: Second; Order w.r.t. B: Zero

Solution:

Concept:

- Write the experimental rate law as $r = k[A]^m[B]^n$, where m, n are the respective orders.
- Compare experiments with one concentration fixed to isolate the order of the other reactant.

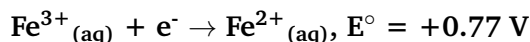
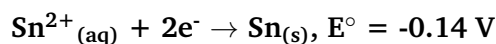
Step 1: Find the order in B Between experiments 1 and 2, $[A]$ is fixed at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, while $[B]$ doubles. The rate remains $1.89 \times 10^{-4} \text{ mol dm}^{-3}\text{s}^{-1}$. Therefore $2^n = 1$, giving $n = 0$.

Step 2: Find the order in A and compare Between experiments 2 and 3, $[B]$ is fixed while $[A]$ doubles. The rate ratio is $7.56/1.89 = 4$; hence $2^m = 4$ and $m = 2$. Option A reverses these orders, B gives the wrong order for A, and D incorrectly makes the rate depend on B.

Step 3: Conclusion The orders in A and B are second and zero, respectively. Hence, the correct option is (C).

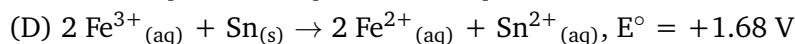
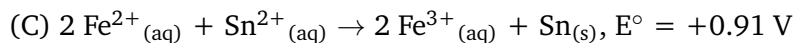
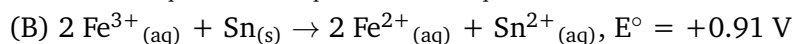
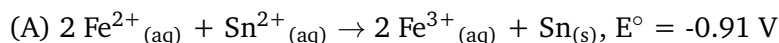
Quick Tip to Solve: Use experiments 1 and 2 for B, then 2 and 3 for A; never infer order from the balanced equation.

3. Consider the following standard electrode potential values:



What is the cell reaction and potential for the spontaneous reaction that occurs ?

[1 mark]



Correct Answer: (B) $2 \text{Fe}^{3+}_{(\text{aq})} + \text{Sn}_{(\text{s})} \rightarrow 2 \text{Fe}^{2+}_{(\text{aq})} + \text{Sn}^{2+}_{(\text{aq})}, E^{\circ} = +0.91 \text{ V}$

Solution:

Concept:

- The half-cell with the larger standard reduction potential undergoes reduction.
- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$; a positive value gives a spontaneous standard cell reaction.

Step 1: Balance the half-reactions Iron(III) has the larger reduction potential, so $2\text{Fe}^{3+} + 2\text{e}^{-} \rightarrow 2\text{Fe}^{2+}$. Tin must undergo oxidation: $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^{-}$. Adding cancels the two electrons and conserves both atoms and charge.

Step 2: Calculate the potential and test choices Using the reduction potentials, $E^{\circ}_{\text{cell}} = 0.77 - (-0.14) = +0.91 \text{ V}$. Multiplying the iron half-reaction by two does not multiply its potential. A is the nonspontaneous reverse reaction, C gives that reverse reaction a wrong positive potential, and D incorrectly changes the voltage.

Step 3: Conclusion $2\text{Fe}^{3+}_{(\text{aq})} + \text{Sn}_{(\text{s})} \rightarrow 2\text{Fe}^{2+}_{(\text{aq})} + \text{Sn}^{2+}_{(\text{aq})}$, with $E^{\circ} = +0.91 \text{ V}$. Hence, the correct option is (B).

Quick Tip to Solve: Balance electrons by multiplying equations, but never multiply electrode potentials by stoichiometric coefficients.

4. Which of the following cell was used in Apollo space programme ?

[1 mark]

(A) Mercury cell

(B) Daniel cell

(C) H_2 - O_2 Fuel cell

(D) Dry cell

Correct Answer: (C) H_2 - O_2 Fuel cell

Solution:

Concept:

- A fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.
- The hydrogen-oxygen fuel cell has overall reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.

Step 1: Identify the cell The Apollo space programme used hydrogen-oxygen fuel cells for its electrical

Quick Tip to Solve: Link Apollo with hydrogen plus oxygen: electrical energy and water are produced together.

supply. Hydrogen acts as the fuel and oxygen as the oxidant; their electrochemical reaction supplies current while producing water, which is useful in a spacecraft.

Step 2: Check the alternatives A mercury cell uses zinc amalgam and mercury(II) oxide, a Daniell cell uses zinc and copper half-cells, and a dry cell uses a zinc container with a manganese dioxide cathode mixture. These are different cell systems and do not identify the hydrogen-oxygen fuel cell used in Apollo.

Step 3: Conclusion The cell was the $\text{H}_2\text{-O}_2$ fuel cell. Hence, the correct option is (C).

Quick Tip to Solve: Link Apollo with hydrogen plus oxygen: electrical energy and water are produced together.

5. Which of the following alcohols will not undergo oxidation ?

[1 mark]

- (A) Butanol
- (B) Butan-2-ol
- (C) 2-Methylbutan-2-ol
- (D) 3-Methylbutan-2-ol

Correct Answer: (C) 2-Methylbutan-2-ol

Solution:

Concept:

- Ordinary oxidation of an alcohol to a carbonyl compound requires a hydrogen on the carbon bearing the hydroxyl group.
- Primary alcohols form aldehydes and then acids; secondary alcohols form ketones.

Step 1: Classify the listed alcohols Butanol is primary and has hydrogen on its hydroxyl-bearing carbon. Butan-2-ol is secondary, as is 3-methylbutan-2-ol; both have one hydrogen on that carbon. In 2-methylbutan-2-ol, the carbon bearing -OH is bonded to three carbon groups and has no hydrogen.

Step 2: Apply the oxidation requirement The tertiary alcohol 2-methylbutan-2-ol therefore resists ordinary alcohol oxidation. The primary and secondary choices undergo oxidation to carbonyl products. Under drastic conditions tertiary alcohols can suffer carbon-carbon bond cleavage, but that is not the usual oxidation tested by this question.

Step 3: Conclusion 2-Methylbutan-2-ol will not undergo ordinary oxidation. Hence, the correct option is (C).

Quick Tip to Solve: Inspect only the carbon bearing OH: three carbon neighbours mean no hydrogen is available for ordinary oxidation.

6. The unit of molar conductivity is

[1 mark]

- (A) $\text{S cm}^{-2}\text{mol}^{-1}$
- (B) $\text{S cm}^2\text{mol}^{-1}$
- (C) $\text{S}^{-1}\text{cm}^2\text{mol}^{-1}$
- (D) $\text{S cm}^2\text{mol}$

Correct Answer: (B) $\text{S cm}^2\text{mol}^{-1}$

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa/c$ when concentration c is in mol cm^{-3} .
- Conductivity κ has unit S cm^{-1} , where S denotes siemens.

Step 1: Derive the dimensions Dividing conductivity by amount concentration gives

$$[\Lambda_m] = \frac{\text{S cm}^{-1}}{\text{mol cm}^{-3}} = \text{S cm}^2\text{mol}^{-1}.$$

If concentration is instead in mol per litre, the numerical conversion factor 1000 must also be included.

Step 2: Check each printed option Option A has the wrong power of centimetres. Option C uses inverse siemens, which corresponds to resistance rather than conductance. Option D multiplies by moles instead of dividing by them. The required unit has siemens, squared centimetres and inverse moles, exactly as in printed option B.

Step 3: Conclusion The unit is $\text{S cm}^2\text{mol}^{-1}$. Hence, the correct option is (B).

Quick Tip to Solve: Divide conductivity units by concentration units; subtracting -3 from -1 gives the required centimetre power +2.

7. Out of the following 1.0 M aqueous solutions, which one will show largest freezing point depression ?

[1 mark]

- (A) NaCl
- (B) Na_2SO_4
- (C) $\text{C}_6\text{H}_{12}\text{O}_6$
- (D) $\text{Al}_2(\text{SO}_4)_3$

Correct Answer: (D) $\text{Al}_2(\text{SO}_4)_3$

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor and m is molality.
- For the intended comparison of equally concentrated aqueous solutions, the solute producing the greatest number of particles gives the largest depression.

Step 1: Count the dissolved particles NaCl produces two ions per formula unit, and Na_2SO_4 produces

Quick Tip to Solve: Count ions after writing dissociation: aluminium sulfate gives two aluminium ions plus three sulfate ions.

three. Glucose $C_6H_{12}O_6$ does not dissociate, so its factor is one. Aluminium sulfate dissociates as $Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$, producing five ions.

Step 2: Compare the colligative effects Using the usual complete-dissociation comparison, the factors are 2, 3, 1 and 5 for A, B, C and D. The solvent factor is common. Consequently aluminium sulfate yields the greatest effective particle concentration and hence the largest freezing-point depression; each other choice yields fewer particles.

Step 3: Conclusion $Al_2(SO_4)_3$ gives the largest freezing-point depression. Hence, the correct option is (D).

Quick Tip to Solve: Count ions after writing dissociation: aluminium sulfate gives two aluminium ions plus three sulfate ions.

8. Which of the following molecules has a chiral centre correctly labelled with an asterisk (*) ?

[1 mark]

- (A) $CH_3C^*HBrCH_3$
(B) $CH_3C^*HClCH_2Br$
(C) $HOCH_2C^*H(OH)CH_2OH$
(D) $CH_3C^*Br_2CH_3$

Correct Answer: (B) $CH_3C^*HClCH_2Br$

Solution:

Concept:

- A chiral centre is usually an sp^3 -hybridised carbon bonded to four different groups.
- Compare complete substituents attached to the starred carbon, not just the first atom of each substituent.

Step 1: Inspect the four groups in option (B) The starred carbon in $CH_3CHClCH_2Br$ is bonded to H, Cl, CH_3 and CH_2Br . These four groups are all different, so this carbon is a chiral centre.

Step 2: Reject the other labelled centres In (A), two groups are identical methyl groups. In (C), two groups are identical CH_2OH groups. In (D), both bromine substituents are identical, and the two methyl groups are also identical. Thus none of these three starred carbons satisfies the four-different-groups condition.

Step 3: Conclusion The correctly labelled chiral centre is in $CH_3C^*HClCH_2Br$. Hence, the correct option is (B).

Quick Tip to Solve: List all four groups on the starred carbon; one repeated group immediately excludes chirality.

9. In the reaction

$\text{C}_6\text{H}_5\text{NH}_2 + \text{CHCl}_3 + 3 \text{KOH} \rightarrow \text{A} + 3\text{B} + 3\text{C}$ the product A is

[1 mark]

- (A) $\text{C}_6\text{H}_5\text{NC}$
- (B) $\text{C}_6\text{H}_5\text{CN}$
- (C) $\text{C}_6\text{H}_5\text{Cl}$
- (D) $\text{C}_6\text{H}_5\text{NHCH}_3$

Correct Answer: (A) $\text{C}_6\text{H}_5\text{NC}$

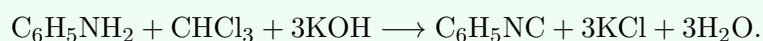
Solution:

Concept:

- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide.
- An isocyanide has the connectivity $\text{R} - \text{N} \equiv \text{C}$, whereas a nitrile has $\text{R} - \text{C} \equiv \text{N}$.

Step 1: Identify the amine and its product Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, is a primary aromatic amine and therefore undergoes the carbylamine reaction. Its phenyl group remains attached to nitrogen, giving phenyl isocyanide, $\text{C}_6\text{H}_5\text{NC}$.

Step 2: Balance the reaction and compare the choices



Thus B is potassium chloride and C is water. Option (B) is benzonitrile, with the wrong connectivity. Neither chlorobenzene in (C) nor the secondary amine in (D) is the carbylamine product.

Step 3: Conclusion Product A is phenyl isocyanide, $\text{C}_6\text{H}_5\text{NC}$. Hence, the correct option is (A).

Quick Tip to Solve: For the carbylamine test, retain the original amine nitrogen next to the organic group: write RNC, not RCN.

10. β -pleated sheet structure in proteins refers to

[1 mark]

- (A) primary structure
- (B) secondary structure
- (C) tertiary structure
- (D) quaternary structure

Correct Answer: (B) secondary structure

Solution:

Concept:

- The primary structure of a protein specifies the amino-acid sequence in its polypeptide chain.
- Secondary structure describes regular arrangements of the polypeptide backbone stabilised by hydrogen bonds; examples are the α -helix and β -pleated sheet.

Step 1: Recognise the sheet arrangement In a β -pleated sheet, extended stretches of polypeptide

Quick Tip to Solve: Associate alpha-helix and beta-pleated sheet with backbone hydrogen bonding and the secondary level.

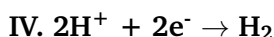
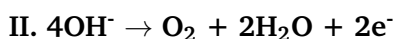
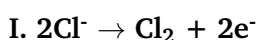
lie beside one another and are connected by hydrogen bonds between backbone C = O and N – H groups. This produces a regular, folded sheet arrangement.

Step 2: Distinguish the levels of protein structure Option (A) concerns amino-acid order rather than this arrangement. Tertiary structure, option (C), is the overall three-dimensional folding of one polypeptide. Quaternary structure, option (D), concerns the association of multiple polypeptide subunits. The regular sheet arrangement belongs to the secondary level.

Step 3: Conclusion The β -pleated sheet is a secondary structure of proteins. Hence, the correct option is (B).

Quick Tip to Solve: Associate alpha-helix and beta-pleated sheet with backbone hydrogen bonding and the secondary level.

11. Four half reactions I to IV are shown below:



Which two of these reactions are most likely to occur when concentrated brine is electrolysed ?

[1 mark]

- (A) I and III
- (B) I and IV
- (C) II and III
- (D) II and IV

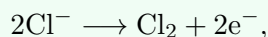
Correct Answer: (B) I and IV

Solution:

Concept:

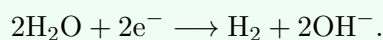
- At an electrolytic anode oxidation occurs; at the cathode reduction occurs.
- Concentrated aqueous sodium chloride gives chlorine at the anode and hydrogen at the cathode; sodium ions remain in solution.

Step 1: Select the anode process In concentrated brine, the high chloride concentration and the oxygen-evolution overpotential favour discharge of chloride ions. The anode reaction is



which is reaction I. Oxygen evolution is not the selected process under these conditions.

Step 2: Select the cathode process and eliminate alternatives Water is reduced preferentially to Na^+ , giving hydrogen rather than sodium metal. In aqueous alkaline notation,



Quick Tip to Solve: For concentrated aqueous brine, remember chlorine at the anode and hydrogen at the cathode; molten salt behaves differently.

Among the printed choices, IV denotes hydrogen evolution. Thus (A) and (C) incorrectly include sodium deposition, while (D) chooses oxygen instead of chlorine. The printed reaction II also has an electron imbalance: balanced hydroxide oxidation would release four electrons.

Step 3: Conclusion The selected processes are I and IV: chlorine evolution and hydrogen evolution. Hence, the correct option is (B).

Quick Tip to Solve: For concentrated aqueous brine, remember chlorine at the anode and hydrogen at the cathode; molten salt behaves differently.

12. Which property of transition metals enables them to behave as catalysts ?

[1 mark]

- (A) High melting point
- (B) High ionisation enthalpy
- (C) Alloy formation
- (D) Variable oxidation states

Correct Answer: (D) Variable oxidation states

Solution:

Concept:

- Transition metals can exhibit more than one oxidation state because their ns and $(n - 1)d$ electrons can participate in bonding.
- A catalyst provides an alternative reaction pathway and is regenerated during the catalytic cycle.

Step 1: Connect oxidation states with catalysis A transition metal can accept electrons in one stage of a reaction and donate electrons in another. Its ability to change oxidation state permits formation of intermediates and subsequent regeneration of the original catalyst, facilitating a lower-activation-energy pathway.

Step 2: Compare the remaining properties High melting point in (A) is a physical property and does not by itself explain a catalytic cycle. High ionisation enthalpy in (B) is not the relevant general explanation. Alloy formation in (C) concerns mixing metals and is likewise not the property asked for. Variable oxidation states directly enable the electron-transfer steps involved in many catalytic reactions.

Step 3: Conclusion Variable oxidation states enable transition metals to behave as catalysts. Hence, the correct option is (D).

Quick Tip to Solve: When a catalyst undergoes electron transfer and is regenerated, connect its role to variable oxidation states.

13. Which of the following would not be a good choice for reducing nitrobenzene to aniline ? [1 mark]

- (A) LiAlH_4
- (B) H_2/Ni
- (C) Fe and HCl
- (D) Sn and HCl

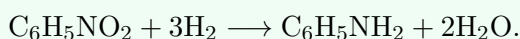
Correct Answer: (A) LiAlH_4

Solution:

Concept:

- Reduction of nitrobenzene to aniline converts $-\text{NO}_2$ to $-\text{NH}_2$ while retaining the benzene ring.
- Standard preparations use catalytic hydrogenation or a metal such as iron or tin in hydrochloric acid, followed by liberation of the free amine.

Step 1: Recognise the suitable methods Catalytic hydrogenation with H_2/Ni gives



Both Fe/HCl and Sn/HCl are also standard nitro-group reducing systems. The acidic reaction mixture contains an anilinium salt, from which the free aniline is obtained by adding base.

Step 2: Identify the unsuitable choice LiAlH_4 is not the standard suitable reagent for converting an aryl nitro compound to its amine under the usual ethereal conditions. A strong reducing agent is not automatically the best choice for every substrate. Hence options (B), (C) and (D) describe established methods, leaving the hydride reagent in (A) as the requested poor choice.

Step 3: Conclusion LiAlH_4 is not a good choice for this conversion. Hence, the correct option is (A).

Quick Tip to Solve: For nitrobenzene to aniline, choose hydrogen with nickel or iron/tin with acid; do not select a hydride just because it is strong.

14. Which one of the following has lowest $\text{p}K_a$ value ?

[1 mark]

- (A) $\text{CH}_3\text{—COOH}$
- (B) $\text{O}_2\text{N—CH}_2\text{—COOH}$
- (C) $\text{Cl—CH}_2\text{—COOH}$
- (D) HCOOH

Correct Answer: (B) $\text{O}_2\text{N—CH}_2\text{—COOH}$

Solution:

Concept:

- $\text{p}K_a = -\log_{10} K_a$: a lower $\text{p}K_a$ indicates a stronger acid.
- Electron-withdrawing groups stabilise the carboxylate conjugate base through the negative inductive effect, increasing acid strength.

Step 1: Compare the substituent effects The nitro group in $\text{O}_2\text{NCH}_2\text{COOH}$ exerts a particularly

Quick Tip to Solve: First rank conjugate-base stability by the inductive effect; reverse the acid-strength order to rank $\text{p}K_a$.

strong electron-withdrawing effect. Chlorine in ClCH_2COOH also withdraws electrons, but less strongly than the nitro group. Both substituents stabilise the negative charge of the carboxylate ion more than hydrogen does.

Step 2: Place the acids in the relevant order A methyl group is electron-releasing and destabilises the acetate ion relative to formate. Consequently the acid-strength order is



The pK_a order is the reverse. Thus chloroacetic acid, formic acid and acetic acid all have higher pK_a values than nitroacetic acid.

Step 3: Conclusion $\text{O}_2\text{NCH}_2\text{COOH}$ has the lowest pK_a . Hence, the correct option is (B).

Quick Tip to Solve: First rank conjugate-base stability by the inductive effect; reverse the acid-strength order to rank pK_a .

15. Assertion (A): The backbone of DNA and RNA molecules is a chain consisting of heterocyclic base, pentose sugar and phosphate group.

Reason (R): Nucleotides and nucleosides mainly differ from each other in presence of phosphate group. [1 mark]

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

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

Solution:

Concept:

- A nucleoside contains a nitrogenous base and a pentose sugar; a nucleotide also contains a phosphate group.
- The nucleic-acid backbone is an alternating sugar-phosphate chain, joined through phosphodiester linkages.

Step 1: Evaluate Assertion (A) The assertion is false. The backbone of DNA and RNA contains alternating pentose-sugar and phosphate units. The heterocyclic nitrogenous bases are attached to the sugars and project from this chain; they are not themselves links in the backbone.

Step 2: Evaluate Reason (R) The reason is true. Addition of a phosphate group to a nucleoside produces a nucleotide: nucleotide = base + sugar + phosphate. A nucleoside lacks this phosphate group.

Step 3: Check the explanation A true reason cannot explain the false statement about the backbone. Options (A) and (B) incorrectly treat the assertion as true, while (C) also incorrectly treats the reason

Quick Tip to Solve: Distinguish the whole nucleotide from its backbone: bases hang from the sugar-phosphate chain.

as false.

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

Quick Tip to Solve: Distinguish the whole nucleotide from its backbone: bases hang from the sugar-phosphate chain.

16. Assertion (A): Order of reaction is applicable to elementary as well as complex reactions.

Reason (R): For a complex reaction molecularity has no meaning.

[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:

- Order is the sum of concentration exponents in the experimentally determined rate law.
- Molecularity counts reacting species in one elementary step; it is not assigned to an overall multistep reaction.

Step 1: Evaluate Assertion (A) The assertion is true. A rate law can be obtained for either an elementary reaction or a complex reaction. For example, if $r = k[A]^m[B]^n$, its order is $m + n$, irrespective of whether the overall reaction takes place in one step or several steps.

Step 2: Evaluate Reason (R) The reason is true. A complex reaction comprises elementary steps with their own molecularities. The overall equation does not represent a single molecular collision, so overall molecularity has no meaning.

Step 3: Check the explanatory connection The reason describes the limitation of molecularity. It does not explain why order applies to both kinds of reactions; that follows from the experimental rate law. Therefore (A) is excluded. Options (C) and (D) are excluded because both statements are true.

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: Use the rate law for order, and a single elementary step for molecularity; then judge the explanatory link separately.

17. Assertion (A): The final product in Aldol condensation is always α,β -unsaturated carbonyl compound.

Reason (R): α,β -unsaturated carbonyl compounds are stabilised due to conjugation. [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:

- Aldol addition gives a β -hydroxy carbonyl compound, which loses water during aldol condensation.
- An α,β -unsaturated carbonyl compound has conjugated $C = C$ and $C = O$ bonds.

Step 1: Evaluate Assertion (A) The assertion is true in the usual aldol-condensation reaction: dehydration of the initially formed aldol gives the final α,β -unsaturated aldehyde or ketone. For ethanal, the initial product is 3-hydroxybutanal, which on heating loses water to give but-2-enal.

Step 2: Evaluate Reason (R) The reason is true. In the dehydration product, the carbon-carbon double bond lies adjacent to the carbonyl group. The resulting conjugated system permits delocalisation of electrons and stabilises the unsaturated carbonyl product.

Step 3: Check the explanatory connection The stability gained through conjugation accounts for formation of the dehydrated final product. The intermediate hydroxy compound belongs to aldol addition; it must not be confused with the final condensation product. Thus (B), (C) and (D) do not describe the true statements and their causal link.

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: Separate aldol addition from condensation: the latter includes dehydration to a conjugated carbonyl product.

18. Assertion (A): $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ gives a white precipitate with silver nitrate solution.

Reason (R): The complex dissociates to give Cl^- and SO_4^{2-} ions.

[1 mark]

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

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

Solution:

Concept:

- Only counter-ions outside the coordination sphere are freely released by ordinary dissociation.
- Free chloride ions react with silver ions to form white AgCl .

Step 1: Evaluate Assertion (A) The assertion is true. Chloride lies outside the square brackets and is released in solution:



The chloride reacts with silver nitrate: $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(\text{s})$, giving a white precipitate.

Step 2: Evaluate Reason (R) The reason is false. Sulphate is inside the coordination sphere and remains bonded to cobalt in the complex ion. Ordinary dissociation releases the chloride counter-ion, not free sulphate ions as well.

Step 3: Check the explanation The white precipitate is correctly explained by release of chloride alone. The reason adds the incorrect claim that sulphate is released. Therefore options (A) and (B), which declare the reason true, and (D), which declares the assertion false, are excluded.

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

Quick Tip to Solve: Read square brackets first: an anion inside them is coordinated, while an anion outside is a counter-ion.

Section B (14 marks)

19. For the pair phenol and cyclohexanol, answer the following:

- (a) Why is phenol more acidic than cyclohexanol ?
(b) Give one chemical test to distinguish between the two.

[2 marks]

Solution:

Concept:

- Acid strength increases when the conjugate base produced on loss of H^+ is more stable.
- Phenols give a characteristic colour with neutral aqueous ferric chloride, whereas ordinary alcohols do not.

Quick Tip to Solve: Compare conjugate-base stability for acidity; use neutral ferric chloride when distinguishing phenol from an ordinary alcohol.

Step 1: (a) Compare the conjugate bases Phenol loses a proton to form phenoxide, $\text{C}_6\text{H}_5\text{O}^-$. Its negative charge is delocalised from oxygen into the aromatic ring by resonance. Cyclohexanol forms cyclohexoxide, whose negative charge remains localised on oxygen because its saturated ring cannot provide this conjugation. The cyclohexyl group also has an electron-releasing inductive effect, which does not stabilise the negative charge. The greater stability of phenoxide favours proton loss from phenol, so phenol is more acidic.

Step 2: (b) Perform the ferric chloride test Add a few drops of freshly prepared neutral aqueous FeCl_3 solution separately to the two samples. Phenol produces a violet or purple colour through formation of a coloured iron(III)-phenolate complex. Cyclohexanol does not give this characteristic violet colour. This difference distinguishes the two compounds.

Step 3: Conclusion (a) Phenol is more acidic because its phenoxide ion is resonance-stabilised. (b) Neutral ferric chloride gives a violet colour with phenol, but no characteristic violet colour with cyclohexanol.

Quick Tip to Solve: Compare conjugate-base stability for acidity; use neutral ferric chloride when distinguishing phenol from an ordinary alcohol.

20. (a) Which of the following species cannot act as a ligand ? Give reason.

OH^- , NH_4^+ , CH_3NH_2 , H_2O

(b) The complex $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ is red in colour. Give IUPAC name of its linkage isomer.

[2 marks]

Solution:

Concept:

- A ligand must possess an available lone pair of electrons for donation to a metal ion.
- An ambidentate ligand can attach through different donor atoms, giving linkage isomers.

Step 1: (a) Identify the species that cannot donate a lone pair NH_4^+ cannot act as a ligand. Nitrogen has used its lone pair to bond to a proton in forming the ammonium ion, so no lone pair remains available for donation to a metal. In contrast, OH^- and H_2O have available oxygen lone pairs, while CH_3NH_2 has an available nitrogen lone pair and can coordinate through nitrogen.

Step 2: (b) Identify the linkage isomer and name it The red complex contains the oxygen-bound nitrito ligand. Its linkage isomer contains the same NO_2^- ligand attached through nitrogen, and is represented by $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ with N-bonding specified. The complex ion has charge +2. Since the five ammine ligands are neutral and nitrito has charge -1 , cobalt has oxidation state +3. The IUPAC name of this N-bound linkage isomer is pentaamminenitrito-N-cobalt(III) chloride (also called pentaamminenitrocobalt(III) chloride).

Step 3: Conclusion (a) NH_4^+ , because it has no available lone pair. (b) Pentaamminenitrito-N-cobalt(III) chloride, the nitrogen-bound linkage isomer.

Quick Tip to Solve: For nitrite linkage isomers, specify the donor atom: red corresponds to O-bonding, and its linkage isomer is N-bound.

21. What happens to the rate constant k and activation energy E_a as the temperature of a chemical reaction is increased ? Justify. [2 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a is activation energy, R is the gas constant and T is absolute temperature.
- Activation energy is the energy barrier for a given reaction pathway; heating changes the distribution of molecular energies.

Step 1: Effect on the rate constant When temperature increases, $E_a/(RT)$ decreases for a fixed reaction pathway. Therefore the exponent $-E_a/(RT)$ becomes less negative and $e^{-E_a/(RT)}$ increases. Thus the rate constant k increases. Physically, a larger fraction of reactant molecules now has energy equal to or greater than the activation energy, so more collisions are effective.

Step 2: Effect on activation energy The activation energy E_a remains unchanged when only temperature is increased, provided the reaction mechanism is unchanged. It is the energy difference between the reactants and the activated complex for the same pathway. Heating supplies energy to molecules; it does not lower this barrier. A catalyst, by providing a different pathway, can change the activation energy.

Step 3: Conclusion On increasing temperature, k increases, whereas E_a remains unchanged for the same reaction pathway.

Quick Tip to Solve: In the Arrhenius equation, change T while keeping the barrier E_a fixed; heating increases the fraction crossing it.

22. Why haloarenes are not reactive towards nucleophilic substitution reaction ? Give two reasons. [2 marks]

Solution:

Concept:

- Nucleophilic substitution requires cleavage of the carbon-halogen bond and replacement of the halogen by a nucleophile.
- In a haloarene, the halogen lone pair interacts with the benzene ring and the halogen-bearing carbon is sp^2 -hybridised.

Step 1: Resonance strengthens the carbon-halogen bond A lone pair on the halogen is delocalised into the aromatic ring by resonance. Consequently, the carbon-halogen bond acquires partial double-bond character. This makes the bond shorter and stronger than a normal carbon-halogen single bond in a haloalkane. Cleavage of this bond, required for nucleophilic substitution, is therefore difficult.

Step 2: The carbon atom is sp^2 -hybridised The halogen-bearing carbon in a haloarene is sp^2 -hybridised, whereas it is sp^3 -hybridised in a haloalkane. An sp^2 orbital has greater s-character and holds the bonding electron pair closer to the carbon nucleus. As a result, the carbon-halogen bond in a haloarene is shorter and stronger, making displacement of the halogen by a nucleophile more

Quick Tip to Solve: Give two distinct causes of the strong aryl-halogen bond: resonance and the greater s-character of sp^2 carbon.

difficult under ordinary conditions.

Step 3: Conclusion Haloarenes resist nucleophilic substitution because resonance gives the carbon-halogen bond partial double-bond character and the sp^2 -hybridised carbon forms a shorter, stronger bond.

Quick Tip to Solve: Give two distinct causes of the strong aryl-halogen bond: resonance and the greater s-character of sp^2 carbon.

23(a). (i) What should be the signs (positive/negative) for E°_{cell} and ΔG° for a spontaneous redox reaction occurring under standard conditions ?

(ii) State Faraday's first law of electrolysis.

[2 marks]

Solution:

Concept:

- For a cell reaction, $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- The charge passed during electrolysis is $Q = It$, where I is current and t is time.

Step 1: (i) Signs for a spontaneous standard cell reaction A reaction is spontaneous under standard conditions when its standard Gibbs energy change is negative: $\Delta G^\circ < 0$. Since n and F are positive, the relation $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ then requires $E^\circ_{\text{cell}} > 0$. Hence the standard cell potential is positive and the standard Gibbs energy change is negative.

Step 2: (ii) Faraday's first law The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte. Thus

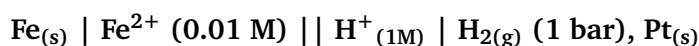
$$m \propto Q, \quad m = ZQ = ZIt.$$

Here m is the deposited or liberated mass and Z is the electrochemical equivalent of the substance. For a fixed substance, doubling the charge doubles the mass deposited or liberated.

Step 3: Conclusion (i) E°_{cell} is positive and ΔG° is negative. (ii) Faraday's first law states $m \propto Q$, or $m = ZIt$.

Quick Tip to Solve: Use the minus sign in $\Delta G^\circ = -nFE^\circ_{\text{cell}}$; for electrolysis, first convert current and time into charge.

23(b). Calculate the emf of the following cell at 298 K:



Given $E^\circ_{\text{cell}} = 0.44 \text{ V}$.

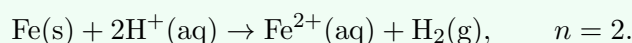
[2 marks]

Solution:

Concept:

- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, with base-10 logarithm.
- Pure solids have unit activity; hydrogen gas activity is its pressure relative to 1 bar. Solute activities are represented here by their molar concentrations relative to 1 M.

Step 1: Write the cell reaction and reaction quotient Iron is oxidised at the left electrode: $\text{Fe}_{(s)} \rightarrow \text{Fe}^{2+}_{(aq)} + 2e^-$. Hydrogen ions are reduced at the right electrode: $2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_{2(g)}$. Therefore the cell reaction is



With unit hydrogen pressure and $[\text{H}^+] = 1 \text{ M}$, the dimensionless reaction quotient is

$$Q = \frac{[\text{Fe}^{2+}] (p_{\text{H}_2}/1 \text{ bar})}{[\text{H}^+]^2} = \frac{0.01 \times 1}{1^2} = 0.01,$$

where the concentrations in this expression are their numerical values relative to 1 M.

Step 2: Substitute into the Nernst equation Using $E^\circ_{\text{cell}} = 0.44 \text{ V}$ and $\log(0.01) = -2$,

$$\begin{aligned} E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \log(0.01) \\ &= 0.44 - \frac{0.0591}{2} (-2) \\ &= 0.4991 \text{ V}. \end{aligned}$$

Since $Q < 1$, the logarithmic correction increases the emf above its standard value, consistent with the low product-ion concentration.

Step 3: Conclusion The emf of the cell at 298 K is $E_{\text{cell}} = 0.4991 \text{ V} \approx 0.50 \text{ V}$.

Quick Tip to Solve: Write the overall reaction before Q ; hydrogen ions are squared and $n = 2$, so $\log 0.01 = -2$ cancels the denominator.

24(a). (i) Draw the zwitter ion structure for sulphanilic acid.

(ii) How can the activating effect of -NH_2 group in aniline be controlled ?

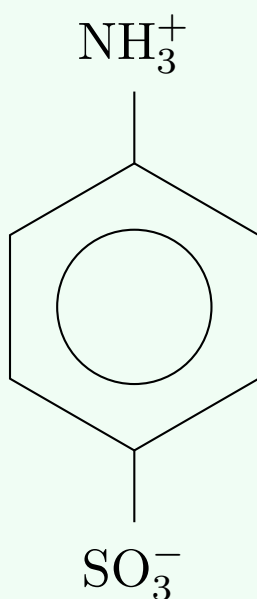
[2 marks]

Solution:

Concept:

- A zwitterion contains both positive and negative charges in the same molecule, but has zero net charge.
- Acetylation converts the strongly activating amino group into an amide group, whose nitrogen lone pair is less available to the benzene ring.

Step 1: (i) Form the zwitterion In sulphanilic acid the $\text{-SO}_3\text{H}$ and -NH_2 groups occupy para positions. Transfer of the acidic proton from the sulphonic acid group to the amino group gives -SO_3^- and -NH_3^+ . Thus the structure is $^+\text{H}_3\text{N} - \text{C}_6\text{H}_4 - \text{SO}_3^-$, with the two substituents opposite each other. The labelled drawing shows both charges explicitly.



Zwitterionic structure of sulphanilic acid

Step 2: (ii) Control activation by acetylation Treat aniline with acetic anhydride to form acetanilide:



The nitrogen lone pair is delocalised towards the carbonyl group in -NHCOCH_3 , so its donation into the benzene ring is reduced. Acetylation therefore moderates activation and makes controlled electrophilic substitution possible. The protecting acetyl group can subsequently be removed by hydrolysis.

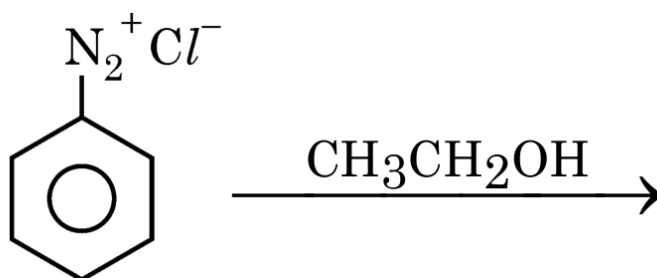
Step 3: Conclusion (i) The para zwitterion is $^+\text{H}_3\text{N} - \text{C}_6\text{H}_4 - \text{SO}_3^-$. (ii) Acetylate aniline to acetanilide to control its activating effect.

Quick Tip to Solve: Put both ionic charges on sulphanilic acid, and use acetylation to reduce nitrogen lone-pair donation.

24(b). (i) Complete the reaction with the main product formed:

(ii) Convert Bromoethane to Propanamine.

[2 marks]

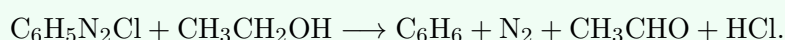


Solution:

Concept:

- Ethanol reduces an aryl diazonium salt: the diazonium group is replaced by hydrogen and nitrogen gas is liberated.
- Alcoholic KCN substitutes bromide by cyanide, extending the carbon chain by one carbon; reduction of the nitrile gives a primary amine.

Step 1: (i) Identify the main product The starting compound is benzenediazonium chloride. Ethanol replaces $-\text{N}_2^+$ by hydrogen, producing benzene as the main organic product. Ethanol itself is oxidised to ethanal:



The ring remains intact. Formation of phenol would require water as the reagent, whereas the printed reagent here is ethanol.

Step 2: (ii) Extend the chain and reduce the nitrile First heat bromoethane with alcoholic potassium cyanide to form propanenitrile:



Then reduce propanenitrile with LiAlH_4 in dry ether, followed by hydrolysis:



The carbon of the cyanide group becomes the terminal $-\text{CH}_2\text{NH}_2$ carbon. Thus the product has three carbon atoms, as required for propan-1-amine. Direct ammonolysis of bromoethane would give ethanamine and would not extend the chain.

Step 3: Conclusion (i) Benzene, C_6H_6 , is the main product. (ii) Treat bromoethane with alcoholic KCN to obtain propanenitrile, then reduce it with lithium aluminium hydride to obtain propan-1-amine.

Quick Tip to Solve: Count carbon atoms: KCN adds one carbon before nitrile reduction gives propan-1-amine.

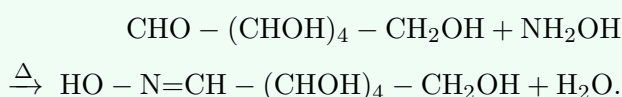
25. Give the reaction of heating glucose with hydroxylamine. Presence of which group is confirmed by this reaction ? [2 marks]

Solution:

Concept:

- Hydroxylamine, NH_2OH , condenses with an aldehyde or ketone carbonyl group to form an oxime, with elimination of water.
- The open-chain form of glucose contains a terminal aldehyde group, $-\text{CHO}$, and five hydroxyl groups.

Step 1: Write the oxime-forming reaction On heating glucose with hydroxylamine, its carbonyl group reacts to give glucose oxime:



The former aldehyde carbon now bears the $\text{C}=\text{N}-\text{OH}$ group. The hydroxyl groups along the remaining carbon chain are retained.

Step 2: Identify the functional group indicated Oxime formation demonstrates the presence of a carbonyl group in glucose. In its open-chain structure, that carbonyl occurs at the end of the chain as an aldehyde group, $-\text{CHO}$. Hydroxylamine is a reagent for the carbonyl group; it does not establish the number of alcoholic hydroxyl groups. Although glucose exists mainly in cyclic forms in solution, equilibrium supplies the open-chain form, which reacts and is replenished as it is consumed.

Step 3: Conclusion Glucose forms glucose oxime and water with hydroxylamine. This confirms its carbonyl group, present as an aldehydic $-\text{CHO}$ group in open-chain glucose.

Quick Tip to Solve: For hydroxylamine, replace the carbonyl $\text{C}=\text{O}$ by $\text{C}=\text{N}-\text{OH}$ and show water as the coproduct.

Section C (15 marks)

26. Give reasons for any 3 of the following observations:

- Penta-acetate of glucose does not react with hydroxylamine.
- Amino acids behave like salts.
- Water soluble vitamins must be taken regularly in diet.
- The two strands in DNA are complimentary to each other.

[3 marks]

Solution:

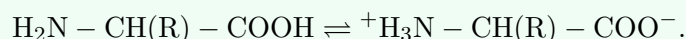
Concept:

- Chemical reactivity depends on whether a functional group is free and available to the reagent.
- Zwitterions have internal ionic charges; complementary DNA bases pair specifically through hydrogen bonds.

Quick Tip to Solve: Use a direct cause for each observation: blocked carbonyl, zwitterion, limited storage, and specific base pairing.

Step 1: (a) Glucose pentaacetate and hydroxylamine Glucose pentaacetate has a cyclic structure in which the anomeric hydroxyl group has also been acetylated. The aldehydic carbonyl is not present as a free $-\text{CHO}$ group, and the acetylated cyclic form cannot readily open to supply that group. Hydroxylamine therefore cannot form the oxime. This observation supports the cyclic structure of glucose.

Step 2: (b) Salt-like behaviour of amino acids An amino acid contains both an acidic $-\text{COOH}$ group and a basic $-\text{NH}_2$ group. Internal proton transfer produces the zwitterion:



These internal positive and negative ions cause salt-like properties, such as relatively high melting points and substantial water solubility. The molecule has zero overall charge while retaining ionic character.

Step 3: (c) Regular dietary supply of water-soluble vitamins Water-soluble vitamins are generally not stored in appreciable amounts in the body. Excess amounts are eliminated in urine, so reserves are limited. A regular dietary supply is therefore needed to replace losses and meet metabolic requirements. This is the general behaviour of water-soluble vitamins; vitamin B12 is an exception because it can be stored in the body.

Step 4: (d) Complementarity of DNA strands The bases pair specifically: adenine pairs with thymine through two hydrogen bonds, and guanine pairs with cytosine through three hydrogen bonds. Each purine pairs with a pyrimidine, preserving the width of the double helix. Consequently, the sequence on one strand determines the complementary sequence on the opposite strand. For example, an A on one strand requires T at the corresponding position on the other.

Step 5: Conclusion (a) No free aldehyde group is available in cyclic glucose pentaacetate. (b) Amino acids exist as zwitterions. (c) Water-soluble vitamins are generally not stored and are excreted. (d) Specific A-T and G-C pairing makes DNA strands complementary. Any three reasons answer the question.

Quick Tip to Solve: Use a direct cause for each observation: blocked carbonyl, zwitterion, limited storage, and specific base pairing.

27. (a) On the basis of crystal field theory, write the electronic configuration for d^4 with a strong field ligand for which $\Delta_o > P$.

(b) A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green but a solution of $[\text{Ni}(\text{CO})_4]$ is colourless. Explain.

[Atomic number: Ni = 28]

[3 marks]

Solution:

Concept:

- An octahedral crystal field splits the metal d orbitals into the lower t_{2g} and upper e_g sets. Δ_o is this separation, and P is the pairing energy.
- If $\Delta_o > P$, pairing is energetically preferred to occupying the higher set. Visible colour can result

Quick Tip to Solve: Determine oxidation state before counting d electrons: neutral CO gives Ni(0), while the aqua cation contains Ni(II).

from transitions between partially filled metal d levels.

Step 1: (a) Obtain the low-spin configuration The first three electrons occupy the three lower t_{2g} orbitals singly. The fourth electron pairs in one of these orbitals because pairing costs P , less than the excitation energy Δ_o needed to enter an e_g orbital. Therefore the electronic configuration is $(t_{2g})^4(e_g)^0$. One lower orbital contains a pair, the other two each contain one electron, and the higher orbitals are empty. This is a low-spin configuration with two unpaired electrons.

Step 2: (b) Account for the green aqua complex Nickel has atomic configuration $[\text{Ar}]3d^84s^2$. In $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, neutral water ligands leave nickel in oxidation state +2, with configuration $3d^8$. Its octahedral occupancy is $(t_{2g})^6(e_g)^2$. Partially filled d orbitals allow d-d transitions. Absorption of selected visible wavelengths for these transitions leaves transmitted light giving the solution its green colour.

Step 3: (b) Account for colourless nickel tetracarbonyl CO is neutral, so nickel in neutral $[\text{Ni}(\text{CO})_4]$ has oxidation state zero. Under the strong-field influence of CO, the valence electrons pair to give a completely filled $3d^{10}$ subshell in the complex. All the metal d orbitals are occupied, so there is no available vacant d level for a d-d transition. Thus visible absorption through d-d excitation does not occur and nickel tetracarbonyl is colourless. The different oxidation states and d occupancies must be considered before comparing these complexes.

Step 4: Conclusion (a) $(t_{2g})^4(e_g)^0$, with two unpaired electrons. (b) The aqua complex is d^8 and shows visible d-d absorption; nickel tetracarbonyl has a filled d^{10} subshell and is colourless.

Quick Tip to Solve: Determine oxidation state before counting d electrons: neutral CO gives Ni(0), while the aqua cation contains Ni(II).

28(a). (i) Why is the C—O bond length in phenols less than that in methanol ?

(ii) Arrange the following in order of increasing boiling point:

Ethoxyethane, Butanal, Butanol, n-butane

(iii) How can phenol be prepared from anisole ? Give reaction.

[3 marks]

Solution:

Concept:

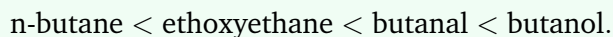
- Conjugation of an oxygen lone pair with an aromatic ring gives the aryl C—O bond partial double-bond character. Stronger bonds are generally shorter.
- For comparable molecular sizes, boiling points increase as intermolecular attraction increases: dispersion, dipole interactions and intermolecular hydrogen bonding.
- Aryl alkyl ethers undergo cleavage by hot concentrated HI at the alkyl–oxygen bond; the aryl–oxygen bond is retained.

Step 1: (i) Compare the C—O bonds In phenol, an oxygen lone pair overlaps with the conjugated aromatic ring and is delocalised by resonance. The C—O bond therefore acquires partial double-bond character and is shorter than the ordinary single C—O bond in methanol. Also, the carbon attached to oxygen in phenol is sp^2 -hybridised, whereas the corresponding carbon in methanol is

Quick Tip to Solve: In anisole cleavage, keep oxygen on the aromatic ring and attach iodine to the methyl group; compare boiling points by self-hydrogen bonding first.

sp^3 -hybridised; greater s character further favours a shorter bond. Methanol lacks the aromatic conjugation responsible for this shortening.

Step 2: (ii) Order the boiling points The increasing order is



Nonpolar n-butane has only dispersion forces. Ethoxyethane is polar and has dipole interactions, but cannot hydrogen-bond to itself because it has no O–H bond. The carbonyl group gives butanal stronger dipole interactions than the ether. Butanol has an O–H group and forms extensive intermolecular hydrogen bonds, so the most energy is needed to separate its molecules.

Step 3: (iii) Prepare phenol from anisole Heat anisole with concentrated hydrogen iodide:



Protonation of ether oxygen is followed by iodide attack at the methyl carbon. Cleavage occurs at the methyl–oxygen bond through substitution, producing phenol and methyl iodide. The aromatic C–O bond has partial double-bond character and its sp^2 carbon does not undergo the usual backside substitution; hence iodobenzene is not the product.

Step 4: Conclusion Resonance shortens phenol's C–O bond. Boiling points increase as n-butane, ethoxyethane, butanal, butanol. Hot concentrated HI converts anisole into phenol and methyl iodide.

Quick Tip to Solve: In anisole cleavage, keep oxygen on the aromatic ring and attach iodine to the methyl group; compare boiling points by self-hydrogen bonding first.

OR

28(b). (i) Give mechanism of the following reaction:



(ii) Illustrate hydroboration–oxidation reaction with an example.

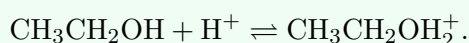
[3 marks]

Solution:

Concept:

- Acid-catalysed intermolecular dehydration of ethanol at 413 K forms ethoxyethane. Protonation converts the poor leaving group OH into a water leaving group.
- Hydroboration followed by alkaline peroxide oxidation adds water across an alkene in the anti-Markovnikov orientation: OH reaches the less substituted carbon.

Step 1: (i) Protonate ethanol Sulphuric acid supplies the proton that activates the alcohol:

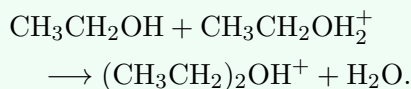


Oxygen donates a lone pair to the proton. The resulting ethyloxonium ion contains a positively charged oxygen and can lose neutral water. This makes substitution possible under the reaction

Quick Tip to Solve: For ether formation write the protonated alcohol and protonated ether explicitly; for hydroboration put OH on the less substituted alkene carbon.

conditions.

Step 2: (i) Form the new C–O bond and regenerate acid A second ethanol molecule acts as the nucleophile. Its oxygen attacks the primary ethyl carbon of protonated ethanol while water leaves, in a concerted substitution:

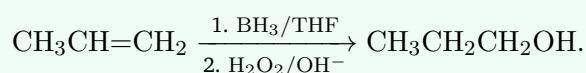


The product is a protonated ether. Loss of its oxygen-bound proton gives neutral diethyl ether and regenerates the acid catalyst:



Thus two ethanol molecules undergo intermolecular dehydration at 413 K, producing one ether molecule and one water molecule. A free primary ethyl carbocation is not required for this mechanism.

Step 3: (ii) Illustrate hydroboration–oxidation Propene gives propan-1-ol when treated first with borane and then with hydrogen peroxide in alkaline solution:



In hydroboration, boron bonds to the less substituted terminal carbon and hydrogen to the other carbon in a concerted addition. Oxidation replaces the C–B bond by a C–OH bond with retention of configuration. Overall, hydrogen and OH add syn, with OH on the terminal carbon; this is anti-Markovnikov hydration and does not involve carbocation rearrangement.

Step 4: Conclusion (i) Protonation, ethanol attack with water loss, and deprotonation yield ethoxyethane. (ii) Hydroboration–oxidation of propene yields propan-1-ol with OH at the less substituted carbon.

Quick Tip to Solve: For ether formation write the protonated alcohol and protonated ether explicitly; for hydroboration put OH on the less substituted alkene carbon.

29. (a) Illustrate Sandmeyer's reaction with an equation.

(b) Explain, why $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in aqueous solution.

[3 marks]

Solution:

Concept:

- Sandmeyer reaction replaces the diazonium group of an aromatic diazonium salt by chloride, bromide or cyanide using the appropriate cuprous salt.
- An amine is a base because its nitrogen lone pair accepts a proton. In water its basicity depends on the electron-donating effect of alkyl groups and the hydration of the conjugate acid.

Step 1: (a) Illustrate the Sandmeyer reaction Benzene diazonium chloride reacts with cuprous

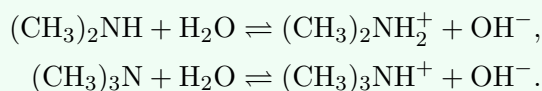
Quick Tip to Solve: For aqueous methylamines, compare hydration of the protonated ions as well as the number of electron-donating methyl groups.

chloride in hydrochloric acid to give chlorobenzene, with evolution of nitrogen gas:



The aromatic ring is retained, while the diazonium group is replaced by chlorine. Analogously, cuprous bromide gives bromobenzene and cuprous cyanide gives benzonitrile.

Step 2: (b) Compare protonation and hydration The two bases accept a proton as follows:

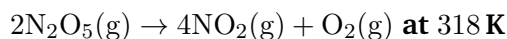


Although three methyl groups donate electron density to nitrogen more strongly than two, basicity in aqueous solution cannot be decided by this effect alone. The dimethylammonium ion has two N–H bonds and is less sterically crowded; water can hydrate it more effectively through hydrogen bonding. Trimethylammonium has only one N–H bond, and its three methyl groups hinder approach of water molecules. The greater hydration stabilisation of the conjugate acid of dimethylamine outweighs the additional electron-donating effect in trimethylamine, favouring proton acceptance by dimethylamine.

Step 3: Conclusion Sandmeyer chlorination gives $\text{C}_6\text{H}_5\text{Cl}$ from benzene diazonium chloride using CuCl/HCl . In aqueous solution, $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ because its conjugate acid is better hydrated.

Quick Tip to Solve: For aqueous methylamines, compare hydration of the protonated ions as well as the number of electron-donating methyl groups.

30. (a) For the reaction



calculate the rate of reaction if rate of disappearance of $\text{N}_2\text{O}_5(\text{g})$ is $1.4 \times 10^{-3} \text{ m s}^{-1}$.

(b) For a first order reaction derive the relationship $t_{99\%} = 2t_{90\%}$.

[3 marks]

Solution:

Concept:

- For a balanced reaction, its rate is the disappearance or appearance rate divided by the corresponding stoichiometric coefficient.
- For a first order reaction, $kt = \ln([A]_0/[A]_t)$, where k is the rate constant and $[A]_0, [A]_t$ are initial and remaining concentrations.

Step 1: (a) Apply the stoichiometric definition For the given reaction, the normalized rate is

$$r = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}.$$

The given disappearance rate is positive; the minus sign in the definition converts the decreasing

Quick Tip to Solve: Divide a species rate by its equation coefficient; for percentage completion, put the fraction remaining inside the first order logarithm.

reactant concentration into a positive rate. Divide its magnitude by the coefficient 2:

$$r = \frac{1.4 \times 10^{-3}}{2} = 7.0 \times 10^{-4}.$$

The printed question gives the unit ms^{-1} ; the factor of one-half preserves that supplied unit. A rate expressed as change of molar concentration would conventionally have units $\text{mol L}^{-1} \text{s}^{-1}$. No temperature correction is required: the given rate already applies at 318 K.

Step 2: (b) Calculate the time for 90 percent completion If the initial concentration is a , then 90 percent completion leaves $0.10a$. The integrated first order law gives

$$t_{90\%} = \frac{1}{k} \ln \frac{a}{0.10a} = \frac{\ln 10}{k}.$$

Use the amount remaining, not the amount reacted, in the denominator.

Step 3: (b) Calculate the time for 99 percent completion At 99 percent completion the concentration remaining is $0.01a$. Thus

$$t_{99\%} = \frac{1}{k} \ln \frac{a}{0.01a} = \frac{\ln 100}{k} = \frac{2 \ln 10}{k}.$$

Both times refer to the same first order reaction at the same temperature, so k is identical and cancels when their ratio is taken. The initial concentration also cancels, so the relationship holds for any nonzero initial concentration.

Step 4: Conclusion Using the supplied printed unit, $r = 7.0 \times 10^{-4} \text{ms}^{-1}$. Also, $t_{99\%}/t_{90\%} = \ln 100/\ln 10 = 2$, hence $t_{99\%} = 2t_{90\%}$.

Quick Tip to Solve: Divide a species rate by its equation coefficient; for percentage completion, put the fraction remaining inside the first order logarithm.

Section D (8 marks)

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

31. Nucleophilic Substitution

Nucleophilic Substitution reaction of haloalkane can be conducted according to both S_N1 and S_N2 mechanisms. S_N1 is a two step reaction while S_N2 is a single step reaction. For any haloalkane which mechanism is followed depends on factors such as structure of haloalkane, properties of leaving group, nucleophilic reagent and solvent.

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1 . Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water).

[4 marks]

31(a). Why racemisation occurs in S_N1 ?

[1 mark]

Solution:

Concept:

- An S_N1 substitution proceeds through a carbocation intermediate after the leaving group departs.
- The carbocation carbon is sp^2 -hybridised and trigonal planar, allowing nucleophilic attack from either face.

Step 1: Form the planar intermediate The C–halogen bond breaks heterolytically to form a carbocation. If the reacting carbon was a chiral centre, its tetrahedral configuration is lost when it becomes planar.

Step 2: Attack from both faces The nucleophile can approach either side of the plane. Attack from one face produces retention of configuration and attack from the other produces inversion, yielding both enantiomers. Consequently the product undergoes racemisation; their formation need not be exactly equal because the departing group can partly shield one face.

Step 3: Conclusion Racemisation occurs because the planar carbocation in S_N1 permits nucleophilic attack from both faces, producing both enantiomers.

Quick Tip to Solve: Link racemisation to the planar carbocation and two-face attack, rather than merely calling the mechanism a two-step process.

31(b). Why is ethanol less polar than water ?

[1 mark]

Solution:

Concept:

- Water and ethanol contain polar O–H bonds, but a molecule's overall solvent polarity also depends on its nonpolar part.
- An alkyl group is comparatively nonpolar; increasing its contribution reduces the polarity of an alcohol relative to water.

Step 1: Compare the molecular structures Water, H_2O , is a small polar molecule with no hydrocarbon group. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, contains a polar hydroxyl group attached to a nonpolar ethyl group.

Step 2: Relate structure to solvent polarity The nonpolar ethyl group reduces ethanol's overall polarity relative to water. Water also forms a more extensive hydrogen-bonded network and screens electrostatic attractions more effectively; as the passage states, its dielectric constant is about 79 compared with about 24 for ethanol. Ethanol can hydrogen bond, but this does not make the two solvents equally polar.

Step 3: Conclusion Ethanol is less polar than water because its nonpolar ethyl group reduces the contribution of its polar hydroxyl group to the overall solvent polarity.

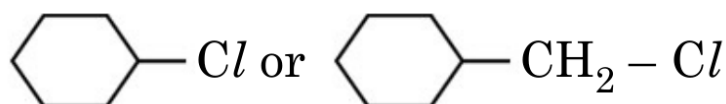
Quick Tip to Solve: Identify the nonpolar ethyl group in ethanol; do not claim that ethanol lacks an O–H bond or cannot form hydrogen bonds.

31(c). Which one of the following in each pair is more reactive towards $\text{S}_{\text{N}}2$ reaction ?

(i) $\text{CH}_3\text{—CH}_2\text{—I}$ or $\text{CH}_3\text{CH}_2\text{—Cl}$

(ii)

[2 marks]



Solution:

Concept:

- An $\text{S}_{\text{N}}2$ reaction occurs in one step: the nucleophile attacks the carbon from the side opposite the leaving group while the carbon-halogen bond breaks.
- With comparable alkyl groups, leaving-group ability follows $\text{I}^- > \text{Br}^- > \text{Cl}^-$. With the same leaving group, lower steric hindrance favours backside attack.

Step 1: Compare the leaving groups in pair (i) Both ethyl iodide, $\text{CH}_3\text{CH}_2\text{I}$, and ethyl chloride, $\text{CH}_3\text{CH}_2\text{Cl}$, have the same primary ethyl group. Their steric environments are therefore comparable. The C–I bond is weaker than the C–Cl bond, and iodide is a better leaving group than chloride. Thus ethyl iodide undergoes nucleophilic displacement faster under comparable conditions.

Step 2: Compare the reacting carbons in pair (ii) In chlorocyclohexane, the carbon bonded directly to chlorine lies within the ring and is secondary; two carbon groups hinder backside approach. In cyclohexylmethyl chloride, $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, chlorine is bonded to an external primary CH_2 carbon.

Quick Tip to Solve: First identify the carbon directly bonded to the halogen; a bulky ring nearby does not make an external CH_2 carbon secondary.

Although the ring is bulky, the carbon undergoing substitution is less hindered than the secondary ring carbon. The common chloride leaving group means that this steric difference controls the comparison.

Step 3: Conclusion The more reactive compounds are: (i) $\text{CH}_3\text{CH}_2\text{I}$; (ii) $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, cyclohexyl-methyl chloride.

Quick Tip to Solve: First identify the carbon directly bonded to the halogen; a bulky ring nearby does not make an external CH_2 carbon secondary.

OR

31(c). Arrange the following in the increasing order of their reactivity towards $\text{S}_{\text{N}}1$ reactions:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane

[2 marks]

Solution:

Concept:

- In an $\text{S}_{\text{N}}1$ reaction, slow ionisation of the carbon-halogen bond forms a carbocation: $\text{RBr} \longrightarrow \text{R}^+ + \text{Br}^-$.
- For these saturated alkyl compounds, carbocation stability and hence reactivity increase as primary < secondary < tertiary. Alkyl groups stabilise positive charge through their electron-releasing effect and hyperconjugation.

Step 1: Classify the bromides in set (i) 1-Bromopentane has bromine on a primary carbon and would generate a primary carbocation. 2-Bromopentane has bromine on a secondary carbon and generates a secondary carbocation. In 2-bromo-2-methylbutane, the carbon bearing bromine is bonded to three carbon groups, so ionisation generates a tertiary carbocation. Since all three compounds have bromide as their leaving group, the stability of the initially formed carbocation determines their relative ionisation rates.

Step 2: Classify the bromides in set (ii) 1-Bromo-3-methylbutane has a primary bromine-bearing carbon despite branching farther along the chain. 2-Bromo-3-methylbutane has a secondary bromine-bearing carbon. 2-Bromo-2-methylbutane has a tertiary bromine-bearing carbon. Hence the same primary-to-secondary-to-tertiary sequence applies. Classification must be made at the carbon from which bromide leaves; a possible rearrangement after ionisation does not convert the initially primary substrate into a tertiary substrate for this rate comparison.

Step 3: Conclusion (i) 1-Bromopentane < 2-Bromopentane < 2-bromo-2-methylbutane.
(ii) 1-Bromo-3-methylbutane < 2-bromo-3-methylbutane < 2-bromo-2-methylbutane.

Quick Tip to Solve: Count carbon groups attached to the bromine-bearing carbon, rather than counting all branches in the molecule.

32. Rahul set-up an experiment to find resistance of aqueous KCl solution for different concentrations at 298 K using a conductivity cell connected to a Wheatstone bridge. He fed the Wheatstone bridge with a.c. power in the audio frequency range 550 to 5000 cycles per second. Once the resistance was calculated from null point he also calculated the conductivity κ and molar conductivity Λ_m and recorded his readings in tabular form.

S.No.	Conc.(M)	$\kappa \text{ S cm}^{-1}$	$\Lambda_m \text{ S cm}^2 \text{ mol}^{-1}$
1.	1.00	111.3×10^{-3}	111.3
2.	0.10	12.9×10^{-3}	129.0
3.	0.01	1.41×10^{-3}	141.0

Answer the following questions :

[4 marks]

32(a). Why does conductivity increase though the conductivity decrease with dilution ?

[1 mark]

Solution:

Concept:

- Conductivity κ measures conduction by ions in a unit volume; molar conductivity Λ_m refers to the ions supplied by one mole of electrolyte.
- For c in mol L^{-1} and κ in S cm^{-1} , $\Lambda_m = 1000\kappa/c$.

Step 1: Explain the fall in conductivity Dilution lowers the number of KCl ions per unit volume. Thus fewer charge carriers contribute to conduction in that volume and conductivity κ decreases, as the table shows.

Step 2: Explain the increase per mole The increasing quantity in the table is molar conductivity: it rises from 111.3 to 141.0 $\text{S cm}^2 \text{ mol}^{-1}$. On dilution, interionic attractions weaken and ionic mobility increases. Hence the ions from one mole conduct more effectively even though their number per unit volume falls.

Step 3: Conclusion On dilution, conductivity decreases because ion concentration per unit volume falls, whereas molar conductivity increases because ionic mobility increases.

Quick Tip to Solve: Distinguish conduction per unit volume from conduction by one mole before interpreting a dilution trend.

32(b). If Λ_m° of KCl is $150.0 \text{ S cm}^2 \text{ mol}^{-1}$, calculate the degree of dissociation of 0.01 M KCl.

[1 mark]

Solution:

Concept:

- The conductivity-ratio relation used to estimate degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m° is limiting molar conductivity.
- The table gives $\Lambda_m = 141.0 \text{ S cm}^2 \text{ mol}^{-1}$ for 0.01 M KCl.

Step 1: Select the concentration-specific value Use the row for 0.01 M, rather than the rows for 1.00 or 0.10 M. Its molar conductivity is $141.0 \text{ S cm}^2 \text{ mol}^{-1}$; the supplied limiting value is $150.0 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: Read molar conductivity at the stated concentration and divide by the limiting value; conductivity itself is not the numerator.

Step 2: Calculate the conductivity ratio Both quantities have identical units, so their ratio is dimensionless:

$$\alpha = \frac{141.0}{150.0} = 0.94, \quad 100\alpha = 94\%.$$

This is the degree of dissociation obtained using the requested conductivity-ratio method. KCl is a strong electrolyte; departures of its finite-concentration conductivity from the limiting value also reflect interionic effects.

Step 3: Conclusion The conductivity-ratio estimate is $\alpha = 0.94$, or 94% .

Quick Tip to Solve: Read molar conductivity at the stated concentration and divide by the limiting value; conductivity itself is not the numerator.

32(c). If Rahul had used HCl instead to KCl then would you expect the Λ_m values to be more or less than those per KCl for a given concentration. Justify. [2 marks]

Solution:

Concept:

- Molar conductivity, Λ_m , measures the conducting ability of all ions supplied by one mole of electrolyte at a stated concentration.
- For strong electrolytes, both ion mobility and interionic interactions determine molar conductivity. Hydrogen ions have exceptionally high mobility in water.

Step 1: Compare the ions present Both HCl and KCl are strong electrolytes and are substantially ionised in aqueous solution. HCl supplies H^+ and Cl^- , whereas KCl supplies K^+ and Cl^- . At the same concentration and temperature, the common chloride ion cannot account for the main difference between their molar conductivities.

Step 2: Explain the difference in mobility The mobility of H^+ in water is much higher than that of K^+ . Protons can be transferred rapidly through the hydrogen-bonded water network, in addition to transport associated with hydrated ions. Consequently, the hydrogen-ion contribution to charge transport is larger, and HCl has a greater molar conductivity than KCl at the given concentration. This comparison concerns Λ_m , rather than simply counting the two ions formed per formula unit.

Step 3: Conclusion Rahul would obtain higher Λ_m values with HCl because H^+ has a much greater ionic mobility than K^+ .

Quick Tip to Solve: When comparing HCl with KCl, cancel the common chloride ion and compare the mobilities of the cations.

32(c). Amit, a classmate of Rahul repeated the same experiment with CH_3COOH solution instead of KCl solution. Give one point that would be similar and one that would be different in his observations as compared to Rahul. [2 marks]

Solution:

Concept:

- Dilution increases molar conductivity, Λ_m , by reducing interionic hindrance; for a weak electrolyte it also increases ionisation.
- KCl is a strong electrolyte, while acetic acid is weak and establishes $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$.

Step 1: State a similar observation For both aqueous KCl and aqueous acetic acid, molar conductivity increases as the solution is diluted. Thus Amit would observe the same direction of change in Λ_m as Rahul when concentration is decreased. Molar conductivity refers to the conducting ability per mole, so this trend must not be confused with the decrease in conductivity caused by fewer ions per unit volume.

Step 2: State a different observation For KCl , which is already substantially ionised, the increase in Λ_m on dilution is comparatively small and gradual; reduced interionic interactions make ion motion easier. For acetic acid, dilution increases its degree of ionisation considerably, producing more charge carriers per mole of acid. Its molar conductivity therefore increases much more sharply and nonlinearly, particularly at low concentrations. A plot of Λ_m against $\sqrt{c}$ is approximately linear for dilute KCl , whereas the weak-acid curve does not follow this straight-line behaviour.

Step 3: Conclusion Similarity: Λ_m increases on dilution for both solutions. Difference: the increase is gradual for KCl but much sharper for CH_3COOH , owing to increased ionisation of the weak acid.

Quick Tip to Solve: Compare molar conductivity per mole: dilution changes mainly mobility for KCl but also ionisation for acetic acid.

Section E (15 marks)

33(a). (i) Write the reaction involved in Cannizzaro's reaction.

(ii) Why are the boiling point of aldehydes and ketones lower than that of corresponding carboxylic acids ?

(iii) An organic compound 'A' with molecular formula $\text{C}_5\text{H}_8\text{O}_2$ is reduced to n-pentane with hydrazine followed by heating with NaOH and Glycol. 'A' forms a dioxime with hydroxylamine and gives a positive Iodoform and Tollen's test. Identify 'A' and give its reaction for Iodoform and Tollen's test. [5 marks]

Solution:

Concept:

- An aldehyde without an α -hydrogen undergoes Cannizzaro disproportionation in concentrated alkali, giving an alcohol and a carboxylate salt.

Quick Tip to Solve: Use the dioxime to count two carbonyls, then assign one aldehyde and one methyl ketone before checking the five-carbon chain.

- Carboxylic acids form strongly hydrogen-bonded associates. The iodoform test detects a methyl ketone group, $\text{CH}_3\text{CO}-$, and Tollens' reagent oxidises an aldehyde group.
- Wolff-Kishner reduction converts carbonyl groups to methylene groups without changing the carbon skeleton; hydroxylamine forms an oxime with each reactive carbonyl group.

Step 1: (i) Write the Cannizzaro reaction For example, benzaldehyde has no α -hydrogen and undergoes disproportionation in concentrated sodium hydroxide:



One aldehyde molecule is reduced to benzyl alcohol while the other is oxidised to sodium benzoate. Acidification of the salt gives benzoic acid.

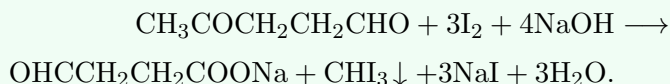
Step 2: (ii) Compare boiling points Carboxylic acids contain an $\text{O}-\text{H}$ group as well as a carbonyl oxygen and form strong intermolecular hydrogen bonds, commonly producing dimers. Aldehydes and ketones lack an $\text{O}-\text{H}$ hydrogen and cannot form such hydrogen bonds among their own molecules. Their intermolecular attraction is therefore weaker, so corresponding aldehydes and ketones have lower boiling points than carboxylic acids.

Step 3: (iii) Identify the compound from the tests Formation of a dioxime shows that A contains two carbonyl groups. A positive Tollens' test indicates an aldehyde group, while a positive iodoform test requires a methyl ketone group. Reduction to *n*-pentane requires a straight chain of five carbon atoms. These observations give

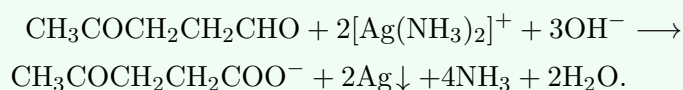


named 4-oxopentanal. Its formula is $\text{C}_5\text{H}_8\text{O}_2$. Under Wolff-Kishner conditions the ketone and aldehyde carbonyl groups are reduced, yielding $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$. With hydroxylamine it forms $\text{CH}_3\text{C}(=\text{NOH})\text{CH}_2\text{CH}_2\text{CH}=\text{NOH}$, consistent with the dioxime observation.

Step 4: Write the iodoform and Tollens reactions The methyl ketone group undergoes the iodoform reaction:



The yellow precipitate is iodoform. With Tollens' reagent, the aldehyde group is oxidised while the ketone group remains unchanged:



Deposition of metallic silver gives the positive silver-mirror test.

Step 5: Conclusion Cannizzaro disproportionation produces an alcohol and a carboxylate. Carboxylic acids boil higher because of strong intermolecular hydrogen bonding. Compound A is $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$, 4-oxopentanal; its methyl ketone gives yellow iodoform, and its aldehyde gives a silver mirror.

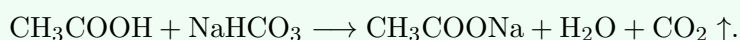
Quick Tip to Solve: Use the dioxime to count two carbonyls, then assign one aldehyde and one methyl ketone before checking the five-carbon chain.

- 33(b).** (i) Give a chemical test to distinguish between ethanal acid and ethanoic acid.
 (ii) Why is the α -hydrogens of aldehydes and ketones are acidic in nature ?
 (iii) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.
 (1) Identify 'A', 'B' and 'C'.
 (2) Out of 'B' and 'C', which will have higher boiling point ? Give reason. [5 marks]

Solution:**Concept:**

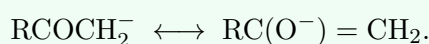
- Carboxylic acids liberate carbon dioxide from sodium hydrogen carbonate; aldehydes do not give this effervescence.
- An α -hydrogen is attached to the carbon next to a carbonyl group. Its removal produces a resonance-stabilised enolate ion.
- Ester hydrolysis gives a carboxylic acid and an alcohol; soda-lime decarboxylation removes the carboxyl carbon.

Step 1: (i) Apply the sodium hydrogen carbonate test The printed name "ethanal acid" is read as ethanal, the aldehyde contrasted with ethanoic acid. Add aqueous $NaHCO_3$ separately to the samples. Ethanoic acid gives brisk effervescence of carbon dioxide, whereas ethanal gives no effervescence. The gas turns limewater milky:



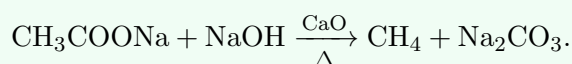
This distinguishes the acidic carboxyl group from the aldehyde group.

Step 2: (ii) Explain alpha-hydrogen acidity The electron-withdrawing carbonyl group favours removal of a neighbouring hydrogen as a proton. The resulting conjugate base is stabilised by delocalisation of its negative charge between carbon and oxygen:



This resonance stabilisation makes removal of an α -hydrogen easier than removal of a hydrogen from an ordinary alkane. It explains the acidic character of these hydrogens in aldehydes and ketones.

Step 3: (iii)(1) Use the decarboxylation and oxidation clues A sodium carboxylate loses its carboxyl carbon on heating with soda lime. Since methane is formed, B must be ethanoic acid, CH_3COOH :



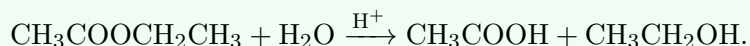
Hydrolysis of an ester gives an alcohol C. The alcohol that oxidises to ethanoic acid is ethanol, CH_3CH_2OH :



Step 4: Identify and verify A Combining the ethanoic acid and ethanol fragments gives ethyl ethanoate,

Quick Tip to Solve: Start with the soda-lime clue: methane fixes the acid fragment as ethanoic acid before you identify the ester.

$\text{CH}_3\text{COOCH}_2\text{CH}_3$. This has the required molecular formula $\text{C}_4\text{H}_8\text{O}_2$. Its acid hydrolysis is



Thus the proposed ester satisfies the molecular formula, hydrolysis products and subsequent oxidation condition.

Step 5: (iii)(2) Compare boiling points Ethanoic acid B has a higher boiling point than ethanol C. Carboxylic acid molecules associate through strong intermolecular hydrogen bonding and form cyclic dimers containing two hydrogen bonds. More energy is required to separate these associated molecules during vaporisation. Ethanol also forms hydrogen bonds, but the strong dimeric association of ethanoic acid gives the higher boiling point.

Step 6: Conclusion Ethanoic acid alone gives CO_2 with sodium hydrogen carbonate. Alpha-hydrogens are acidic because the enolate conjugate base is resonance stabilised. A is ethyl ethanoate, B is ethanoic acid and C is ethanol. B has the higher boiling point.

Quick Tip to Solve: Start with the soda-lime clue: methane fixes the acid fragment as ethanoic acid before you identify the ester.

34(a). (i) Why is boiling point of 1M NaCl solution more than that of 1M glucose solution ?

(ii) A non-volatile solute 'X' (molar mass = 50 g mol^{-1}) when dissolved in 78 g of benzene reduced its vapour pressure to 90%. Calculate the mass of X dissolved in the solution.

(iii) Calculate the boiling point elevation for a solution prepared by adding 10 g of MgCl_2 to 200 g of water assuming MgCl_2 is completely dissociated.

(K_b for Water = $0.512 \text{ K kg mol}^{-1}$, Molar mass $\text{MgCl}_2 = 95 \text{ g mol}^{-1}$)

[5 marks]

Solution:

Concept:

- Boiling point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.
- For a non-volatile solute, Raoult's law gives $p = x_1 p^0$. Hence $(p^0 - p)/p^0 = x_2 = n_2/(n_1 + n_2)$.
- Complete dissociation of MgCl_2 gives three ions per formula unit, so $i = 3$.

Step 1: (i) Compare sodium chloride and glucose solutions Glucose is a non-electrolyte and remains as molecules in water, so its van't Hoff factor is approximately 1. Sodium chloride dissociates into Na^+ and Cl^- , producing approximately two particles per formula unit and having i close to 2. At the stated equal concentration, the NaCl solution contains more solute particles. It therefore shows a larger lowering of solvent vapour pressure and a greater elevation of boiling point than the glucose solution. Colligative effects depend on the number of particles rather than their chemical identity.

Step 2: (ii) Translate the vapour pressure into mole fraction The final vapour pressure is 90 percent of the pure solvent vapour pressure, so $p/p^0 = 0.90$. The relative lowering is therefore $1 - 0.90 = 0.10$,

Quick Tip to Solve: When vapour pressure is reduced to 90 percent, use a relative lowering of 0.10 and retain the exact mole-fraction denominator.

not 0.90. Benzene has molar mass 78 g mol^{-1} , giving

$$n_1 = \frac{78}{78} = 1.00 \text{ mol}, \quad \frac{n_2}{1 + n_2} = 0.10.$$

Keep both solvent and solute moles in the denominator because the stated lowering is appreciable.

Step 3: Find the amount and mass of X Rearranging the exact mole-fraction relation,

$$\begin{aligned} n_2 &= 0.10(1 + n_2), \\ 0.90n_2 &= 0.10, \\ n_2 &= \frac{1}{9} \text{ mol.} \end{aligned}$$

With molar mass $M_X = 50 \text{ g mol}^{-1}$, the required mass is

$$w_X = n_2 M_X = \frac{50}{9} = 5.56 \text{ g.}$$

This corresponds to a solvent mole fraction of 0.90 and therefore reproduces the specified vapour pressure.

Step 4: (iii) Determine molality and the dissociation factor For the added salt,

$$n = \frac{10}{95} = 0.10526 \text{ mol}, \quad m = \frac{0.10526}{0.200} = 0.52632 \text{ mol kg}^{-1}.$$

Use the mass of water, not the total solution mass, in molality. Complete dissociation is



so the number of solute particles triples and $i = 3$.

Step 5: Calculate the boiling point elevation Substitution in the colligative-property equation gives

$$\Delta T_b = iK_b m = 3(0.512)(0.52632) = 0.8084 \text{ K.}$$

The units cancel as $(\text{K kg mol}^{-1})(\text{mol kg}^{-1}) = \text{K}$. The question asks for an elevation, so this positive temperature difference is the required quantity.

Step 6: Conclusion (i) NaCl dissociation produces more solute particles and a higher boiling point than glucose. (ii) The mass of X is 5.56 g. (iii) The boiling point elevation is 0.808 K.

Quick Tip to Solve: When vapour pressure is reduced to 90 percent, use a relative lowering of 0.10 and retain the exact mole-fraction denominator.

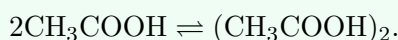
- 34(b).** (i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5 ?
 (ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at $25^\circ C$, assuming that K_2SO_4 is completely dissociated.
 ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, Molar mass $K_2SO_4 = 174 \text{ g mol}^{-1}$)
 (iii) When 25.6 g of Sulphur was dissolved in 1000 g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of Sulphur (S_x).
 (K_f for benzene = $5.12 \text{ K kg mol}^{-1}$, Atomic mass of Sulphur = 32 g mol^{-1})

[5 marks]

Solution:**Concept:**

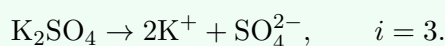
- The van't Hoff factor i is the ratio of the actual number of solute particles to the number expected without association or dissociation. Association decreases i , whereas dissociation increases it.
- Osmotic pressure is $\pi = i(n/V)RT$, where n is the amount of solute in moles, V the solution volume and T the absolute temperature.
- Freezing-point depression obeys $\Delta T_f = K_f m$, where m is moles of dissolved particles per kilogram of solvent. The molecular mass of S_x is $32x$.

Step 1: (i) Association of ethanoic acid In nonpolar benzene, ethanoic acid molecules associate in pairs through intermolecular hydrogen bonding to form cyclic dimers:



Two molecules therefore behave as one dissolved particle. For nearly complete dimerisation, the number of particles becomes approximately half the original number, so i is close to $1/2$. More generally, if the fraction associated is α , then $i = 1 - \alpha/2$; as α approaches unity, i approaches 0.5.

Step 2: (ii) Count the ions and calculate osmotic pressure Complete dissociation gives



Convert the temperature before substituting: $T = 25 + 273 = 298 \text{ K}$. The solute amount and concentration are

$$n = \frac{2.32 \times 10^{-2}}{174} = 1.3333 \times 10^{-4} \text{ mol},$$

$$C = \frac{n}{2} = 6.6667 \times 10^{-5} \text{ mol L}^{-1}.$$

Thus

$$\pi = 3(6.6667 \times 10^{-5})(0.082)(298) = 4.8872 \times 10^{-3} \text{ atm}.$$

The factor of three is necessary because each formula unit supplies three ions; the volume used here is the stated total solution volume.

Step 3: (iii) Find the molecular mass and sulphur formula The benzene mass is $1000 \text{ g} = 1.000 \text{ kg}$.

Quick Tip to Solve: Count all three ions of potassium sulphate before using osmotic pressure; for sulphur, divide the measured molecular mass by 32 to obtain x .

The measured depression determines the molality of dissolved sulphur molecules:

$$m = \frac{0.512}{5.12} = 0.100 \text{ mol kg}^{-1}.$$

Hence 1.000 kg of benzene contains 0.100 mol of sulphur molecules. Their molar mass is

$$M = \frac{25.6 \text{ g}}{0.100 \text{ mol}} = 256 \text{ g mol}^{-1}, \quad x = \frac{256}{32} = 8.$$

As a check, $25.6/256 = 0.100 \text{ mol}$, which gives $5.12 \times 0.100 = 0.512 \text{ K}$, exactly the observed depression.

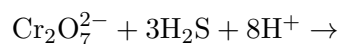
Step 4: Conclusion (i) Hydrogen-bonded dimerisation gives $i \approx 0.5$. (ii) $\pi = 4.89 \times 10^{-3} \text{ atm}$. (iii) S_8 , with molar mass 256 g mol^{-1} .

Quick Tip to Solve: Count all three ions of potassium sulphate before using osmotic pressure; for sulphur, divide the measured molecular mass by 32 to obtain x .

35. (a) Write the number of unpaired electrons in Cr^{3+} .

(Atomic number of Cr = 24)

(b) Complete the reaction mentioning all the products formed:



(c) Account for the following:

(i) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.

(ii) Copper has exceptionally positive $E_{\text{M}^{2+}/\text{M}}^\circ$ value.

(iii) Eu^{2+} with electronic configuration $[\text{Xe}] 4f^7 6s^2$ is a strong reducing agent.

[5 marks]

Solution:

Concept:

- Transition-metal ions lose their outer $4s$ electrons before $3d$ electrons. Hund's rule places electrons singly in degenerate orbitals before pairing.
- Half-filled d^5 configurations have extra stability. Oxidation removes an electron, so compare both the initial and final electronic configurations.
- A standard reduction potential reflects the overall energy balance of atomisation, ionisation and hydration. A reducing agent donates electrons and is itself oxidised.

Step 1: (a) Electronic configuration of chromium(III) Neutral chromium has configuration $[\text{Ar}] 3d^5 4s^1$. Remove the $4s$ electron first, then two $3d$ electrons to obtain

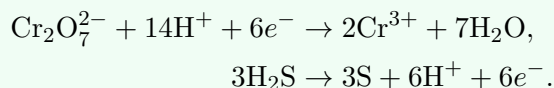


The three d electrons occupy three different orbitals with parallel spins by Hund's rule. Consequently, all three are unpaired.

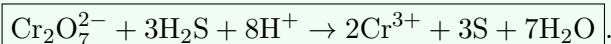
Step 2: (b) Complete and check the redox reaction Acidified dichromate oxidises hydrogen sulphide

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons, and compare both sides of an oxidation: Mn^{2+} loses d^5 stability, whereas Fe^{2+} gains it on forming Fe^{3+} .

to elemental sulphur while chromium is reduced from +6 to +3. The half-reactions are



Adding them cancels the six electrons and six hydrogen ions, giving



Both sides contain two Cr, seven O, three S and fourteen H atoms, and both have net charge +6.

Step 3: (c)(i) Relative resistance to oxidation Mn^{2+} has the stable half-filled $3d^5$ configuration. Its oxidation to Mn^{3+} , which is $3d^4$, destroys that stability and requires relatively more energy. By contrast, Fe^{2+} is $3d^6$, and oxidation produces Fe^{3+} with the stable half-filled $3d^5$ configuration. Thus manganese(II) resists oxidation to +3 more strongly than iron(II).

Step 4: (c)(ii) Exceptionally positive copper reduction potential Converting solid copper to aqueous Cu^{2+} requires atomisation and the first two ionisations. Copper has a high atomisation enthalpy and high ionisation enthalpies; the second ionisation removes an electron from the stable $3d^{10}$ configuration of Cu^+ . The energy required is not adequately compensated by the hydration enthalpy of Cu^{2+} . Therefore oxidation of copper to aqueous copper(II) is energetically unfavourable, and the reverse reduction has an exceptionally positive standard potential.

Step 5: (c)(iii) Reducing character of europium(II) The $[\text{Xe}] 4f^7 6s^2$ configuration stated in the question is the neutral europium configuration. The ion Eu^{2+} is actually $[\text{Xe}] 4f^7$, after loss of both $6s$ electrons. Despite its half-filled shell, europium(II) readily donates another electron to form the usual, thermodynamically favoured +3 oxidation state of lanthanoids:



The overall energy balance in aqueous solution favours this oxidation. By supplying an electron to another species, Eu^{2+} reduces that species and therefore acts as a strong reducing agent. Its explanation is the favourability of oxidation to +3, not acquisition of a half-filled shell on oxidation.

Step 6: Conclusion (a) $\boxed{3}$ unpaired electrons. (b) The products are $2\text{Cr}^{3+} + 3\text{S} + 7\text{H}_2\text{O}$. (c) Half-filled d^5 stability explains the Mn/Fe contrast; copper's atomisation and ionisation costs explain its positive reduction potential; Eu^{2+} reduces other species by being oxidised to Eu^{3+} .

Quick Tip to Solve: Remove 4s electrons before 3d electrons, and compare both sides of an oxidation: Mn^{2+} loses d^5 stability, whereas Fe^{2+} gains it on forming Fe^{3+} .