

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-5-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **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. Which one of the following has lowest pK_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:

- Acid strength increases with the acid dissociation constant K_a ; since $pK_a = -\log K_a$, the strongest acid has the lowest pK_a .
- Electron-withdrawing groups stabilise the carboxylate ion through the negative inductive effect and increase acidity.

Step 1: Compare the substituent effects The NO_2 group in $\text{O}_2\text{N—CH}_2\text{—COOH}$ withdraws electrons strongly and stabilises the conjugate base. The chlorine atom in $\text{Cl—CH}_2\text{—COOH}$ also withdraws electrons, but its effect is weaker than that of the nitro group at the same position.

Step 2: Eliminate the other acids The methyl group in CH_3COOH has a positive inductive effect, which destabilises the carboxylate ion relative to HCOOH . Formic acid lacks the strong electron-withdrawing substituent present in nitroacetic acid. Thus neither (A), (C), nor (D) gives the greatest conjugate-base stabilisation.

Step 3: Conclusion $\text{O}_2\text{N—CH}_2\text{—COOH}$ is the strongest acid listed and has the lowest pK_a . Hence, the correct option is (B).

Quick Tip to Solve: For these acids, compare the electron-withdrawing power of the group next to COOH ; the strongest withdrawal gives the lowest pK_a .

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

[1 mark]

- (A) Mercury cell
- (B) Daniell cell
- (C) $\text{H}_2\text{-O}_2$ Fuel cell
- (D) Dry cell

Correct Answer: (C) $\text{H}_2\text{-O}_2$ Fuel cell

Solution:

Concept:

- A fuel cell continuously converts the chemical energy of externally supplied fuel and oxidant into electrical energy.
- The hydrogen-oxygen fuel cell produces water through the overall reaction $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$.

Quick Tip to Solve: Associate Apollo with the fuel cell that supplies both electrical energy and useful water: hydrogen plus oxygen.

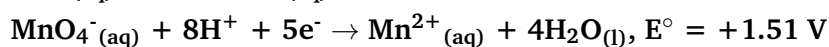
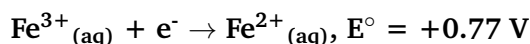
Step 1: Identify the cell used in Apollo The Apollo space programme used the hydrogen-oxygen fuel cell. Hydrogen acts as the fuel and oxygen as the oxidant; their electrochemical reaction supplies electricity, while the water formed is also useful to the astronauts.

Step 2: Check the alternatives A mercury cell and a dry cell are primary cells containing their reactants within the cell. A Daniell cell is the conventional zinc-copper galvanic cell. None of these is the hydrogen-oxygen system used for the stated space programme.

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

Quick Tip to Solve: Associate Apollo with the fuel cell that supplies both electrical energy and useful water: hydrogen plus oxygen.

3. Consider the following standard electrode potential values:



What is the cell potential for the redox reaction ?

[1 mark]

- (A) -2.28 V
(B) -0.74 V
(C) +0.74 V
(D) +2.28 V

Correct Answer: (C) +0.74 V

Solution:

Concept:

- The half-cell with the greater standard reduction potential undergoes reduction at the cathode of a spontaneous galvanic cell.
- Using reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Electrode potentials are not multiplied by stoichiometric coefficients.

Step 1: Select the reduction and oxidation Since $1.51 > 0.77$, MnO_4^- is reduced to Mn^{2+} , while Fe^{2+} is oxidised to Fe^{3+} . Electron balancing requires five iron ions per permanganate ion, giving



Step 2: Subtract the reduction potentials

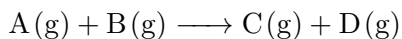
$$E^\circ_{\text{cell}} = 1.51 - 0.77 = +0.74 \text{ V}.$$

Adding the two reduction potentials would incorrectly give the positive or negative sum options. The negative difference belongs to the reverse, nonspontaneous reaction; the spontaneous cell has a positive potential.

Step 3: Conclusion The standard cell potential is +0.74 V. Hence, the correct option is (C).

Quick Tip to Solve: Subtract the smaller reduction potential from the larger; never multiply E° by five when balancing the iron half-reaction.

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



Initial [A(g)] mol dm ⁻³	Initial [B(g)] mol dm ⁻³	Initial rate mol dm ⁻³ 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 $r = k[\text{A}]^m[\text{B}]^n$, where m and n are the respective reaction orders and k is the rate constant.
- Compare two experiments in which one concentration is unchanged; the rate ratio then determines the order in the other reactant.

Step 1: Determine the order in B Between experiments 1 and 2, [A] stays at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, while [B] doubles. The rate remains $1.89 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Thus

$$\frac{r_2}{r_1} = 2^n = 1 \Rightarrow n = 0.$$

This excludes the second-order and first-order assignments for B in (A) and (D).

Step 2: Determine the order in A Between experiments 2 and 3, [B] is fixed and [A] doubles. The rate rises by a factor of four:

$$\frac{r_3}{r_2} = \frac{7.56 \times 10^{-4}}{1.89 \times 10^{-4}} = 4 = 2^m \Rightarrow m = 2.$$

First order in A would only double the rate, so (B) is also excluded.

Step 3: Conclusion The reaction is second order with respect to A and zero order with respect to B; $r = k[\text{A}]^2$. Hence, the correct option is (C).

Quick Tip to Solve: Use rows 1 and 2 for B, then rows 2 and 3 for A: no rate change means order zero, while a fourfold rate after doubling means order two.

5. 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 $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons and BM denotes Bohr magneton.
- Chloride is a weak-field ligand; the tetrahedral $[\text{NiCl}_4]^{2-}$ complex of Ni^{2+} has two unpaired electrons.

Step 1: Find the metal ion configuration Let the nickel oxidation state be x . Then $x + 4(-1) = -2$, so $x = +2$. Neutral nickel is $[\text{Ar}] 3d^8 4s^2$; loss of the two outer $4s$ electrons gives Ni^{2+} the configuration $[\text{Ar}] 3d^8$.

Step 2: Count unpaired electrons and calculate In the tetrahedral weak-field complex, the eight d electrons leave two electrons unpaired. Therefore

$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.828 \dots \text{ BM.}$$

This corresponds to the listed value 2.82 BM. The other values do not correspond to the two unpaired electrons of this complex; square-planar pairing must not be applied to this chloride complex.

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

Quick Tip to Solve: For $[\text{NiCl}_4]^{2-}$, first identify tetrahedral d^8 with two unpaired electrons, then insert $n = 2$ into the spin-only formula.

6. Which of the following ions has the electronic configuration $3d^6$? (Atomic number : Mn = 25, Co = 27, Ni = 28)

[1 mark]

- (A) Ni^{3+}
- (B) Co^{3+}
- (C) Mn^{2+}
- (D) Mn^{3+}

Correct Answer: (B) Co^{3+}

Solution:

Concept:

- Transition-metal cations lose their $4s$ electrons before their $3d$ electrons, although the $4s$ orbital fills first in the neutral atom.

Quick Tip to Solve: Remove both $4s$ electrons first: cobalt starts with seven $3d$ electrons, so its third ionisation leaves six.

- Neutral manganese, cobalt and nickel have the configurations $[\text{Ar}] 3d^5 4s^2$, $[\text{Ar}] 3d^7 4s^2$ and $[\text{Ar}] 3d^8 4s^2$, respectively.

Step 1: Determine the cobalt ion configuration To form Co^{3+} , remove the two $4s$ electrons and one $3d$ electron from cobalt. The resulting configuration is $[\text{Ar}] 3d^6$, as required.

Step 2: Check the remaining printed ions The same removal rule gives Ni^{3+} the configuration $[\text{Ar}] 3d^7$. For Mn^{2+} , only the two $4s$ electrons are removed, leaving $[\text{Ar}] 3d^5$; removing one further electron gives Mn^{3+} the configuration $[\text{Ar}] 3d^4$. Thus (A), (C) and (D) do not have six d electrons.

Step 3: Conclusion Co^{3+} has the electronic configuration $[\text{Ar}] 3d^6$. Hence, the correct option is (B).

Quick Tip to Solve: Remove both $4s$ electrons first: cobalt starts with seven $3d$ electrons, so its third ionisation leaves six.

7. Which of the following aqueous solution will have highest boiling point ?

[1 mark]

- (A) 1.0 M KCl
- (B) 1.0 M K_2SO_4
- (C) 2.0 M KCl
- (D) 2.0 M K_2SO_4

Correct Answer: (D) 2.0 M K_2SO_4

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 is the solvent's ebullioscopic constant and m is molality.
- Under the usual ideal-electrolyte comparison, a larger concentration of dissolved particles produces a larger boiling-point elevation in the same solvent.

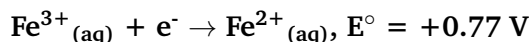
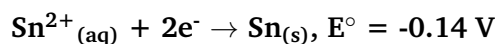
Step 1: Count the ions formed by each electrolyte Potassium chloride dissociates as $\text{KCl} \longrightarrow \text{K}^+ + \text{Cl}^-$, giving $i = 2$. Potassium sulphate dissociates as $\text{K}_2\text{SO}_4 \longrightarrow 2\text{K}^+ + \text{SO}_4^{2-}$, giving $i = 3$ for complete dissociation.

Step 2: Compare the particle concentrations For the intended comparison using the given molar concentrations, multiply each concentration by its ion count. The relative particle concentrations for (A), (B), (C) and (D) are respectively $2 \times 1 = 2$, $3 \times 1 = 3$, $2 \times 2 = 4$ and $3 \times 2 = 6$. Option (D) therefore gives the greatest particle concentration; the other three yield smaller elevations.

Step 3: Conclusion The 2.0 M aqueous K_2SO_4 solution has the highest boiling point. Hence, the correct option is (D).

Quick Tip to Solve: For this electrolyte comparison, count two ions for KCl and three for K_2SO_4 , then multiply by the given concentration.

8. A voltaic cell is made by connecting two half cells represented by half equations below:



Which statement is correct about this voltaic cell ?

[1 mark]

- (A) Fe^{2+} is oxidised and the voltage of the cell is -0.91 V
(B) Sn is oxidised and the voltage of the cell is 0.91 V
(C) Fe^{2+} is oxidised and the voltage of the cell is 0.91 V
(D) Sn is oxidised and the voltage of the cell is 0.63 V

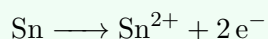
Correct Answer: (B) Sn is oxidised and the voltage of the cell is 0.91 V

Solution:

Concept:

- In a spontaneous voltaic cell, the half-cell with the higher standard reduction potential undergoes reduction at the cathode.
- The standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, using reduction potentials for both electrodes.

Step 1: Identify oxidation and reduction Since +0.77 V exceeds -0.14 V, Fe^{3+} is reduced to Fe^{2+} . The tin half-reaction reverses, so tin is oxidised:



Combining it with twice the iron reduction gives $\text{Sn} + 2\text{Fe}^{3+} \longrightarrow \text{Sn}^{2+} + 2\text{Fe}^{2+}$. Thus options (A) and (C), which oxidise Fe^{2+} , are inconsistent with the spontaneous direction.

Step 2: Calculate the cell potential Subtract the anode reduction potential without multiplying potentials by electron coefficients:

$$E^{\circ}_{\text{cell}} = 0.77 - (-0.14) = 0.91 \text{ V}.$$

The positive value confirms spontaneity. Option (D) incorrectly adds the signed reduction potentials and obtains 0.63 V.

Step 3: Conclusion Tin is oxidised and the standard cell voltage is 0.91 V. Hence, the correct option is (B).

Quick Tip to Solve: Choose the more positive reduction potential as the cathode, then subtract the other value with its sign intact.

9. Amides can be converted into amines by the reaction named

[1 mark]

- (A) Hoffmann degradation
- (B) Ammonolysis
- (C) Carbylamine
- (D) Diazotisation

Correct Answer: (A) Hoffmann degradation

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine using bromine and aqueous alkali.
- The product amine contains one carbon atom fewer than the starting amide because its carbonyl carbon is lost.

Step 1: Recognise the amide-to-amine reaction For an amide RCONH_2 , where R is an alkyl or aryl group, bromine and sodium hydroxide give RNH_2 :



For example, ethanamide gives methanamine, illustrating the loss of the carbonyl carbon.

Step 2: Distinguish the other named reactions Ammonolysis commonly prepares amines from alkyl halides and ammonia, not from amides. The carbylamine reaction converts primary amines into isocyanides and is used as their test. Diazotisation converts a primary aromatic amine into a diazonium salt under cold acidic conditions. These do not describe the stated conversion.

Step 3: Conclusion The named conversion is Hoffmann degradation, conventionally called Hofmann bromamide degradation. Hence, the correct option is (A).

Quick Tip to Solve: Link an amide becoming an amine with one fewer carbon to the bromine-and-alkali Hofmann reaction.

10. Which of the following statements is not true about glucose ?

[1 mark]

- (A) It is an aldohexose.
- (B) On heating with HI it forms n-hexane.
- (C) It is present in pyranose form.
- (D) It gives 2, 4 DNP test.

Correct Answer: (D) It gives 2, 4 DNP test.

Solution:

Concept:

- Glucose is an aldohexose: its open-chain structure has six carbon atoms and an aldehyde group.
- Glucose exists predominantly as cyclic hemiacetal forms; its usual six-membered ring is called the pyranose form.

Quick Tip to Solve: For glucose, distinguish the open-chain aldehyde classification from tests suppressed by its predominant cyclic hemiacetal structure.

Step 1: Verify the structural statements Statement (A) is true because glucose is a six-carbon aldose. Prolonged heating with HI yields n-hexane, supporting an unbranched chain of six carbon atoms, so (B) is true. Its aldehyde group reacts internally with a hydroxyl group to form a cyclic hemiacetal, and the stable pyranose forms make (C) true.

Step 2: Check the carbonyl test The 2,4-dinitrophenylhydrazine test ordinarily detects free aldehyde or ketone groups by forming a hydrazone precipitate. Glucose does not give this test under the usual test conditions: its carbonyl group is predominantly tied up in the cyclic hemiacetal form. Thus the claim in (D) is false, even though glucose is classified as an aldohexose from its open-chain structure.

Step 3: Conclusion The statement that glucose gives the 2,4-DNP test is not true. Hence, the correct option is (D).

Quick Tip to Solve: For glucose, distinguish the open-chain aldehyde classification from tests suppressed by its predominant cyclic hemiacetal structure.

11. 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 a primary or secondary alcohol removes hydrogen from the hydroxyl group and from the carbon bearing that group to form a carbonyl compound.
- A tertiary alcohol has no hydrogen on the carbon bonded to the hydroxyl group, so it resists ordinary oxidation without carbon-carbon bond cleavage.

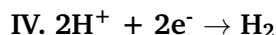
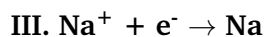
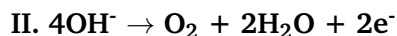
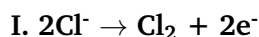
Step 1: Classify the alcohols Butanol, understood here as butan-1-ol, is primary and can be oxidised to butanal and then butanoic acid. Butan-2-ol is secondary and gives butan-2-one. In 3-methylbutan-2-ol, the hydroxyl-bearing carbon remains secondary and has one hydrogen, so this alcohol can also be oxidised to a ketone.

Step 2: Inspect the hydroxyl-bearing carbon in option (C) The condensed structure of 2-methylbutan-2-ol is $\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{CH}_3$. Its hydroxyl-bearing carbon is attached to three carbon groups and has no hydrogen. It is therefore tertiary and does not undergo the usual alcohol-to-carbonyl oxidation. Very vigorous conditions can break carbon-carbon bonds, but that is different from ordinary alcohol oxidation.

Step 3: Conclusion 2-Methylbutan-2-ol resists ordinary oxidation. Hence, the correct option is (C).

Quick Tip to Solve: Count hydrogens on the carbon directly attached to the hydroxyl group; zero identifies a tertiary alcohol resistant to normal oxidation.

12. 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

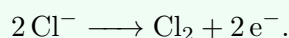
Correct Answer: (B) I and IV

Solution:

Concept:

- In electrolysis of concentrated aqueous sodium chloride, chlorine is liberated at the anode and hydrogen at the cathode.
- Electrode products depend on reduction potentials, concentrations and overpotentials; water is reduced in preference to aqueous sodium ions.

Step 1: Select the anode process High chloride concentration and the overpotential for oxygen evolution favour chloride oxidation:



This is reaction I. The oxygen-evolution process represented by II is not the favoured anode process in concentrated brine. Also, the printed equation II has an electron-balance error: the balanced oxygen half-reaction would release four electrons, not two.

Step 2: Select the cathode process Aqueous Na^+ is not discharged as sodium metal; instead water is reduced to hydrogen:



Among the supplied choices, IV represents hydrogen evolution in its proton form. Thus III is excluded, eliminating (A) and (C); (D) has the wrong anode process. The solution becomes alkaline because hydroxide ions remain with sodium ions.

Step 3: Conclusion The appropriate listed pair is I and IV, corresponding to chlorine 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; sodium metal is obtained from the molten salt.

13. 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:

- A catalyst increases the rate by providing a reaction pathway with lower activation energy and is regenerated overall.
- Transition metals can adopt several oxidation states because electrons in their d and outer s orbitals can participate in bonding.

Step 1: Connect oxidation states with catalytic action A transition-metal species can accept electrons in one step and donate them in another. By cycling between accessible oxidation states, it forms intermediate species and transfers electrons between reactants. The catalyst returns to its original state when the cycle finishes. This explains why variable oxidation states promote catalytic behaviour.

Step 2: Eliminate unrelated properties A high melting point may allow operation at elevated temperature, but it does not explain a lower-energy reaction pathway. High ionisation enthalpy likewise does not itself create a catalytic cycle. Alloy formation describes mixing metals in the solid state, not the characteristic electron-transfer ability asked for here. Thus (A), (B) and (C) are not the relevant property.

Step 3: Conclusion Variable oxidation states enable the catalytic action described. Hence, the correct option is (D).

Quick Tip to Solve: When catalytic activity is linked to transition metals, look for their ability to change oxidation state and return to the starting state.

14. 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:

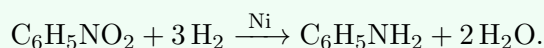
Concept:

- Reduction of nitrobenzene to aniline changes the nitro group into an amino group while retaining the benzene ring.
- Catalytic hydrogenation and metals in acidic medium are standard methods for reducing aromatic

Quick Tip to Solve: For nitrobenzene to aniline, choose hydrogen with a metal catalyst or iron/tin with acid; do not select a reagent only because it is strongly reducing.

nitro compounds to primary aromatic amines.

Step 1: Identify the suitable reagents Hydrogen with nickel catalyses the reduction:



Iron with hydrochloric acid and tin with hydrochloric acid also reduce the nitro group effectively. In acidic medium the amine is present as an anilinium salt; subsequent treatment with alkali releases aniline. Therefore (B), (C) and (D) are suitable choices.

Step 2: Distinguish the hydride reagent Although LiAlH_4 is a powerful reducing agent for many functional groups, it is not the standard suitable choice for selectively preparing aniline from nitrobenzene in this comparison. Reduction of aromatic nitro compounds with it can lead to azo products such as azobenzene rather than the desired primary amine. A strong reducing agent is not automatically the right selective reagent for every substrate.

Step 3: Conclusion LiAlH_4 would not be a good choice among the listed reagents. Hence, the correct option is (A).

Quick Tip to Solve: For nitrobenzene to aniline, choose hydrogen with a metal catalyst or iron/tin with acid; do not select a reagent only because it is strongly reducing.

15. Assertion (A): Vitamin C cannot be stored in our body.

Reason (R): Vitamin C is fat soluble and is excreted from the body in urine.

[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:

- Water-soluble vitamins dissolve in body fluids, and excess amounts are eliminated in urine.
- Vitamin C (ascorbic acid) is water soluble; vitamins A, D, E and K are fat soluble.

Step 1: Evaluate the assertion Vitamin C is not stored in appreciable amounts in the body and must be supplied regularly in the diet. Thus, the assertion is true in the standard classification of vitamins.

Step 2: Evaluate the reason The reason calls vitamin C fat soluble, which is incorrect. Vitamin C is water soluble. Although excess vitamin C is excreted in urine, the complete reason is false because its solubility statement is wrong.

Step 3: Check the explanatory link A false reason cannot explain a true assertion. Options (A) and (B) incorrectly regard the reason as true, while (D) incorrectly regards the assertion as false. Water

Quick Tip to Solve: Remember A, D, E and K as the fat-soluble vitamins; vitamin C belongs to the water-soluble group.

solubility, rather than fat solubility, explains why a regular dietary supply is needed.

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

Quick Tip to Solve: Remember A, D, E and K as the fat-soluble vitamins; vitamin C belongs to the water-soluble group.

16. Assertion (A): The half life of a reaction is the time in which the concentration of the reactant is reduced to one half of its initial concentration.

Reason (R): In first order kinetics when concentration of reactant is doubled, its half life is doubled.

[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:

- Half-life, $t_{1/2}$, is the time required for the reactant concentration to fall from its initial value $[A]_0$ to $[A]_0/2$.
- For a first-order reaction, $t = (1/k) \ln([A]_0/[A]_t)$, where k is the rate constant and $[A]_t$ is the concentration at time t .

Step 1: Evaluate the assertion The assertion gives the definition of half-life exactly: after one half-life, half of the initial reactant concentration remains. Therefore the assertion is true.

Step 2: Evaluate the reason Substitute $[A]_t = [A]_0/2$ into the integrated first-order rate equation:

$$t_{1/2} = \frac{1}{k} \ln \frac{[A]_0}{[A]_0/2} = \frac{\ln 2}{k} = \frac{0.693}{k}.$$

The initial concentration cancels. At fixed temperature, doubling it leaves the half-life unchanged, so the reason is false.

Step 3: Check the explanatory link Since the reason is false, it cannot explain the assertion. Options (A) and (B) wrongly take the reason as true; option (D) wrongly takes the definition in the assertion as false.

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

Quick Tip to Solve: For first-order half-life questions, write $t_{1/2} = 0.693/k$ before considering any change in initial concentration.

17. Assertion (A): Bromination of benzoic acid gives m-bromobenzoic acid.

Reason (R): Carboxyl group increases the electron density at the meta position.

[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:

- Electrophilic aromatic substitution is directed by the substituent already present on the benzene ring.
- The carboxyl group, $-\text{COOH}$, withdraws electrons through both inductive and resonance effects; it deactivates the ring and directs further substitution mainly to the meta position.

Step 1: Evaluate the assertion In benzoic acid, the electron-withdrawing $-\text{COOH}$ group is meta directing. Therefore bromination gives m-bromobenzoic acid as the major substitution product, and the assertion is true.

Step 2: Evaluate the reason The carboxyl group does not increase the ring's electron density. It withdraws electron density, with the ortho and para positions more strongly depleted by resonance. The meta position is relatively less electron deficient; this is different from an increase in its absolute electron density. Thus the reason is false.

Step 3: Check the explanatory link A false statement cannot explain the observed directing effect. Options (A) and (B) fail because they treat the reason as true, while option (D) fails because the assertion correctly identifies the major product.

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

Quick Tip to Solve: A meta-directing electron-withdrawing group makes meta relatively less depleted; do not describe it as donating electrons to meta.

18. Assertion (A): EDTA is a hexadentate ligand.

Reason (R): EDTA has 2 nitrogen and 4 oxygen donor atoms.

[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:

- Denticity is the number of donor atoms of a single ligand that can bond simultaneously to the same central metal ion.
- The ethylenediaminetetraacetate ion, EDTA^{4-} , contains two amine nitrogen donor atoms and four carboxylate oxygen donor atoms.

Step 1: Evaluate the assertion EDTA can bind a metal ion through six donor atoms in its usual chelating mode. A ligand with six such attachment sites is called hexadentate. Therefore the assertion is true.

Step 2: Evaluate the reason The ligand has two nitrogen atoms, each donating a lone pair, and four carboxylate groups, each supplying one oxygen donor atom. Thus the number of donor sites is $2 + 4 = 6$, and the reason is true.

Step 3: Check the explanatory link The count of six donor atoms directly explains the term hexadentate. Option (B) wrongly denies this connection, while (C) and (D) each incorrectly label one of the true statements as false. Count coordinating donor atoms, not all atoms in the ligand.

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

Quick Tip to Solve: For EDTA, count two nitrogen donors plus one oxygen from each of four carboxylate groups: six donor sites.

Section B (14 marks)

19. (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 acts as a Lewis base by donating an available lone pair of electrons to a metal ion to form a coordinate bond.
- Linkage isomers arise when an ambidentate ligand bonds through different donor atoms. The nitrite ion, NO_2^- , can coordinate through nitrogen or oxygen.

Step 1: Identify the species without a donor lone pair (a) In NH_4^+ , nitrogen forms four bonds and has no available lone pair for donation. Hence it cannot act as a ligand. In contrast, OH^- and H_2O possess oxygen lone pairs, while CH_3NH_2 has a nitrogen lone pair; all three can donate an electron pair to a metal ion.

Step 2: Identify and name the linkage isomer (b) The red complex contains the oxygen-bonded nitrito form, represented more explicitly as $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$. Its linkage isomer has nitrogen-bonded nitrite, $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$, and is yellow. The two chloride counter-ions give the complex ion a charge of +2. If cobalt has oxidation state x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The requested name is **pentaamminenitrito-N-cobalt(III) chloride** (also called pentaamminenitrocobalt(III) chloride).

Step 3: Conclusion (a) NH_4^+ cannot act as a ligand because it has no available lone pair. (b) The linkage isomer is pentaamminenitrito-N-cobalt(III) chloride, the nitrogen-bonded form.

Quick Tip to Solve: Use the red colour to identify O-bonded nitrito; its linkage isomer is N-bonded. Keep five ammine ligands and cobalt(III) unchanged.

20. 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.

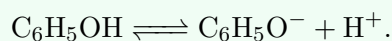
[2 marks]

Solution:

Concept:

- Acid strength depends on the stability of the conjugate base formed after loss of H^+ ; greater conjugate-base stability favours ionisation.
- Phenol gives a violet colour with neutral aqueous ferric chloride, FeCl_3 , because it forms a coloured iron(III) complex.

Step 1: Compare the conjugate bases (a) Phenol loses a proton to give the phenoxide ion:



Quick Tip to Solve: Compare the ions left after removing H^+ ; for identification, pair phenol with the violet neutral ferric chloride test.

In phenoxide, the negative charge is delocalised by resonance between oxygen and the aromatic ring, stabilising the ion. Cyclohexanol gives cyclohexoxide, whose negative charge remains localised on oxygen because the saturated ring has no conjugated system. The electron-releasing alkyl group also destabilises the negative charge. Thus proton loss is easier from phenol.

Step 2: Apply the neutral ferric chloride test (b) Add a few drops of neutral aqueous FeCl_3 solution to separate samples. Phenol produces a violet coloration due to complex formation with iron(III). Cyclohexanol gives no such violet coloration, so the two samples can be distinguished by this observation.

Step 3: Conclusion Phenol is more acidic because its conjugate base is resonance stabilised. With neutral FeCl_3 , phenol gives a violet colour, whereas cyclohexanol does not.

Quick Tip to Solve: Compare the ions left after removing H^+ ; for identification, pair phenol with the violet neutral ferric chloride test.

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

(ii) How can the activating effect of $-\text{NH}_2$ group in aniline be controlled ?

[2 marks]

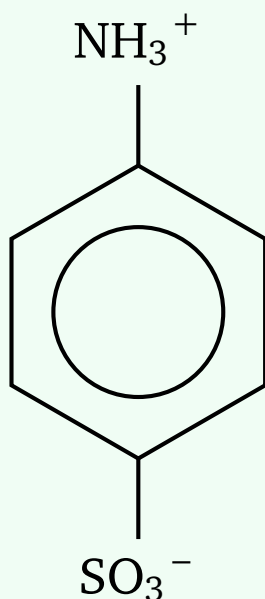
Solution:

Concept:

- A zwitterion contains both positive and negative charges within the same molecule but has no net charge.
- Acetylation converts the strongly activating amino group of aniline into an acetamido group, whose nitrogen lone pair is less available to the benzene ring.

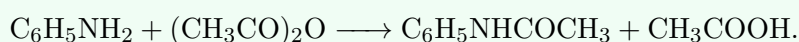
Step 1: (i) Transfer the acidic proton to the amino group Sulphanilic acid has an amino group and a sulphonic acid group at para positions. Transfer of the acidic proton from $-\text{SO}_3\text{H}$ to $-\text{NH}_2$ produces $-\text{SO}_3^-$ and $-\text{NH}_3^+$, respectively. Thus its zwitterion is $^+\text{H}_3\text{N}-\text{C}_6\text{H}_4-\text{SO}_3^-$, with the two substituents opposite one another on the ring, as drawn below. The charges cancel overall; the molecule is an internal salt.

Quick Tip to Solve: In the zwitterion, move the proton from sulphonic acid to nitrogen; keep the two groups para and retain both opposite charges.



Zwitterion of sulphanilic acid: para ammonium and sulphonate groups

Step 2: (ii) Protect the amino group by acetylation Treat aniline with acetic anhydride to form acetanilide:



The nitrogen lone pair is now delocalised towards the carbonyl group as well as the ring. Its donation to the ring decreases, so the activating effect is controlled and excessive substitution is reduced. The protecting acetyl group can subsequently be removed by hydrolysis.

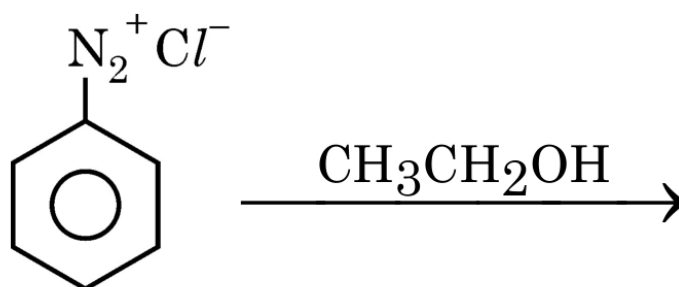
Step 3: Conclusion (i) The zwitterion is para- $^+\text{H}_3\text{N}-\text{C}_6\text{H}_4-\text{SO}_3^-$. (ii) Control activation by acetylating aniline to acetanilide.

Quick Tip to Solve: In the zwitterion, move the proton from sulphonic acid to nitrogen; keep the two groups para and retain both opposite charges.

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

(ii) Convert Bromoethane to Propanamine.

[2 marks]

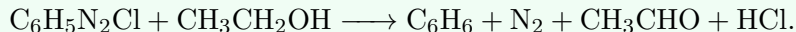


Solution:

Concept:

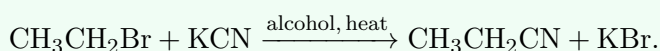
- Ethanol reduces an aromatic diazonium salt by replacing its diazonium group with hydrogen; nitrogen gas is liberated.
- Substitution with alcoholic potassium cyanide extends an alkyl chain by one carbon, and reduction of the nitrile gives a primary amine.

Step 1: (i) Replace the diazonium group by hydrogen The printed reactant is benzenediazonium chloride and the reagent is ethanol. Ethanol supplies hydrogen and is itself oxidised to ethanal. The balanced reaction is



The main organic product formed from the aromatic substrate is benzene. This is reduction of the diazonium group, rather than substitution by an ethoxy group.

Step 2: (ii) Add one carbon and reduce the nitrile Bromoethane contains two carbons whereas propanamine contains three. First heat bromoethane with alcoholic KCN; the carbon of the cyanide group becomes the third carbon:



Reduce the resulting propanenitrile with LiAlH_4 in dry ether, followed by hydrolysis:



The nitrile carbon remains in the chain and becomes the carbon bonded to the amino group, giving propan-1-amine.

Step 3: Conclusion (i) The main product is benzene, C_6H_6 . (ii) Use alcoholic KCN, then LiAlH_4 in dry ether followed by hydrolysis, to convert bromoethane through propanenitrile into propan-1-amine.

Quick Tip to Solve: For a primary amine with one more carbon than the haloalkane, use KCN followed by nitrile reduction; direct ammonia substitution does not extend the chain.

22. Write equations for the following:

(a) Oxidation of chloroform by air and light

(b) Reaction of chlorobenzene with CH_3Cl / anhyd. AlCl_3

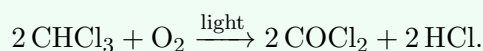
[2 marks]

Solution:

Concept:

- Chloroform undergoes oxidation by oxygen in air in the presence of light to form carbonyl chloride, also called phosgene.
- Chlorine deactivates a benzene ring by its inductive effect but directs electrophilic substitution to the ortho and para positions through resonance donation.

Step 1: (a) Write the oxidation equation Oxygen converts chloroform into phosgene with elimination of hydrogen chloride. The balanced equation is



Both sides contain two carbon atoms, two hydrogen atoms, six chlorine atoms and two oxygen atoms. The product COCl_2 is highly poisonous; this oxidation explains why chloroform is stored in dark bottles protected from air and light.

Step 2: (b) Carry out Friedel–Crafts methylation Anhydrous AlCl_3 activates methyl chloride for electrophilic substitution. Methyl substitution occurs at the ortho and para positions relative to chlorine, giving the corresponding chlorotoluenes. Each equation represents one of the alternative product pathways:



Para-chlorotoluene is the major product because substitution there suffers less steric crowding than substitution next to chlorine. The existing carbon–chlorine bond is retained.

Step 3: Conclusion (a) Chloroform gives phosgene and hydrogen chloride on oxidation by air and light. (b) Chlorobenzene gives ortho- and para-chlorotoluene, with the para isomer predominating, on methylation with CH_3Cl /anhydrous AlCl_3 .

Quick Tip to Solve: For halobenzenes, separate reactivity from direction: chlorine deactivates the ring but still directs incoming methyl groups ortho and para.

23. 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 k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.

Quick Tip to Solve: Read heating as increasing the number of molecules above the barrier, and catalysis as providing a different barrier; do not confuse their effects on E_a .

- Activation energy is the energy barrier for the reaction pathway. Raising temperature changes the fraction of molecules able to cross this barrier.

Step 1: Determine how the rate constant changes For a given reaction with positive activation energy, increasing T makes the exponent $-E_a/(RT)$ less negative. Therefore the exponential factor and hence k increase. For two temperatures $T_2 > T_1$, the usual Arrhenius treatment gives

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) > 0,$$

so $k_2 > k_1$. Physically, a greater fraction of molecules has energy at least equal to the activation barrier, producing more effective collisions.

Step 2: Distinguish the barrier from molecular energy The activation energy remains unchanged for the same reaction pathway in the usual temperature range. Heating raises the molecular energies; it does not itself lower the energy difference between the reactants and the activated complex. A catalyst can change the pathway and its activation barrier, but simply increasing the temperature does not have that effect.

Step 3: Conclusion The rate constant k increases with temperature, while the activation energy E_a remains unchanged for the same reaction pathway. The increase in rate occurs because more molecules can overcome the existing barrier.

Quick Tip to Solve: Read heating as increasing the number of molecules above the barrier, and catalysis as providing a different barrier; do not confuse their effects on E_a .

24(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:

- Under standard conditions, a redox reaction is spontaneous in the forward direction when its standard Gibbs energy change is negative: $\Delta G^\circ < 0$.
- The relation $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ connects Gibbs energy and cell potential; n is the number of electrons transferred and F is the Faraday constant.
- The charge passed by a constant current I in time t is $Q = It$.

Step 1: (i) Determine the signs from the energy relation Both n and F are positive. Therefore, the minus sign in $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ makes the two quantities opposite in sign. A spontaneous standard-state reaction requires $\Delta G^\circ < 0$, so its standard cell potential must satisfy $E^\circ_{\text{cell}} > 0$. Zero potential would correspond to equilibrium, not a spontaneous forward reaction.

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

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

Quick Tip to Solve: Use the minus sign in $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ to fix the signs, and remember that electrolysis depends on total charge It , not current alone.

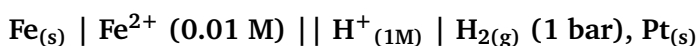
Here m is the deposited or liberated mass and Z is the electrochemical equivalent, namely the mass deposited by unit charge. Thus, for the same substance, doubling the charge doubles the deposited mass.

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

Quick Tip to Solve: Use the minus sign in $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$ to fix the signs, and remember that electrolysis depends on total charge It , not current alone.

OR

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



Given $E_{\text{cell}}^{\circ} = 0.44 \text{ V}$.

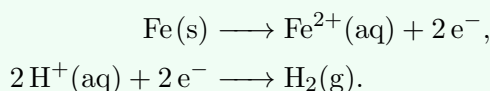
[2 marks]

Solution:

Concept:

- For a cell reaction transferring n electrons, the Nernst equation at 298 K is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0591/n) \log Q$, where Q is the dimensionless reaction quotient and potentials are in volts.
- Pure solids have unit activity; dilute-solution activities are approximated by concentrations relative to 1 M, and gas activity by pressure relative to 1 bar.

Step 1: Write the half-reactions and reaction quotient The left electrode undergoes oxidation, while hydrogen ions are reduced at the right electrode:



Thus the overall reaction is $\text{Fe}_{(\text{s})} + 2\text{H}^{+}(\text{aq}) \longrightarrow \text{Fe}^{2+}(\text{aq}) + \text{H}_{2(\text{g})}$, and $n = 2$. Iron and platinum do not enter the quotient. With the given pressure and concentrations,

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

Step 2: Substitute in the Nernst equation Using the supplied standard emf directly and $\log(0.01) = -2$,

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

The low concentration of the product ion increases the forward driving force, so an emf greater than the standard value is consistent with the reaction.

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

Quick Tip to Solve: Write the cell reaction before forming Q : iron(II) is a product, so its concentration goes in the numerator and the two hydrogen ions give a squared denominator.

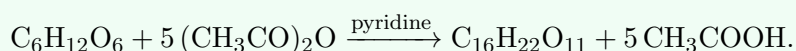
25. Give the reaction of glucose with acetic anhydride. Presence of which group is confirmed by this reaction ? [2 marks]

Solution:

Concept:

- Acetic anhydride acetylates an alcohol group: the hydrogen of —OH is replaced by an acetyl group, giving an ester group —OCOCH_3 .
- Glucose contains five hydroxyl groups. Their acetylation gives glucose pentaacetate, so the number of acetyl groups identifies the number of hydroxyl groups present.

Step 1: Write the acetylation reaction On treatment with excess acetic anhydride, usually in pyridine, glucose forms glucose pentaacetate. The overall reaction can be written using molecular formulae as



Here $\text{C}_{16}\text{H}_{22}\text{O}_{11}$ is glucose pentaacetate. Each of the five hydroxyl groups becomes an acetate ester group; one molecule of acetic acid is formed for each hydroxyl group acetylated.

Step 2: Identify the functional group confirmed Formation of a pentaacetate shows that glucose has five acetylatable —OH groups. These hydroxyl groups are attached to five different carbon atoms. The reaction tests the hydroxyl groups because acetylation occurs at their oxygen atoms; this observation is not a test for the aldehyde group. The prefix “penta” records the participation of all five hydroxyl groups.

Step 3: Conclusion Glucose reacts with acetic anhydride to form glucose pentaacetate. This confirms the presence of **five hydroxyl groups** in glucose.

Quick Tip to Solve: Link “pentaacetate” to five original —OH groups: each acetylated hydroxyl group produces one ester group and one molecule of acetic acid.

Section C (15 marks)

26(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:

- Resonance delocalisation of an oxygen lone pair into an aromatic ring gives the aryl carbon–oxygen bond partial double-bond character, making it shorter than an ordinary single bond.
- For molecules of comparable size, stronger intermolecular attractions generally raise the boiling point: hydrogen bonding is stronger than ordinary dipole–dipole attractions, which add to dispersion forces.
- Hot concentrated hydrogen iodide cleaves an aryl alkyl ether at the alkyl carbon–oxygen bond,

Quick Tip to Solve: For anisole, preserve the aryl–oxygen bond and break the methyl–oxygen bond. For the boiling-point comparison, identify the nonpolar compound, the carbonyl dipole and the hydrogen-bond donor.

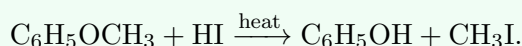
yielding a phenol and an alkyl iodide.

Step 1: (i) Explain the shorter carbon–oxygen bond in phenol In phenol, an oxygen lone pair overlaps with the conjugated aromatic system. Resonance structures therefore give the bond between oxygen and the ring carbon partial double-bond character. In methanol, CH_3OH , this delocalisation is absent, so its carbon–oxygen bond remains an ordinary single bond. Also, oxygen is bonded to an sp^2 -hybridised carbon in phenol but an sp^3 -hybridised carbon in methanol; the greater s -character of the former favours a shorter bond.

Step 2: (ii) Compare the intermolecular forces Nonpolar n -butane has only weak dispersion forces and boils first. Ethoxyethane is polar and has dipole–dipole attractions, but no hydroxyl group to form hydrogen bonds between its own molecules. Butanal has a more strongly polar carbonyl group, giving stronger dipole attractions. Butanol forms intermolecular hydrogen bonds through its hydroxyl group and has the highest boiling point. Hence the increasing order is



Step 3: (iii) Cleave anisole with hydrogen iodide Heat anisole with concentrated HI:



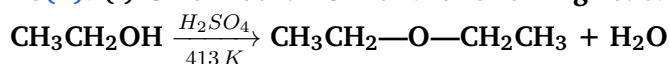
Protonation of the ether oxygen is followed by attack of iodide on the methyl carbon through an S_N2 step. The methyl–oxygen bond breaks, producing phenol and methyl iodide. The aryl–oxygen bond is not cleaved because it has partial double-bond character and an sp^2 aryl carbon does not undergo the ordinary S_N2 displacement.

Step 4: Conclusion (i) Resonance gives phenol's carbon–oxygen bond partial double-bond character and reduces its length. (ii) n -butane < ethoxyethane < butanal < butanol. (iii) Anisole gives phenol and CH_3I on heating with concentrated HI.

Quick Tip to Solve: For anisole, preserve the aryl–oxygen bond and break the methyl–oxygen bond. For the boiling-point comparison, identify the nonpolar compound, the carbonyl dipole and the hydrogen-bond donor.

OR

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



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

[3 marks]

Solution:

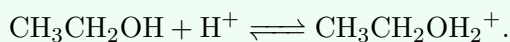
Concept:

- Concentrated H_2SO_4 catalyses intermolecular dehydration of ethanol at 413 K. Protonation converts the poor leaving group —OH into water.
- A second ethanol molecule acts as the nucleophile. A primary alcohol forms ether through substitution without a free primary carbocation.

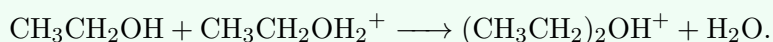
Quick Tip to Solve: For ethanol at 413 K, show attack by a second alcohol molecule to obtain ether. For hydroboration–oxidation, place OH on the less substituted alkene carbon.

- Hydroboration followed by alkaline peroxide oxidation converts an alkene into an anti-Markovnikov alcohol: the hydroxyl group enters at the less substituted carbon.

Step 1: (i) Protonate the ethanol oxygen An oxygen lone pair of ethanol accepts a proton supplied by the acid. This produces protonated ethanol, in which water is a good leaving group:



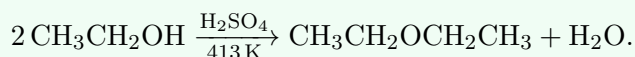
Step 2: Allow a second ethanol molecule to attack The oxygen lone pair of unprotonated ethanol attacks the primary carbon of protonated ethanol. The carbon–oxygen bond to the leaving water breaks simultaneously, giving protonated diethyl ether in an S_N2 step:



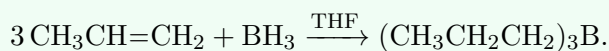
Step 3: Remove the proton to regenerate the catalyst Loss of a proton from the oxonium ion gives neutral ether and regenerates the acid catalyst:



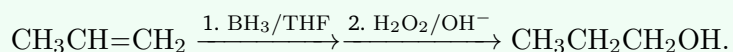
Adding the steps gives the balanced overall dehydration:



Step 4: (ii) Illustrate hydroboration–oxidation using propene Borane in tetrahydrofuran (THF) adds with boron at the less substituted carbon. Three propene molecules form a trialkylborane:



Alkaline peroxide oxidation replaces carbon–boron bonds by carbon–oxygen bonds, giving propan-1-ol:



Step 5: Conclusion (i) Protonation, nucleophilic substitution by ethanol and deprotonation produce diethyl ether at 413 K. (ii) Hydroboration–oxidation of propene gives propan-1-ol, the anti-Markovnikov alcohol.

Quick Tip to Solve: For ethanol at 413 K, show attack by a second alcohol molecule to obtain ether. For hydroboration–oxidation, place OH on the less substituted alkene carbon.

27. (a) On the basis of crystal field theory write the electronic configuration for d^5 ion with a weak ligand for which $\Delta_o < P$.

(b) Explain $[\text{Fe}(\text{CN})_6]^{3-}$ is an inner orbital complex whereas $[\text{FeF}_6]^{3-}$ is an outer orbital complex.

[Atomic number : Fe = 26]

[3 marks]

Solution:

Concept:

- In an octahedral crystal field, the five d orbitals split into three lower-energy t_{2g} orbitals and two higher-energy e_g orbitals. The energy separation is Δ_o .
- If $\Delta_o < P$, where P is the electron-pairing energy, electrons occupy the upper orbitals singly before pairing in the lower orbitals. This gives a high-spin complex.
- In valence bond theory, inner orbital octahedral complexes use $(n-1)d$ orbitals for d^2sp^3 hybridisation, whereas outer orbital complexes use nd orbitals for sp^3d^2 hybridisation.

Step 1: (a) Distribute the five electrons for a weak ligand As the splitting is smaller than the pairing energy, promoting an electron to e_g costs less energy than pairing it in t_{2g} . Hund's rule therefore gives one electron in each of the five orbitals:

$$d^5 : (t_{2g})^3(e_g)^2.$$

All five electrons are unpaired. The t_{2g} orbitals contain three singly occupied states and the e_g orbitals contain two singly occupied states.

Step 2: (b) Find the metal oxidation state and configuration Each cyanide ion and each fluoride ion has charge -1 . In either complex, the oxidation state x of iron satisfies

$$x + 6(-1) = -3, \quad x = +3.$$

The neutral iron atom has configuration $[\text{Ar}] 3d^6 4s^2$. Removal of two $4s$ electrons and one $3d$ electron gives Fe^{3+} with configuration $[\text{Ar}] 3d^5$.

Step 3: Explain the inner orbital cyanide complex The ligand CN^- produces a strong field. Here $\Delta_o > P$, so electrons pair in the lower t_{2g} set, giving $(t_{2g})^5(e_g)^0$ with one unpaired electron. In the valence bond description, pairing leaves two inner $3d$ orbitals vacant. These two $3d$ orbitals, one $4s$ orbital and three $4p$ orbitals form six d^2sp^3 hybrid orbitals. Thus $[\text{Fe}(\text{CN})_6]^{3-}$ is an octahedral inner orbital complex.

Step 4: Explain the outer orbital fluoride complex The ligand F^- produces a weak field, so $\Delta_o < P$ and the configuration remains $(t_{2g})^3(e_g)^2$, with five unpaired electrons. No two inner $3d$ orbitals are available for accepting ligand electron pairs. The complex therefore uses one $4s$, three $4p$ and two outer $4d$ orbitals for sp^3d^2 hybridisation. Hence $[\text{FeF}_6]^{3-}$ is an octahedral outer orbital complex.

Step 5: Conclusion (a) The weak-field d^5 configuration is $(t_{2g})^3(e_g)^2$. (b) $[\text{Fe}(\text{CN})_6]^{3-}$ is low spin and inner orbital, with d^2sp^3 hybridisation; $[\text{FeF}_6]^{3-}$ is high spin and outer orbital, with sp^3d^2 hybridisation.

Quick Tip to Solve: Find Fe^{3+} , hence d^5 , first. Then use strong-field CN^- to pair electrons and weak-field F^- to retain five unpaired electrons.

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

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

[3 marks]

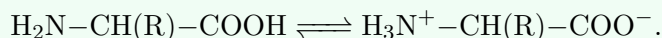
Solution:

Concept:

- Hydroxylamine, NH_2OH , reacts with a free aldehyde or ketone carbonyl group to form an oxime; a protected carbonyl group does not undergo this reaction.
- Amino acids contain both acidic carboxyl and basic amino groups. In the zwitterionic form they contain positive and negative charges within the same molecule.
- Vitamin requirements depend on storage and excretion. DNA strand sequences are related by specific complementary base pairing through hydrogen bonds.

Step 1: (a) Examine the functional group in glucose penta-acetate Glucose normally exists mainly in a cyclic hemiacetal form, which can open to provide the free aldehyde group needed for oxime formation. Acetylation of its five hydroxyl groups includes the anomeric hydroxyl group and locks the cyclic structure in an acetal-like form. Glucose penta-acetate therefore cannot open in the usual way to expose a free $-\text{CHO}$ group. Since the free aldehyde carbonyl is unavailable, it does not react with hydroxylamine to form an oxime.

Step 2: (b) Identify the ionic form of an amino acid The carboxyl group can donate a proton, and the amino group can accept it. Internal proton transfer produces a dipolar ion, or zwitterion:



Although the net charge is zero, the molecule has separate $-\text{NH}_3^+$ and $-\text{COO}-$ centres. Electrostatic attractions between such ions give amino acids salt-like properties, including high melting points and appreciable water solubility compared with similar non-ionic organic compounds.

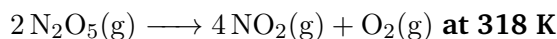
Step 3: (c) Relate regular vitamin intake to loss from the body Most water-soluble vitamins, such as vitamin C and many B-group vitamins, are not stored in large amounts. Excess quantities are readily eliminated in urine, so a large occasional intake does not generally maintain a lasting reserve. Regular dietary intake is therefore required to replenish losses and maintain their metabolic functions. Vitamin B_{12} , which can be stored substantially in the liver, is an exception to the general storage rule.

Step 4: (d) Apply the specific pairing rules in DNA The nitrogenous bases of opposite DNA strands pair specifically: adenine pairs with thymine through two hydrogen bonds, while guanine pairs with cytosine through three hydrogen bonds. Thus an adenine at any position on one strand requires thymine opposite it, and guanine requires cytosine. The sequence of either strand therefore determines the sequence of the other. The two strands run antiparallel, and each complementary pair contains one purine and one pyrimidine, maintaining the double helix's uniform width.

Step 5: Conclusion Glucose penta-acetate lacks a free aldehyde group; amino acids exist as zwitterions; most water-soluble vitamins require regular replenishment; and DNA strands are complementary because of specific adenine–thymine and guanine–cytosine pairing.

Quick Tip to Solve: Match each observation to its cause: free carbonyl availability, zwitterionic charges, limited vitamin storage, and specific DNA base pairing. Select any three complete explanations.

29. (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:

- The rate of reaction is the rate of disappearance or appearance of a species divided by its stoichiometric coefficient. This makes the reaction rate independent of the species selected.
- For a first order reaction, $t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations.

Step 1: (a) Relate the reaction rate to disappearance For $2\text{N}_2\text{O}_5(\text{g}) \longrightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$, the coefficient of N_2O_5 is 2. Therefore,

$$r = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{2}(1.4 \times 10^{-3}) = 7.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

The supplied disappearance rate is already positive, so no extra negative sign is attached to its numerical value. The temperature identifies the conditions at which this measured rate applies.

Step 2: (b) Express the time for 90 percent completion Let the initial concentration be a . At 90 percent completion the unreacted concentration is $0.10a$, not $0.90a$. The integrated first order equation gives

$$t_{90\%} = \frac{2.303}{k} \log_{10} \frac{a}{0.10a} = \frac{2.303}{k} \log_{10} 10 = \frac{2.303}{k}.$$

Step 3: Express the time for 99 percent completion At 99 percent completion only $0.01a$ remains. Using the same rate constant for the reaction at the same temperature,

$$t_{99\%} = \frac{2.303}{k} \log_{10} \frac{a}{0.01a} = \frac{2.303}{k} \log_{10} 100 = \frac{2(2.303)}{k}.$$

Hence $t_{99\%}/t_{90\%} = 2$. The initial concentration cancels in both expressions, as expected for the time required to complete a fixed fraction of a first order reaction.

Step 4: Conclusion (a) The rate of reaction is $7.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$. (b) For the first order reaction,

$$t_{99\%} = 2t_{90\%}.$$

Quick Tip to Solve: Divide a species disappearance rate by its balanced coefficient; in a completion-time formula insert the percentage remaining, not the percentage reacted.

30. (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.

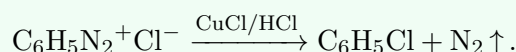
[3 marks]

Solution:

Concept:

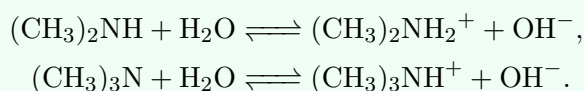
- In the Sandmeyer reaction, an aromatic diazonium group is replaced by chloride, bromide or cyanide using the corresponding copper(I) salt, with evolution of N_2 .
- Basicity in water depends on the availability of the nitrogen lone pair and the stability of the protonated amine in aqueous solution. Both the electron-releasing inductive effect and hydration must be considered.

Step 1: (a) Illustrate substitution of the diazonium group Benzenediazonium chloride reacts with cuprous chloride in hydrochloric acid to give chlorobenzene. An equation illustrating Sandmeyer's reaction is



Thus, the $-\text{N}_2^+$ group attached to the aromatic ring is replaced by chlorine. The copper reagent is copper(I) chloride; the nitrogen leaves as a gas.

Step 2: (b) Compare the protonated amines in water Dimethylamine and trimethylamine accept a proton using the lone pair on nitrogen:



The conjugate acid of dimethylamine has two N–H bonds, whereas that of trimethylamine has only one. The dimethylammonium ion is less sterically shielded and is hydrated more effectively by water through hydrogen bonding.

Step 3: Combine hydration with the inductive effect The three methyl groups of trimethylamine have a stronger combined electron-releasing $+I$ effect than the two methyl groups of dimethylamine. This effect alone would favour trimethylamine. In aqueous solution, however, the greater hydration and stabilization of $(\text{CH}_3)_2\text{NH}_2^+$ outweigh this advantage. Proton acceptance by dimethylamine is consequently more favourable, so its K_b is larger.

Step 4: Conclusion (a) Conversion of benzenediazonium chloride to chlorobenzene using CuCl/HCl illustrates the Sandmeyer reaction. (b) $(\text{CH}_3)_2\text{NH}$ is more basic than $(\text{CH}_3)_3\text{N}$ in water because its conjugate acid is better hydrated and stabilized.

Quick Tip to Solve: For aqueous methylamine basicity, compare the hydration of the protonated ions as well as the methyl groups' inductive effect; counting methyl groups alone gives the wrong order.

Section D (8 marks)

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

31. 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]

31(a). Why does conductivity decrease with dilution ?

[1 mark]

Solution:

Concept:

- Conductivity κ describes the ability of a solution of specified dimensions to conduct electric current through mobile ions.
- Conductivity depends on the number of charge carriers per unit volume as well as their mobilities; it differs from molar conductivity, which refers to one mole of electrolyte.

Step 1: Consider the effect of adding water Dilution distributes the dissolved K^+ and Cl^- ions through a larger volume of solution. Consequently, the number of ions available to carry current in each unit volume decreases.

Step 2: Relate ion concentration to the observed trend Although reduced interionic interactions allow ions to move more freely, this increase in mobility does not compensate for the decrease in their number per unit volume. The table accordingly shows conductivity decreasing from 111.3×10^{-3} to $1.41 \times 10^{-3} \text{ S cm}^{-1}$ as the solution is diluted from 1.00 to 0.01 M.

Step 3: Conclusion Conductivity decreases on dilution because the number of current-carrying ions per unit volume decreases.

Quick Tip to Solve: For conductivity count ions per unit volume; do not confuse its decrease with the increase of molar conductivity on dilution.

31(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-based estimate requested for degree of dissociation is $\alpha = \Lambda_m / \Lambda_m^\circ$, where Λ_m is molar conductivity at the specified concentration and Λ_m° is its limiting value.
- The ratio is dimensionless because both molar conductivities have units of $\text{S cm}^2 \text{ mol}^{-1}$; percentage dissociation is obtained by multiplying it by 100.

Step 1: Select the correct concentration row For 0.01 M KCl , the table gives $\Lambda_m = 141.0 \text{ S cm}^2 \text{ mol}^{-1}$. The supplied limiting value is $\Lambda_m^\circ = 150.0 \text{ S cm}^2 \text{ mol}^{-1}$. The conductivity κ itself must not be substituted for Λ_m .

Step 2: Calculate the conductivity ratio Substitution in the relation used by the question gives

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

For a strong electrolyte such as KCl this ratio is an apparent conductivity-based degree: KCl is essentially fully dissociated, and interionic effects reduce ionic mobility at finite concentration. Thus the numerical ratio should not be interpreted as proof that 6% of KCl remains undissociated.

Step 3: Conclusion The requested conductivity-based degree of dissociation is $\alpha = 0.94$, or 94% .

Quick Tip to Solve: Use the 0.01 M row and divide its molar conductivity by the limiting value; the ratio has no units.

31(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 , is the conductivity contribution of one mole of electrolyte in solution. It depends on the number of mobile ions and their ionic mobilities.
- Both HCl and KCl are strong electrolytes. Their anion is the same, Cl^- , so the key difference is the mobility of H^+ compared with K^+ .

Step 1: Compare the ions supplied In water, HCl produces hydrated hydrogen ions and chloride ions, while KCl produces potassium ions and chloride ions. Both are essentially completely ionised at the concentrations being compared. Therefore the comparison is not explained by treating one as a weak electrolyte; the shared chloride contribution is similar.

Step 2: Compare the cation mobilities Hydrated hydrogen ions have exceptionally high effective mobility in water because charge can be transferred rapidly through the hydrogen-bonded water network. Consequently, the ionic conductivity contribution of H^+ is much greater than that of K^+ . The same amount of HCl therefore transports charge more effectively than KCl at the given concentration and temperature.

Quick Tip to Solve: When comparing strong electrolytes with the same anion, compare the cation mobilities; hydrogen ions are exceptionally mobile in water.

Step 3: Conclusion The molar conductivity of HCl would be greater than that of KCl at a given concentration, because H^+ has much higher ionic mobility than K^+ .

Quick Tip to Solve: When comparing strong electrolytes with the same anion, compare the cation mobilities; hydrogen ions are exceptionally mobile in water.

OR

31(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]

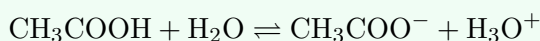
Solution:

Concept:

- Conductivity κ measures the conductance of a solution of specified dimensions; molar conductivity is $\Lambda_m = 1000\kappa/c$ when c is in mol L^{-1} and κ is in S cm^{-1} .
- KCl is a strong electrolyte, whereas acetic acid is a weak electrolyte whose degree of ionisation increases substantially on dilution.

Step 1: Identify a similar observation In both solutions the molar conductivity increases on dilution. Dilution makes ionic motion less hindered by interionic interactions; hence the conductance contribution per mole increases for KCl as well as for acetic acid. Conductivity itself decreases on dilution in both cases because the concentration of ions per unit volume falls.

Step 2: Identify the different observation For KCl, which is already almost completely ionised, the increase in molar conductivity is gradual and chiefly reflects improved ionic mobility. For CH_3COOH , dilution also shifts the equilibrium



towards greater ionisation. Its molar conductivity therefore rises much more sharply on dilution because the fraction of acid molecules producing ions increases substantially.

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

Quick Tip to Solve: Distinguish conductivity per unit volume from conductivity per mole; weak acids show a sharp molar-conductivity rise on dilution.

32. 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]

Answer the following questions:

32(a). Why racemisation occurs in S_N1 ?

[1 mark]

Solution:

Concept:

- An S_N1 reaction proceeds through a carbocation intermediate formed after the leaving group departs.
- A carbocation centre is sp^2 -hybridised and trigonal planar; a nucleophile can approach it from either face.

Step 1: Form the planar intermediate When the leaving group leaves a chiral carbon, the resulting carbocation is planar. Thus the original tetrahedral arrangement at that centre is lost, and the intermediate does not retain the original configuration as a unique tetrahedral structure.

Step 2: Allow attack from either face The nucleophile can attack either side of the plane. Attack from one face gives the product with retained configuration, while attack from the opposite face gives the inverted configuration. Both enantiomeric products are therefore formed. In practice, an ion pair can partly block one face, so the proportions need not be exactly equal.

Step 3: Conclusion Racemisation occurs because nucleophilic attack on the planar carbocation intermediate is possible from both faces, producing both enantiomers.

Quick Tip to Solve: Link racemisation to the planar carbocation and two possible faces of attack, rather than to two separate reaction steps alone.

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

[1 mark]

Solution:**Concept:**

- Solvent polarity describes how effectively the liquid stabilises charge; the dielectric constant is a useful measure in this context.
- Ethanol has a polar hydroxyl group and a nonpolar ethyl group, whereas water has no nonpolar hydrocarbon group.

Step 1: Compare the molecular structures Water is a small bent molecule with two polar O–H bonds whose dipoles do not cancel. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, also contains a polar O–H group, but a substantial part of its molecule is the nonpolar ethyl group. This hydrocarbon portion reduces its overall ability to behave as a strongly polar solvent.

Step 2: Relate structure to solvent behaviour Water therefore stabilises separated charges more effectively than ethanol. This agrees with the passage: water has dielectric constant 79, whereas ethanol has dielectric constant 24. Ethanol can still hydrogen-bond and is a polar protic solvent; it is simply less polar than water.

Step 3: Conclusion Ethanol is less polar than water because it contains a nonpolar ethyl group in addition to its polar hydroxyl group, and it has a much lower dielectric constant.

Quick Tip to Solve: For water versus an alcohol, identify the alcohol's nonpolar alkyl group; do not claim that ethanol cannot form hydrogen bonds.

32(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 concerted step by backside attack of a nucleophile on the carbon bonded to the leaving group.
- For the same alkyl group, a better leaving group increases the rate. For the same leaving group, less steric hindrance at the reacting carbon favours attack.

Step 1: Compare the leaving groups in pair (i) Both $\text{CH}_3\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{Cl}$ contain the same primary ethyl group, so their steric environments are comparable. The C–I bond is weaker than the C–Cl bond, and I^- is a better leaving group than Cl^- . Therefore, iodoethane undergoes nucleophilic displacement more readily than chloroethane.

Step 2: Compare steric hindrance in pair (ii) In chlorocyclohexane, chlorine is directly attached to a secondary ring carbon. In cyclohexylmethyl chloride, $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, chlorine is attached to the primary

Quick Tip to Solve: First locate the carbon directly bonded to the halogen: a ring attached to CH_2Cl does not make that carbon secondary. Compare leaving groups only after comparing the carbon skeletons.

carbon of the side-chain CH_2Cl group. The primary carbon offers less hindrance to the incoming nucleophile's backside approach than the ring carbon. Since both compounds have chloride as the leaving group, the difference in accessibility makes cyclohexylmethyl chloride more reactive.

Step 3: Conclusion The more reactive members are (i) $\text{CH}_3\text{CH}_2\text{I}$, iodoethane, and (ii) $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, cyclohexylmethyl chloride (the second structure).

Quick Tip to Solve: First locate the carbon directly bonded to the halogen: a ring attached to CH_2Cl does not make that carbon secondary. Compare leaving groups only after comparing the carbon skeletons.

OR

32(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

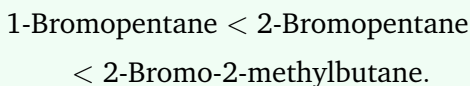
[2 marks]

Solution:

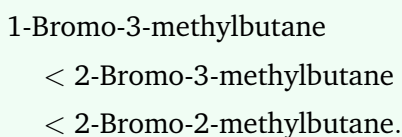
Concept:

- In $\text{S}_{\text{N}}1$, slow ionisation forms a carbocation. Greater carbocation stability makes this rate-determining step easier.
- Alkyl groups stabilise positive charge by the inductive effect and hyperconjugation: primary < secondary < tertiary.

Step 1: Compare set (i) All substrates have bromide as the leaving group. The carbocations initially formed from 1-bromopentane, 2-bromopentane and 2-bromo-2-methylbutane are primary, secondary and tertiary, respectively. Hence the increasing reactivity order is



Step 2: Compare set (ii) Classify the carbon bearing bromine, rather than a remote branch: it is primary in 1-bromo-3-methylbutane, secondary in 2-bromo-3-methylbutane and tertiary in 2-bromo-2-methylbutane. Thus,



Step 3: Conclusion Both orders follow increasing stability of the initially formed carbocation: primary < secondary < tertiary.

Quick Tip to Solve: Count the carbon neighbours of the carbon bearing bromine to compare the initially formed carbocations.

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 $C_5H_8O_2$ 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.

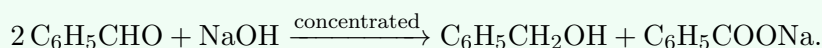
[5 marks]

Solution:

Concept:

- Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one aldehyde molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.
- Carboxylic acids associate by intermolecular hydrogen bonding. Wolff-Kishner reduction converts a carbonyl group to a methylene group without changing the carbon skeleton.
- Hydroxylamine forms one oxime per carbonyl group. A methyl ketone gives the iodoform test, whereas an aldehyde reduces Tollens' reagent to metallic silver.

Step 1: Write the Cannizzaro reaction for part (i) Benzaldehyde has no α -hydrogen and gives benzyl alcohol and sodium benzoate on treatment with concentrated sodium hydroxide:



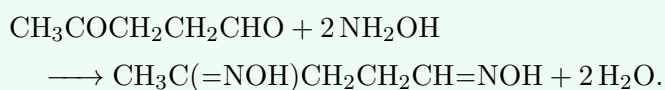
This is a disproportionation because oxidation and reduction occur simultaneously among molecules of the same aldehyde.

Step 2: Explain the boiling-point comparison in part (ii) The $-COOH$ groups of carboxylic acids contain both an O-H hydrogen-bond donor and an oxygen acceptor. Acid molecules form strongly hydrogen-bonded associates, commonly cyclic dimers. More energy is required to separate them during boiling. Aldehydes and ketones have polar carbonyl groups but lack an O-H bond, so their pure liquids do not form comparable intermolecular hydrogen bonds. Their weaker intermolecular attractions give lower boiling points than corresponding carboxylic acids of comparable size.

Step 3: Combine all the structural tests in part (iii) Reduction to n-pentane requires an unbranched five-carbon skeleton. Formation of a dioxime means that both oxygen atoms in $C_5H_8O_2$ belong to carbonyl groups. The positive Tollens' test identifies an aldehyde group, $-CHO$, while the positive iodoform test requires a methyl ketone group, CH_3CO^- . Putting these groups at the ends of the required skeleton gives



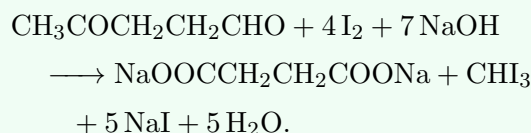
It contains five carbons and eight hydrogens, as required. Both carbonyl groups form oximes:



Quick Tip to Solve: Start from the unchanged straight five-carbon skeleton, then place one aldehyde end for Tollens' test and one CH_3CO^- end for iodoform; finally check the molecular formula and the two oxime sites.

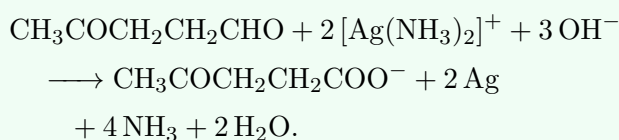
With hydrazine followed by heating with sodium hydroxide in glycol, both carbonyl groups are reduced; the resulting carbon skeleton is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

Step 4: Give the iodoform reaction of A The CH_3CO^- group undergoes haloform cleavage with iodine and sodium hydroxide, producing a yellow precipitate of CHI_3 . Under excess alkaline iodine the aldehyde end is also oxidised, so a balanced overall equation is



The remaining four-carbon chain forms disodium succinate; formation of yellow iodoform is the diagnostic observation for the methyl ketone group.

Step 5: Give the Tollens' reaction of A Tollens' reagent oxidises the aldehyde group to a carboxylate ion while the ketone group remains unchanged. Silver(I) is reduced to metallic silver, producing a silver mirror:



Step 6: Conclusion Benzaldehyde illustrates Cannizzaro disproportionation; stronger hydrogen bonding raises the boiling points of carboxylic acids. Compound A is $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$, 4-oxopentanal, which gives yellow iodoform and a silver mirror in the two tests.

Quick Tip to Solve: Start from the unchanged straight five-carbon skeleton, then place one aldehyde end for Tollens' test and one CH_3CO^- end for iodoform; finally check the molecular formula and the two oxime sites.

OR

33(b). (i) Give a chemical test to distinguish between ethanal 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 $\text{C}_4\text{H}_8\text{O}_2$ 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:

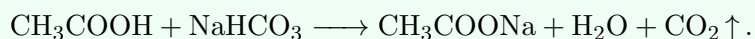
Concept:

- Carboxylic acids liberate carbon dioxide with sodium hydrogen carbonate; aldehydes do not show this acid-base reaction.
- Removal of an α -hydrogen from a carbonyl compound gives an enolate ion whose negative charge is delocalised between carbon and oxygen.

Quick Tip to Solve: Begin the identification with soda lime: methane fixes the acid as ethanoic acid. Then use oxidation to identify ethanol and join the acid and alcohol fragments to obtain the ester.

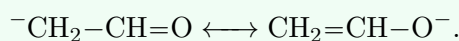
- Acid hydrolysis of an ester gives a carboxylic acid and an alcohol. Soda-lime decarboxylation of a sodium carboxylate gives an alkane containing one fewer carbon atom.
- Boiling point depends on intermolecular attractions; carboxylic acids form strongly hydrogen-bonded associated molecules.

Step 1: (i) Add sodium hydrogen carbonate Add aqueous NaHCO_3 separately to the two samples. Ethanoic acid gives brisk effervescence of CO_2 , whereas ethanal gives no effervescence. The gas turns limewater milky. The distinguishing reaction is



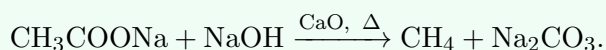
Ethanoic acid is sufficiently acidic to react with hydrogen carbonate. Ethanal lacks a carboxylic acid group and does not liberate this gas under the test conditions.

Step 2: (ii) Explain the stability of the conjugate base An α -hydrogen is attached to the carbon adjacent to the carbonyl group. The electron-withdrawing carbonyl group polarises the neighbouring bonds. On removal of an α -proton by a base, the resulting enolate ion is resonance-stabilised. For ethanal its two contributing structures are



The charge is delocalised over the α -carbon and the electronegative oxygen rather than remaining localised on carbon. Stabilisation of this conjugate base makes the α -hydrogens of aldehydes and ketones acidic relative to ordinary alkane hydrogens. This does not make ethanal acidic enough to give the bicarbonate test above.

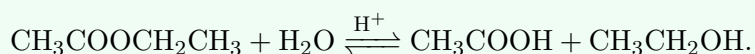
Step 3: (iii)(1) Work backwards from methane Soda lime removes the carboxyl carbon as carbonate. Since the alkane formed is methane, the original sodium salt must contain the methyl group attached to the carboxylate group:



Thus the acid B is ethanoic acid, CH_3COOH . The alcohol C that gives this acid on oxidation is ethanol, $\text{CH}_3\text{CH}_2\text{OH}$:



Here acidified potassium permanganate supplies the oxidising action. An ester yielding ethanoic acid and ethanol on hydrolysis is ethyl ethanoate, so A is $\text{CH}_3\text{COOCH}_2\text{CH}_3$:



Counting its atoms gives $\text{C}_4\text{H}_8\text{O}_2$, in agreement with the given molecular formula. These identities therefore satisfy all three reaction clues.

Step 4: (iii)(2) Compare the boiling points B, ethanoic acid, has the higher boiling point. Its molecules associate through strong intermolecular hydrogen bonding, including cyclic dimers held by two hydrogen bonds. Ethanol also forms hydrogen bonds, but association is stronger in the carboxylic acid; more energy is needed to separate the acid molecules into the vapour. Ethanoic acid also has the

Quick Tip to Solve: Begin the identification with soda lime: methane fixes the acid as ethanoic acid. Then use oxidation to identify ethanol and join the acid and alcohol fragments to obtain the ester.

larger molar mass, reinforcing its stronger intermolecular attraction.

Step 5: Conclusion Ethanoic acid gives CO_2 with NaHCO_3 ; ethanal does not. The α -hydrogens are acidic because their removal produces a resonance-stabilised enolate. A is ethyl ethanoate, B is ethanoic acid and C is ethanol. B has the higher boiling point owing to stronger intermolecular hydrogen bonding and association.

Quick Tip to Solve: Begin the identification with soda lime: methane fixes the acid as ethanoic acid. Then use oxidation to identify ethanol and join the acid and alcohol fragments to obtain 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 $\text{MgCl}_2 = 95 \text{ g mol}^{-1}$)

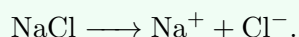
[5 marks]

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 is the molal boiling point elevation constant and m is solute molality.
- For an ideal solution of a non-volatile solute, Raoult's law gives $p = x_1 p^0$, so $(p^0 - p)/p^0 = x_2 = n_2/(n_1 + n_2)$. Here p^0 and p are the vapour pressures of the pure solvent and solution, and n_1, n_2 are solvent and solute amounts.
- Complete dissociation increases the number of dissolved particles. Molality is the amount of solute in moles divided by the mass of solvent in kilograms.

Step 1: (i) Compare the number of dissolved particles Sodium chloride is an electrolyte and dissociates into ions:



Thus each formula unit produces approximately two dissolved particles, giving $i \approx 2$. Glucose remains as molecules, so its van't Hoff factor is $i = 1$. In the usual dilute-solution comparison at the stated equal molarity, sodium chloride therefore produces more solute particles. It lowers the solvent vapour pressure more, so a higher temperature is needed for that pressure to equal the external pressure. Consequently its boiling point is higher. The relevant cause is dissociation, not the relative molar masses of sodium chloride and glucose.

Step 2: (ii) Convert the vapour pressure to a mole fraction The pressure is reduced to 90% of its original value, hence $p = 0.90p^0$; the relative lowering is 0.10, not 0.90. The molar mass of benzene, C_6H_6 , is 78 g mol^{-1} . Therefore

$$n_1 = \frac{78 \text{ g}}{78 \text{ g mol}^{-1}} = 1.00 \text{ mol}.$$

Using the full mole-fraction expression avoids the dilute approximation in which the solute amount is

Quick Tip to Solve: Read "reduced to 90 percent" as a 10 percent lowering and use the full mole fraction. For magnesium chloride, multiply by three and convert only the water mass to kilograms.

neglected in the denominator:

$$\frac{p^0 - p}{p^0} = \frac{n_2}{n_1 + n_2} = 0.10,$$

$$n_2 = 0.10(1.00 + n_2),$$

$$0.90n_2 = 0.10,$$

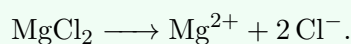
$$n_2 = \frac{1}{9} \text{ mol.}$$

Multiplying by the given solute molar mass gives

$$w_2 = n_2 M_2 = \frac{1}{9} \times 50 = 5.56 \text{ g.}$$

As a check, the solvent mole fraction is $1/(1 + 1/9) = 0.90$, reproducing the given final vapour pressure.

Step 3: (iii) Find the van't Hoff factor and molality Complete dissociation gives one magnesium ion and two chloride ions per formula unit:



Hence $i = 3$. The amount of salt and mass of water are

$$n = \frac{10}{95} = 0.105263 \text{ mol,} \quad w_{\text{water}} = 200 \text{ g} = 0.200 \text{ kg.}$$

Molality uses the mass of water alone, not the total solution mass:

$$m = \frac{0.105263}{0.200} = 0.526316 \text{ mol kg}^{-1}.$$

Step 4: (iii) Calculate the boiling point elevation Substitute the van't Hoff factor and molality in the boiling point elevation formula:

$$\begin{aligned} \Delta T_b &= i K_b m \\ &= 3 \times 0.512 \times 0.526316 \\ &= 0.808421 \text{ K} \approx 0.808 \text{ K.} \end{aligned}$$

This is the rise above the boiling point of pure water at the same pressure. A temperature interval of 0.808 K is also 0.808 °C; it is not the absolute boiling temperature of the solution.

Step 5: Conclusion (i) Sodium chloride produces more solute particles through dissociation and hence a higher boiling point than glucose in the stated comparison. (ii) The mass of X is 5.56 g. (iii) The boiling point elevation is $\Delta T_b \approx 0.808 \text{ K}$.

Quick Tip to Solve: Read "reduced to 90 percent" as a 10 percent lowering and use the full mole fraction. For magnesium chloride, multiply by three and convert only the water mass to kilograms.

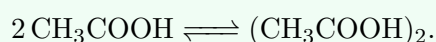
- 34(b).** (i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5 ?
 (ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at 25°C , assuming that K_2SO_4 is completely dissociated.
 ($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, 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 number of solute particles actually present to the number expected without association or dissociation. Association lowers i ; dissociation raises it.
- Osmotic pressure is $\pi = iCRT = i(w/MV)RT$, where w is solute mass, M its molar mass, V the solution volume, R the gas constant and T the absolute temperature.
- Freezing-point depression is $\Delta T_f = K_f m$, where K_f is the solvent's cryoscopic constant and m is the amount of dissolved molecular solute per kilogram of solvent.

Step 1: (i) Explain association of ethanoic acid In the nonpolar solvent benzene, ethanoic acid molecules associate into dimers through intermolecular hydrogen bonds:

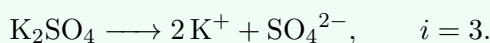


Nearly complete dimerisation changes two independently moving solute particles into one. If the initial amount is n mol, the amount of dimers approaches $n/2$ mol, so

$$i = \frac{n/2}{n} = 0.5.$$

More generally, for a fraction α of acid molecules associated, $i = 1 - \alpha/2$. Thus a value close to 0.5 indicates nearly complete association, rather than ionisation.

Step 2: (ii) Count the dissolved ions Complete dissociation gives three ions for each formula unit:



The concentration before applying the particle factor is

$$C = \frac{w}{MV} = \frac{2.32 \times 10^{-2}}{174 \times 2} = 6.6667 \times 10^{-5} \text{ mol L}^{-1}.$$

Use the stated volume of the solution, 2 L, and convert the temperature to $T = 25 + 273 = 298 \text{ K}$.

Step 3: (ii) Calculate the osmotic pressure With $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, substitute into the

Quick Tip to Solve: Count particles first: dimerisation halves their number, while complete dissociation of K_2SO_4 triples it. For sulphur, divide the colligative molar mass by 32 to obtain its atomicity.

osmotic-pressure equation:

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

The litre, mole and kelvin units cancel, leaving atmospheres. The dissociation factor is applied only once.

Step 4: (iii) Find the molecular mass and atomicity of sulphur The solvent mass is $1000 \text{ g} = 1.000 \text{ kg}$. If M_s is the molar mass of the sulphur molecules, their molality is $(25.6/M_s)/1.000$. Therefore

$$\begin{aligned}0.512 &= 5.12 \times \frac{25.6}{M_s \times 1.000}, \\ M_s &= \frac{5.12 \times 25.6}{0.512 \times 1.000} = 256 \text{ g mol}^{-1}.\end{aligned}$$

Each sulphur atom contributes 32 g mol^{-1} , so the number of atoms in a molecule is

$$x = \frac{256}{32} = 8.$$

The colligative measurement counts the dissolved molecules, so the calculated molecular mass, rather than the atomic mass alone, determines the formula.

Step 5: Conclusion (i) Ethanoic acid forms hydrogen-bonded dimers in benzene, giving $i \approx 0.5$. (ii) The osmotic pressure is $4.89 \times 10^{-3} \text{ atm}$. (iii) Sulphur has molar mass 256 g mol^{-1} and molecular formula S_8 .

Quick Tip to Solve: Count particles first: dimerisation halves their number, while complete dissociation of K_2SO_4 triples it. For sulphur, divide the colligative molar mass by 32 to obtain its atomicity.

35. (a) A transition element X has electronic configuration $[\text{Ar}] 4s^2 3d^3$. Predict its likely oxidation states.

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



(c) Account for the following:

(i) In the 3d transition series, zinc has the lowest enthalpy of atomisation.

(ii) Cu^+ ion is unstable in aqueous solution.

(iii) Actinoids show more number of oxidation states than lanthanoids.

[5 marks]

Solution:

Concept:

- Transition elements show variable oxidation states because the outer ns and $(n-1)d$ orbitals have comparable energies. On ionisation, the outer ns electrons are removed first.
- The enthalpy of atomisation measures the energy needed to form gaseous atoms from the element.

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons when predicting oxidation states. For aqueous copper ions, include hydration in the energy balance instead of deciding stability from the filled d subshell alone.

Stronger metallic bonding generally gives a higher atomisation enthalpy.

- Stability of an aqueous ion depends on both ionisation and hydration energies. Disproportionation is the simultaneous oxidation and reduction of the same oxidation state.
- The range of oxidation states in inner-transition elements depends on how readily their f , d and s valence electrons can participate in bonding.

Step 1: (a) Identify the accessible oxidation states The configuration $[\text{Ar}] 4s^2 3d^3$ contains five electrons beyond the argon core and identifies the element as vanadium. Loss of the two $4s$ electrons gives the +2 state. Successive participation of one, two or all three $3d$ electrons gives +3, +4 and +5, respectively. Thus the likely oxidation states are +2, +3, +4 and +5. The corresponding formal d -electron counts are d^3 , d^2 , d^1 and d^0 .

Step 2: (b) Complete the thermal decomposition On heating, potassium permanganate decomposes to potassium manganate, manganese dioxide and oxygen:



The equation is balanced: both sides contain two potassium atoms, two manganese atoms and eight oxygen atoms. Manganese changes from +7 to +6 in K_2MnO_4 and to +4 in MnO_2 , while part of the oxide oxygen forms O_2 .

Step 3: (c)(i) Relate zinc's configuration to weak metallic bonding Zinc has the configuration $[\text{Ar}] 3d^{10} 4s^2$. Its completely filled $3d$ subshell contains no unpaired d electrons and contributes little to metallic bonding compared with the partially filled d subshells of the other members of the series. Consequently, zinc has relatively weak metallic bonds. Less energy is required to separate its atoms into gaseous atoms, explaining its lowest enthalpy of atomisation in the $3d$ series. This does not mean that zinc has no metallic bonding; its bonding is comparatively weak.

Step 4: (c)(ii) Explain the aqueous instability of copper(I) The greater magnitude of the hydration enthalpy of Cu^{2+} , compared with that of Cu^+ , more than compensates for the energy required to remove the second electron in the overall process. Hence Cu^+ disproportionates in aqueous solution:



One copper(I) ion is oxidised to copper(II), and another is reduced to copper metal. Although Cu^+ has a filled $3d^{10}$ configuration, that electronic feature alone does not determine stability in water; hydration strongly favours Cu^{2+} .

Step 5: (c)(iii) Compare the energies of the valence orbitals In actinoids, the $5f$, $6d$ and $7s$ orbitals have relatively similar energies, so different numbers of electrons from these orbitals can participate in bonding. This produces a wider range of oxidation states. In lanthanoids, the $4f$ electrons are more deeply buried and less available for bonding; the +3 state is therefore predominant, with only a limited number of +2 and +4 exceptions. The smaller energy separations and greater participation of $5f$ electrons account for the greater variability in actinoids.

Step 6: Conclusion (a) The likely oxidation states are $+2, +3, +4, +5$. (b) Heating gives K_2MnO_4 , MnO_2 and O_2 . (c) Zinc has weak metallic bonding associated with its filled $3d$ subshell; Cu^+ disproportionates because aqueous Cu^{2+} is strongly stabilised by hydration; actinoids have more

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons when predicting oxidation states. For aqueous copper ions, include hydration in the energy balance instead of deciding stability from the filled d subshell alone.

accessible $5f$, $6d$ and $7s$ electrons.

Quick Tip to Solve: Remove $4s$ electrons before $3d$ electrons when predicting oxidation states. For aqueous copper ions, include hydration in the energy balance instead of deciding stability from the filled d subshell alone.