

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-5-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **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 of the following molecules has a chiral centre correctly labelled with an asterisk (*) ?

[1 mark]

- (A) $\text{CH}_3\text{C}^*\text{HBrCH}_3$
(B) $\text{CH}_3\text{C}^*\text{HClCH}_2\text{Br}$
(C) $\text{HOCH}_2\text{C}^*\text{H}(\text{OH})\text{CH}_2\text{OH}$
(D) $\text{CH}_3\text{C}^*\text{Br}_2\text{CH}_3$

Correct Answer: (B) $\text{CH}_3\text{C}^*\text{HClCH}_2\text{Br}$

Solution:

Concept:

- A chiral centre is a tetrahedral carbon attached to four different substituents.
- Compare complete substituent groups, not merely the first atom attached to the starred carbon.

Step 1: Examine the starred carbon in option (B) In $\text{CH}_3\text{CHClCH}_2\text{Br}$, the starred carbon is bonded to H, Cl, CH_3 and CH_2Br . These four groups are different; hence this carbon is a chiral centre.

Step 2: Reject the remaining structures Option (A) has two identical CH_3 groups. Option (C) has two identical CH_2OH groups. Option (D) has two identical bromine atoms as well as two identical methyl groups. Each repetition prevents the starred carbon from being a chiral centre.

Step 3: Conclusion Only $\text{CH}_3\text{C}^*\text{HClCH}_2\text{Br}$ has four different groups at the starred carbon. Hence, the correct option is (B).

Quick Tip to Solve: List the four complete groups around the starred carbon; any repeated group rules out chirality.

2. 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 carbon bearing the $-\text{OH}$ group.
- A tertiary alcohol has no hydrogen on this carbon and resists ordinary oxidation without carbon-carbon bond cleavage.

Step 1: Classify the alcohols Butanol is a primary alcohol. Butan-2-ol and 3-methylbutan-2-ol are secondary alcohols. In 2-methylbutan-2-ol, the carbon bearing $-\text{OH}$ is attached to two methyl groups

Quick Tip to Solve: Locate the OH-bearing carbon and check for a C-H bond: a tertiary centre has none.

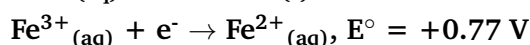
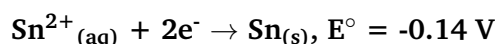
and one ethyl group, so it is tertiary.

Step 2: Apply the oxidation requirement The first, second and fourth alcohols possess a hydrogen on the carbon bearing the hydroxyl group and undergo the usual oxidation to carbonyl compounds. The tertiary alcohol in option (C) lacks this hydrogen, so it does not undergo the usual alcohol oxidation. Very vigorous conditions causing carbon-carbon cleavage are outside this ordinary oxidation comparison.

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

Quick Tip to Solve: Locate the OH-bearing carbon and check for a C-H bond: a tertiary centre has none.

3. 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:

- The half-cell with the higher standard reduction potential acts as the cathode in a spontaneous voltaic cell.
- $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, using both tabulated values as reduction potentials.

Step 1: Identify oxidation and reduction The $\text{Fe}^{3+}/\text{Fe}^{2+}$ reduction potential, +0.77 V, is greater than that of Sn^{2+}/Sn , -0.14 V. Thus Fe^{3+} is reduced at the cathode, while tin is oxidised at the anode: $\text{Sn} \rightarrow \text{Sn}^{2+} + 2\text{e}^{-}$.

Step 2: Calculate the cell voltage and test the statements

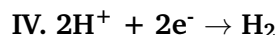
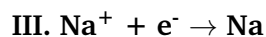
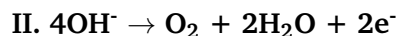
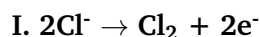
$$E^{\circ}_{\text{cell}} = 0.77 - (-0.14) = 0.91 \text{ V}.$$

Options (A) and (C) incorrectly oxidise Fe^{2+} . Option (D) incorrectly adds the two signed reduction potentials to obtain 0.63 V. Balancing electrons does not multiply an electrode potential.

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

Quick Tip to Solve: Choose the more positive reduction potential as cathode, then subtract the other signed value.

4. 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 aqueous concentrated brine, oxidation occurs at the anode and reduction occurs at the cathode.
- Chloride is preferentially discharged at the anode in concentrated brine; water produces hydrogen at the cathode rather than sodium metal.

Step 1: Select the anodic process The high chloride concentration and oxygen overvoltage favour chlorine evolution: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$. Thus reaction I is selected rather than oxygen evolution in II. The printed reaction II has an incorrect electron coefficient, but it still denotes the competing oxygen-evolution process.

Step 2: Select the cathodic process Water is reduced to hydrogen: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$. Among the listed processes, IV represents hydrogen evolution. Sodium ions are not discharged to sodium metal in aqueous solution, ruling out options (A) and (C). Option (D) gives oxygen rather than chlorine at the anode.

Step 3: Conclusion The products are chlorine at the anode and hydrogen at the cathode, corresponding to I and IV. Hence, the correct option is (B).

Quick Tip to Solve: For concentrated aqueous NaCl, recall chlorine at the anode and hydrogen at the cathode.

5. 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 supplies an alternative reaction pathway with a lower activation energy and is regenerated overall.
- Variable oxidation states let transition-metal species exchange electrons and form intermediate species during catalytic cycles.

Step 1: Relate oxidation states to catalysis Transition metals can change oxidation state by accepting or donating electrons. They can therefore interact with reactants, form intermediates and facilitate successive electron-transfer steps. The catalyst returns to its original state at the end of the cycle.

Step 2: Compare all four properties High melting point concerns thermal stability, while high ionisation enthalpy concerns the energy needed to remove electrons. Alloy formation concerns mixtures of metals. These properties do not directly explain the catalytic electron-transfer cycle. Variable oxidation states provide the relevant chemical mechanism among the stated choices.

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

Quick Tip to Solve: When catalysis is linked to transition metals, look for reversible changes in oxidation state.

6. In the two tetrahedral structures of dichromate ion

[1 mark]

- (A) 4 Cr—O bonds are equivalent in length.
- (B) 6 Cr—O bonds are equivalent in length.
- (C) All Cr—O bonds are equivalent in length.
- (D) All Cr—O bonds are non-equivalent.

Correct Answer: (B) 6 Cr—O bonds are equivalent in length.

Solution:

Concept:

- The dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$, consists of two CrO_4 tetrahedra sharing one oxygen atom.
- Its six terminal Cr—O bonds are equivalent, while the two Cr—O bonds to the bridging oxygen are longer.

Step 1: Count the terminal and bridging bonds Each chromium atom bonds to three terminal oxygen atoms and one shared bridging oxygen. The two tetrahedra therefore contain six terminal Cr—O bonds and two bridging Cr—O bonds, giving eight Cr—O bonds in total.

Quick Tip to Solve: Count three terminal oxygens per chromium: two tetrahedra give six equivalent terminal bonds.

Step 2: Compare their lengths and the options The six terminal bonds have equivalent lengths through the bonding arrangement within the ion. The two bridging bonds have a different, longer bond length. Thus the structural set of equivalent terminal bonds contains six, not four. All eight bonds are not equivalent, and it is also false that every Cr–O bond has a different length.

Step 3: Conclusion Six Cr–O bonds are equivalent in length. Hence, the correct option is (B).

Quick Tip to Solve: Count three terminal oxygens per chromium: two tetrahedra give six equivalent terminal bonds.

7. 1 mole of liquid A and 2 moles of liquid B make a solution having a total vapour pressure 40 torr. The vapour pressure of pure A and pure B are 45 torr and 30 torr respectively. The above solution [1 mark]

- (A) is an ideal solution.
- (B) shows positive deviation.
- (C) shows negative deviation.
- (D) is a maximum boiling azeotrope.

Correct Answer: (B) shows positive deviation.

Solution:

Concept:

- For an ideal binary solution, Raoult's law gives $P_{\text{ideal}} = x_A P_A^\circ + x_B P_B^\circ$, where x denotes liquid mole fraction.
- An observed vapour pressure above the ideal value indicates positive deviation; a lower value indicates negative deviation.

Step 1: Calculate the ideal pressure The total amount is $1 + 2 = 3$ mol, so $x_A = 1/3$ and $x_B = 2/3$. Therefore

$$P_{\text{ideal}} = \frac{1}{3}(45) + \frac{2}{3}(30) = 15 + 20 = 35 \text{ torr.}$$

Step 2: Compare with the measured pressure The actual pressure is 40 torr, greater than the ideal value by 5 torr. Hence the solution shows positive deviation. It is neither ideal nor negatively deviating. A maximum-boiling azeotrope is associated with negative deviation, and a single pressure measurement does not establish an azeotropic composition.

Step 3: Conclusion The solution shows positive deviation from Raoult's law. Hence, the correct option is (B).

Quick Tip to Solve: First compute the mole-fraction-weighted ideal pressure; compare 40 torr with 35 torr.

8. 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

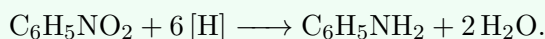
Correct Answer: (A) LiAlH_4

Solution:

Concept:

- Reduction converts the nitro group of nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$, into the amino group of aniline, $\text{C}_6\text{H}_5\text{NH}_2$.
- Catalytic hydrogenation and a metal in acid are standard methods for this conversion; reagent choice must also consider suitability and handling.

Step 1: Identify the standard reduction methods H_2 with nickel gives catalytic reduction of the nitro group. Iron with hydrochloric acid and tin with hydrochloric acid also reduce nitrobenzene to aniline (obtained after the usual alkaline work-up). Thus choices (B), (C) and (D) are established suitable methods. The net conversion is



Step 2: Compare the remaining reagent LiAlH_4 is a strong, moisture-sensitive hydride reagent requiring dry conditions and careful handling. Although nitro-group reduction with hydrides is possible under appropriate conditions, it is not the good practical choice among the listed standard methods. The question asks for reagent suitability, rather than claiming that every powerful reducing agent is equally convenient.

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, first recognise the three standard routes: hydrogen with nickel, iron/HCl and tin/HCl.

9. If molality of a dilute solution is doubled, the value of the molal elevation constant (K_b) will be [1 mark]

- (A) halved
- (B) doubled
- (C) tripled
- (D) unchanged

Correct Answer: (D) unchanged

Solution:

Concept:

- The boiling-point elevation of a dilute solution is $\Delta T_b = K_b m$, where m is molality and K_b is the molal elevation constant.
- K_b is a characteristic of the solvent; changing the amount of solute changes molality, not this constant.

Step 1: Apply the elevation equation Let the initial molality be m . The initial elevation is $\Delta T_b = K_b m$. When the molality becomes $2m$, the new elevation is

$$\Delta T'_b = K_b(2m) = 2\Delta T_b.$$

Thus it is the elevation in boiling point that doubles.

Step 2: Distinguish the constant from the effect The solvent remains the same, so K_b retains its original value. Halving, doubling or tripling K_b would incorrectly treat a solvent property as a concentration-dependent variable. In particular, option (B) confuses the doubled boiling-point elevation with the molal elevation constant.

Step 3: Conclusion The value of K_b is unchanged. Hence, the correct option is (D).

Quick Tip to Solve: Underline the requested quantity: doubling molality doubles ΔT_b , while the solvent constant K_b stays fixed.

10. Hydrolysis of sucrose is called [1 mark]

- (A) inversion
- (B) hydration
- (C) esterification
- (D) saponification

Correct Answer: (A) inversion

Solution:

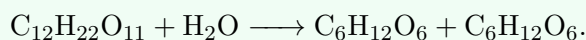
Concept:

- Hydrolysis of sucrose cleaves its glycosidic linkage and produces equimolar D-glucose and D-fructose.

Quick Tip to Solve: Link sucrose hydrolysis to optical rotation: positive sucrose gives a negative glucose-fructose mixture, hence inversion.

- Inversion is a reversal in the sign of optical rotation: dextrorotatory sucrose gives a net laevorotatory product mixture.

Step 1: Identify the hydrolysis products In the presence of dilute acid or the enzyme invertase, sucrose reacts with water:



The two products are glucose and fructose, respectively. This is cleavage of the disaccharide into monosaccharides.

Step 2: Explain the special name Sucrose has positive optical rotation. Fructose has a larger negative rotation in magnitude than the positive rotation of glucose, so the resulting equimolar mixture has negative rotation. This reversal gives the name inversion. Hydration means addition of water, esterification forms an ester, and saponification is alkaline hydrolysis of an ester; none names the optical reversal in this reaction.

Step 3: Conclusion Hydrolysis of sucrose is called inversion. Hence, the correct option is (A).

Quick Tip to Solve: Link sucrose hydrolysis to optical rotation: positive sucrose gives a negative glucose-fructose mixture, hence inversion.

11. 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:

- $pK_a = -\log_{10} K_a$; the lowest pK_a therefore corresponds to the strongest acid.
- An electron-withdrawing substituent stabilises the carboxylate conjugate base by its negative inductive effect, increasing acid strength.

Step 1: Compare the substituent effects The nitro group in $\text{O}_2\text{NCH}_2\text{COOH}$ has a strong negative inductive effect. It withdraws electron density through the carbon chain and stabilises the negative charge of the carboxylate ion. Chlorine in ClCH_2COOH also withdraws electrons, but its effect in this comparison is weaker than that of the nitro group.

Step 2: Compare all four acids Formic acid, HCOOH , lacks an electron-donating alkyl group. Acetic acid, CH_3COOH , has a methyl group with a positive inductive effect, which destabilises its carboxylate relative to formate. Thus acid strength follows



Quick Tip to Solve: For these carboxylic acids, select the strongest electron-withdrawing substituent when asked for the lowest pK_a .

The order of pK_a is the reverse of this strength order.

Step 3: Conclusion O_2NCH_2COOH has the lowest pK_a . Hence, the correct option is (B).

Quick Tip to Solve: For these carboxylic acids, select the strongest electron-withdrawing substituent when asked for the lowest pK_a .

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

[1 mark]

- (A) Mercury cell
- (B) Daniel cell
- (C) H_2-O_2 Fuel cell
- (D) Dry cell

Correct Answer: (C) H_2-O_2 Fuel cell

Solution:

Concept:

- A fuel cell continuously converts the chemical energy of externally supplied fuel and oxidant into electrical energy.
- The hydrogen-oxygen fuel cell has the overall reaction $2H_2 + O_2 \longrightarrow 2H_2O$; water is its reaction product.

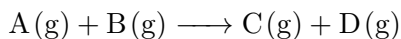
Step 1: Identify the cell used in spacecraft The Apollo space programme used the hydrogen-oxygen fuel cell for electrical power. Hydrogen acts as the fuel and oxygen as the oxidant. Their electrochemical reaction produces water as well as electricity, making this type of cell useful in the spacecraft.

Step 2: Eliminate the other cell types A mercury cell is a small primary cell, commonly associated with compact devices. A Daniell cell uses the zinc-copper electrochemical couple. A dry cell is a primary cell based on zinc and manganese dioxide. These descriptions do not match the hydrogen-oxygen power source used in Apollo, so options (A), (B) and (D) do not answer the question.

Step 3: Conclusion The H_2-O_2 fuel cell was used in the Apollo space programme. Hence, the correct option is (C).

Quick Tip to Solve: Associate Apollo with both electricity and useful product water: hydrogen plus oxygen identifies the fuel cell.

13. 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 with respect to A (g): Zero; order with respect to B (g): Second

(B) Order with respect to A (g): First; order with respect to B (g): Zero

(C) Order with respect to A (g): Second; order with respect to B (g): Zero

(D) Order with respect to A (g): Second; order with respect to B (g): First

Correct Answer: (C) Order with respect to A (g): Second; order with respect to B (g): Zero

Solution:

Concept:

- Write the experimental rate law as $r = k[A]^x[B]^y$, where x and y are the orders with respect to A and B.
- Compare experiments in which only one reactant concentration changes; stoichiometric coefficients do not determine experimental orders.

Step 1: Find the order with respect to B Compare experiments 1 and 2: [A] stays at $3.0 \times 10^{-2} \text{ mol dm}^{-3}$, while [B] doubles from 2.0×10^{-2} to $4.0 \times 10^{-2} \text{ mol dm}^{-3}$. The rate remains $1.89 \times 10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$. Therefore

$$\frac{r_2}{r_1} = 2^y = 1, \quad y = 0.$$

Step 2: Find the order with respect to A Compare experiments 2 and 3: [B] is unchanged, while [A] doubles from 3.0×10^{-2} to $6.0 \times 10^{-2} \text{ mol dm}^{-3}$. The rate increases by a factor of $7.56/1.89 = 4$. Hence

$$\frac{r_3}{r_2} = 2^x = 4, \quad x = 2.$$

Option (A) reverses the effects, option (B) predicts only a twofold rate increase, and option (D) incorrectly predicts dependence on B.

Step 3: Conclusion The order with respect to A is second and that with respect to B is zero. Hence, the correct option is (C).

Quick Tip to Solve: Use rows 1 and 2 for B, then rows 2 and 3 for A: unchanged rate means zero order; fourfold rate on doubling means second order.

14. 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.
- Chloride is a weak-field ligand; $[\text{NiCl}_4]^{2-}$ is a tetrahedral complex of Ni^{2+} .

Step 1: Find the metal ion configuration If the oxidation state of nickel is z , then $z + 4(-1) = -2$, giving $z = +2$. Neutral nickel has configuration $[\text{Ar}] 3d^8 4s^2$; removing its two $4s$ electrons gives Ni^{2+} with $3d^8$.

Step 2: Count unpaired electrons and substitute The weak-field tetrahedral complex has two unpaired electrons in its d^8 configuration. It is therefore paramagnetic. Substitution into the spin-only formula gives

$$\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.82 \text{ BM.}$$

The other values do not correspond to two unpaired electrons and therefore do not fit this complex.

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

Quick Tip to Solve: First obtain Ni^{2+} , then count two unpaired electrons in tetrahedral d^8 ; use $\sqrt{8} = 2.82$.

15. Assertion (A): Proteins are polymers of α -amino acids connected by a peptide bond.

Reason (R): A tetrapeptide contains 4 amino acids linked by 4 peptide bonds.

[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:

- Proteins are polypeptides built from α -amino acids. A peptide linkage is the amide group $-\text{CO}-\text{NH}-$.

Quick Tip to Solve: For a linear peptide, count the junctions: four amino acid residues give three peptide bonds.

- Condensation between the carboxyl group of one amino acid and the amino group of the next forms a peptide bond and eliminates water. A linear chain of n amino acids has $n - 1$ peptide bonds.

Step 1: Judge the assertion Proteins contain many α -amino acid residues joined through peptide linkages. Therefore Assertion (A) is true.

Step 2: Judge the reason A tetrapeptide has four amino acid residues, but only the three junctions between consecutive residues form peptide bonds. Thus the number of peptide bonds is $4 - 1 = 3$, not four, and Reason (R) is false.

Step 3: Select the assertion-reason relation Since the reason is false, it cannot explain the true assertion. Options (A) and (B) incorrectly require both statements to be true; option (D) incorrectly calls the assertion false.

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

Quick Tip to Solve: For a linear peptide, count the junctions: four amino acid residues give three peptide bonds.

16. Assertion (A): For a zero order reaction the unit of rate constant and rate of reaction are same.

Reason (R): Rate of reaction for zero order reaction is independent of concentration of reactant.

[1 mark]

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

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

Solution:

Concept:

- For a reaction of order n , the rate law is $r = k[A]^n$, where r is the reaction rate, k the rate constant, and $[A]$ the reactant concentration.
- For zero order, $[A]^0 = 1$, so $r = k$. Rate has units of concentration divided by time, commonly $\text{mol L}^{-1} \text{s}^{-1}$.

Step 1: Judge the assertion In a zero order reaction, the rate law reduces to $r = k$. Consequently the units of the rate constant are exactly the units of rate, namely $\text{mol L}^{-1} \text{s}^{-1}$ when seconds are used. Assertion (A) is true.

Step 2: Judge the reason The zero power of concentration means the reaction rate does not vary with reactant concentration within the conditions where the zero order law applies. Reason (R) is true.

Step 3: Check the explanation Independence from concentration removes the concentration factor

Quick Tip to Solve: Substitute order zero in the rate law first: rate equals k , so their units must match.

from the rate law, leaving $r = k$. This directly explains why their units coincide. Option (B) misses this causal link; options (C) and (D) incorrectly call one of the statements false.

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

Quick Tip to Solve: Substitute order zero in the rate law first: rate equals k , so their units must match.

17. Assertion (A): Acetic acid but not formic acid can be halogenated in presence of red P and Cl_2 .

Reason (R): Acetic acid is a weaker acid than formic acid.

[1 mark]

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

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

Solution:

Concept:

- The Hell-Volhard-Zelinsky reaction replaces an α -hydrogen of a carboxylic acid by chlorine or bromine in the presence of red phosphorus. The α -carbon is adjacent to the carboxyl carbon.
- An electron-donating alkyl group decreases carboxylic-acid strength by destabilising the carboxylate anion relative to formate.

Step 1: Judge the assertion using the required hydrogen Acetic acid, CH_3COOH , has α -hydrogens and gives chloroacetic acid, ClCH_2COOH , with chlorine and red phosphorus. Formic acid, HCOOH , has no α -carbon and thus no α -hydrogen for this reaction. Assertion (A) is true.

Step 2: Judge the reason using acid strength The methyl group in acetic acid has a positive inductive effect. It makes the acetate ion less stabilised than formate, so acetic acid is a weaker acid than formic acid. Reason (R) is true.

Step 3: Decide whether the reason explains the assertion The difference in halogenation follows from the presence or absence of an α -hydrogen, rather than the relative acid strengths. Thus the true reason does not explain the true assertion. Option (A) asserts an incorrect explanation, while options (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: For red phosphorus and halogen, check for an alpha-hydrogen before comparing acid strengths.

18. Assertion (A): Trans $[\text{CrCl}_2(\text{ox})_2]^{3-}$ shows optical isomerism.

Reason (R): Optical isomerism is common in octahedral complexes involving didentate ligands.

[1 mark]

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

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

Solution:

Concept:

- Optical isomers are non-superimposable mirror images. A complex with a plane of symmetry is achiral and does not show optical isomerism.
- Oxalate, abbreviated ox, is a didentate ligand: it occupies two coordination positions in an octahedral complex. Chelate arrangements can produce chirality, but not every arrangement does.

Step 1: Judge the assertion from the trans geometry In trans- $[\text{CrCl}_2(\text{ox})_2]^{3-}$, the two chloride ligands occupy opposite positions. The two oxalate ligands occupy the remaining four positions. This trans arrangement has a plane of symmetry and its mirror image is superimposable on it. It is optically inactive, so Assertion (A) is false.

Step 2: Judge the general statement in the reason Optical isomerism is indeed common in octahedral complexes containing didentate ligands. For example, suitable cis arrangements of two chelating ligands, and complexes containing three chelating ligands, can form non-superimposable mirror-image pairs. Reason (R) is true.

Step 3: Relate the two statements The general occurrence of optical isomerism with didentate ligands does not make this symmetric trans arrangement chiral. Options (A) and (B) incorrectly accept the assertion; option (C) reverses the truth values.

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

Quick Tip to Solve: For an octahedral complex with two chelates, inspect cis or trans geometry and symmetry before assigning chirality.

Section B (14 marks)

19(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:

- Standard Gibbs energy change and standard cell potential are related by $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, where n is the positive number of electrons transferred and F is Faraday's constant.
- Faraday's first law relates the mass m of substance deposited or liberated at an electrode to the charge Q passed through the electrolyte: $m = ZQ$, where Z is the electrochemical equivalent.

Step 1: Determine the signs for a spontaneous standard reaction For a spontaneous redox reaction under standard conditions, the standard Gibbs energy decreases, so $\Delta G^\circ < 0$. Since n and F are both positive, the equation

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

requires $E^\circ_{\text{cell}} > 0$. Thus the cell potential is positive and the standard Gibbs energy change is negative.

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

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

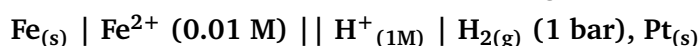
Here I is a constant current and t is the time for which it flows. If the charge passed doubles, the deposited or liberated mass doubles, with the same substance and electrode reaction.

Step 3: Conclusion (i) E°_{cell} is positive and ΔG° is negative. (ii) Faraday's first law states that the mass deposited or liberated is directly proportional to charge passed: $m = ZQ$.

Quick Tip to Solve: Use the minus sign in $\Delta G = -nFE$ for spontaneity, and remember that electrolysis mass follows total charge It .

OR

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



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

[2 marks]

Solution:

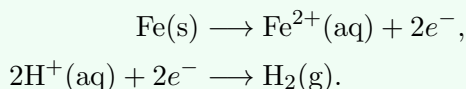
Concept:

- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log_{10} Q$, with potentials in volts, n electrons transferred and Q the reaction quotient.
- Pure solid iron has unit activity. For this calculation, ionic activities are represented by molar

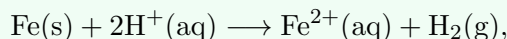
Quick Tip to Solve: Iron transfers two electrons here; with $Q = 0.01$, its negative logarithm makes the emf exceed 0.44 V.

concentrations relative to 1 M, and hydrogen pressure by its ratio to 1 bar.

Step 1: Write the electrode reactions and reaction quotient The left electrode is the anode and the right electrode is the cathode:



Thus the overall reaction is



so $n = 2$. Using the stated concentrations and pressure,

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

The concentration symbols in this quotient denote numerical activities under the concentration approximation.

Step 2: Substitute into the Nernst equation With $E_{\text{cell}}^\circ = 0.44 \text{ V}$ and $\log_{10}(0.01) = -2$,

$$\begin{aligned}E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \log_{10}(0.01) \\ &= 0.44 - \frac{0.0591}{2} (-2) \\ &= 0.4991 \text{ V}.\end{aligned}$$

Since $Q < 1$, the correction increases the emf above the standard value, which checks the sign.

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: Iron transfers two electrons here; with $Q = 0.01$, its negative logarithm makes the emf exceed 0.44 V.

20. 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:

- For a fixed reaction pathway, 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.
- Activation energy is the energy barrier between reactants and the activated complex. Temperature changes the fraction of molecules able to cross this barrier.

Step 1: Effect on the rate constant As T increases, $E_a/(RT)$ decreases and the exponent $-E_a/(RT)$

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

becomes less negative. Thus the exponential factor, and hence k , increases. Equivalently, for $T_2 > T_1$,

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

A greater fraction of molecules has energy at least equal to the activation energy, so more collisions are effective.

Step 2: Effect on activation energy For the same reaction pathway, E_a remains unchanged when temperature is increased. Heating gives reactant molecules more energy but does not lower the energy barrier itself. A catalyst can provide a different pathway with a lower barrier; merely raising temperature does not do so.

Step 3: Conclusion The rate constant k increases, while activation energy E_a remains unchanged for the same reaction pathway.

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

21. (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 donates an available lone pair of electrons to a central metal ion, forming a coordinate bond. Positive charge alone does not determine whether a species is a ligand.
- The nitrite ion NO_2^- is ambidentate: it can coordinate through nitrogen or oxygen, giving linkage isomers. Neutral ammine ligands do not change the metal oxidation state.

Step 1: (a) Identify the species without a donor lone pair NH_4^+ cannot act as a ligand. Nitrogen uses its lone pair in forming the fourth N-H bond, so no lone pair remains available for donation. In contrast, OH^- and H_2O have available oxygen lone pairs, and CH_3NH_2 has an available nitrogen lone pair; these three can act as ligands.

Step 2: (b) Name the linkage isomer The red complex contains oxygen-bound nitrite, $\text{Co}-\text{ONO}$. Its linkage isomer contains nitrogen-bound nitrite, $\text{Co}-\text{NO}_2$, commonly called the nitro form. The complex cation has charge +2 because there are two chloride counterions. If cobalt has oxidation state x , then $x + 5(0) - 1 = +2$, giving $x = +3$. The linkage isomer is named pentaamminenitrito-N-cobalt(III) chloride, also conventionally 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 (pentaamminenitrocobalt(III) chloride).

Quick Tip to Solve: Red nitrite complexes use oxygen attachment; switch to nitrogen attachment for the nitro linkage isomer.

22. Why is boiling point of o-dichlorobenzene higher than p-dichlorobenzene but melting point of para isomer is higher than ortho isomer ? [2 marks]

Solution:

Concept:

- Boiling involves separating molecules from the liquid; stronger intermolecular attractions generally raise the boiling point.
- Melting disrupts the ordered crystal lattice. Molecular symmetry and efficient packing can raise the melting point even when the molecular dipole moment is smaller.

Step 1: Explain the higher boiling point of the ortho isomer In o-dichlorobenzene the two C–Cl bond dipoles do not cancel, so the molecule has a net dipole moment. In the more symmetrical p-dichlorobenzene, the opposite C–Cl bond dipoles cancel. The ortho isomer therefore has stronger dipole–dipole attractions in addition to dispersion forces. More energy is required to separate its molecules on vaporisation, so its boiling point is higher.

Step 2: Explain the higher melting point of the para isomer p-Dichlorobenzene has a more symmetrical molecular shape and packs more regularly and efficiently in the crystal lattice. Its crystal is consequently more stable than that of the less symmetrical ortho isomer. More thermal energy is required to disrupt this well-packed crystal, so the para isomer has the higher melting point. Thus melting-point order depends on crystal packing as well as intermolecular attractions.

Step 3: Conclusion The ortho isomer boils at a higher temperature because of its net dipole and stronger dipole–dipole attractions; the para isomer melts at a higher temperature because its greater symmetry gives better crystal packing.

Quick Tip to Solve: For these isomers, compare dipole cancellation for boiling point and molecular symmetry for melting point.

23. 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:

- Acidity increases when the conjugate base formed after loss of H^+ is more stable. Resonance delocalisation stabilises a conjugate base.
- Phenols form coloured complexes with neutral ferric chloride solution, whereas ordinary aliphatic alcohols do not give this characteristic test.

Step 1: (a) Compare the conjugate bases Phenol loses a proton to form the phenoxide ion, $C_6H_5O^-$. Its negative charge is delocalised by resonance over oxygen and the ortho and para positions of the aromatic ring. Cyclohexanol forms the cyclohexoxide ion; its saturated ring has no conjugated pi system, so the negative charge remains localised on oxygen. The phenoxide ion is therefore more stable, making proton loss from phenol easier and phenol more acidic than cyclohexanol.

Quick Tip to Solve: Draw the conjugate bases mentally: an aromatic ring can delocalise phenoxide charge, while a saturated ring cannot.

Step 2: (b) Apply the neutral ferric chloride test Add a few drops of freshly prepared neutral FeCl_3 solution separately to the two samples. Phenol gives a violet colour because it forms a coloured ferric phenolate complex. Cyclohexanol does not produce this violet colour. The colour appearing with phenol distinguishes the two compounds under the same test conditions.

Step 3: Conclusion (a) Phenol is more acidic because its conjugate base is resonance-stabilised, unlike cyclohexoxide. (b) Neutral FeCl_3 gives a violet colour with phenol but no characteristic violet colour with cyclohexanol.

Quick Tip to Solve: Draw the conjugate bases mentally: an aromatic ring can delocalise phenoxide charge, while a saturated ring cannot.

24(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 ?

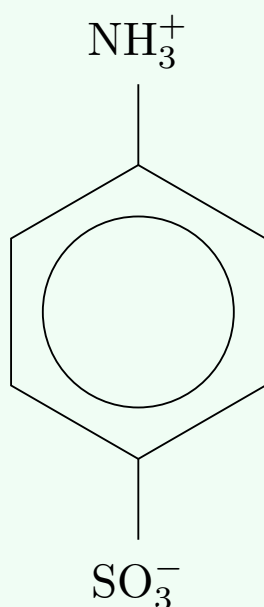
[2 marks]

Solution:

Concept:

- A zwitterion has both a positive and a negative charge within the same molecule, with zero net charge.
- Acetylation converts the strongly activating amino group, $-\text{NH}_2$, into the less activating acetamido group, $-\text{NHCOCH}_3$.

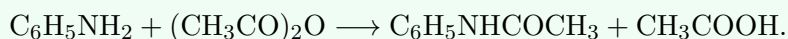
Step 1: (i) Form the zwitterion of sulphanilic acid Sulphanilic acid has an amino group and a sulphonic acid group in para positions on a benzene ring. Transfer of the acidic proton from $-\text{SO}_3\text{H}$ to $-\text{NH}_2$ gives $-\text{SO}_3^-$ and $-\text{NH}_3^+$. The resulting structure is shown below; the charges cancel overall.



Zwitterion of sulphanilic acid (para substituents)

Quick Tip to Solve: Keep the two groups para in the zwitterion, and show both charges; protect aniline as acetanilide before controlled ring substitution.

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



The nitrogen lone pair is now also delocalised towards the carbonyl group. It is therefore less available for donation into the benzene ring, reducing the activating effect. The protected group remains ortho/para directing; after the desired substitution, hydrolysis restores the amino group.

Step 3: Conclusion (i) Sulphanilic acid exists as para- $\text{H}_3\text{N}^+ - \text{C}_6\text{H}_4 - \text{SO}_3^-$. (ii) Acetylation to acetanilide controls the activating effect of the amino group.

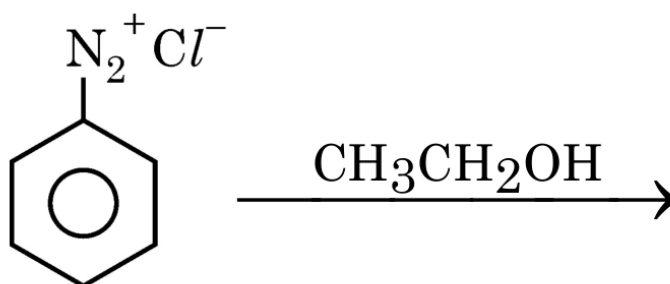
Quick Tip to Solve: Keep the two groups para in the zwitterion, and show both charges; protect aniline as acetanilide before controlled ring substitution.

OR

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

(ii) Convert Bromoethane to Propanamine.

[2 marks]

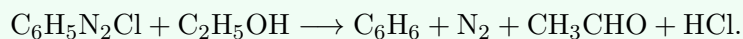


Solution:

Concept:

- Ethanol reduces an aryl diazonium salt to the corresponding arene; the diazonium group is replaced by hydrogen and nitrogen gas is liberated.
- Substitution by cyanide extends an alkyl chain by one carbon. Reduction of the resulting nitrile produces a primary amine.

Step 1: (i) Identify the main product of the diazonium reaction The given salt is benzenediazonium chloride. With ethanol it gives benzene as the main organic product, while ethanol is oxidised to ethanal:

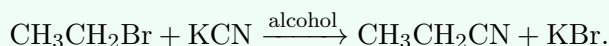


Thus the benzene ring loses the diazonium substituent and acquires a hydrogen atom. Ethanol acts as the reducing agent in this reaction.

Step 2: (ii) Convert bromoethane to propanamine First treat bromoethane with alcoholic potassium

Quick Tip to Solve: For a primary amine with one extra carbon, use KCN first and reduce the nitrile; use KCN rather than AgCN to form the nitrile.

cyanide to obtain propanenitrile:



Reduce the nitrile using LiAlH_4 in dry ether, followed by aqueous work-up:



The carbon of the cyanide group becomes the terminal $-\text{CH}_2\text{NH}_2$ carbon, so the product has the required three-carbon chain. Direct ammonolysis of bromoethane would instead give ethanamine.

Step 3: Conclusion (i) The main product is benzene, C_6H_6 . (ii) Bromoethane gives propanenitrile with alcoholic KCN; nitrile reduction then gives propan-1-amine.

Quick Tip to Solve: For a primary amine with one extra carbon, use KCN first and reduce the nitrile; use KCN rather than AgCN to form the nitrile.

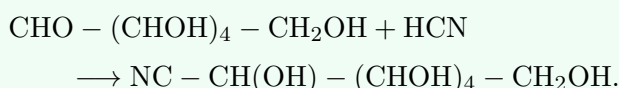
25. Give the reaction of glucose with hydrogen cyanide. Presence of which group is confirmed by this reaction ? [2 marks]

Solution:

Concept:

- Hydrogen cyanide adds across a carbonyl group to form a cyanohydrin: the carbonyl carbon acquires $-\text{CN}$, and oxygen becomes an $-\text{OH}$ group.
- Open-chain glucose is an aldohexose with the structure $\text{CHO} - (\text{CHOH})_4 - \text{CH}_2\text{OH}$. Its terminal carbonyl is an aldehyde group.

Step 1: Write cyanohydrin formation The aldehydic open-chain form of glucose reacts with hydrogen cyanide as follows:



This product is glucose cyanohydrin. The cyanide carbon is added to the molecule; the original aldehyde carbon is now bonded to hydrogen, hydroxyl, cyanide and the rest of the glucose chain.

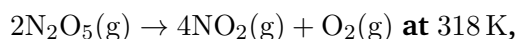
Step 2: Identify the group demonstrated by the reaction Cyanohydrin formation is an addition reaction of a carbonyl group, $> \text{C} = \text{O}$. Cyanide attacks the electrophilic carbonyl carbon, and protonation gives the hydroxyl group. Thus this reaction confirms a carbonyl group in glucose. In its open-chain structure this carbonyl is specifically the aldehyde group, $-\text{CHO}$. HCN addition alone is a test for a carbonyl, because ketones also form cyanohydrins.

Step 3: Conclusion Glucose forms $\text{NC} - \text{CH}(\text{OH}) - (\text{CHOH})_4 - \text{CH}_2\text{OH}$ with HCN. The reaction confirms the presence of a carbonyl group, present as an aldehyde in open-chain glucose.

Quick Tip to Solve: Replace the terminal CHO by $\text{CH}(\text{OH})\text{CN}$ when writing the cyanohydrin; HCN adds to $\text{C}=\text{O}$ and does not replace the chain's hydroxyl groups.

Section C (15 marks)

26. (a) For the reaction



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

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

[3 marks]

Solution:

Concept:

- For $aA \rightarrow bB$, the stoichiometrically normalised rate is $r = -\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt}$; coefficients ensure the same rate is obtained from every species.
- For a first order reaction, $t = \frac{2.303}{k} \log_{10} \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0, [A]_t$ are initial and remaining reactant concentrations.

Step 1: (a) Relate the disappearance rate to reaction rate For the equation as written,

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

The given disappearance rate is already positive, so multiply it by 1/2:

$$r = \frac{1}{2}(1.4 \times 10^{-3}) = 7.0 \times 10^{-4} \text{ m s}^{-1}.$$

The rate is reported in the unit supplied in the question. The stoichiometric factor is dimensionless; the positive sign describes forward progress of the reaction.

Step 2: (b) Obtain the time for 90 percent completion When 90 percent has reacted, 10 percent remains, so $[A]_t = 0.10[A]_0$. Substitution into the integrated first order rate law gives

$$t_{90\%} = \frac{2.303}{k} \log_{10} \frac{[A]_0}{0.10[A]_0} = \frac{2.303}{k} \log_{10} 10 = \frac{2.303}{k}.$$

Use the fraction remaining rather than the fraction consumed in the denominator.

Step 3: Compare with the time for 99 percent completion At 99 percent completion only 1 percent remains, so $[A]_t = 0.01[A]_0$:

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

Both times refer to the same first order reaction at the same conditions, hence the same k . Dividing eliminates k , giving $t_{99\%}/t_{90\%} = 2$. Each successive reduction of the remaining concentration by a factor of ten takes the same time in first order kinetics.

Step 4: Conclusion (a) The reaction rate is $7.0 \times 10^{-4} \text{ m s}^{-1}$. (b) $t_{99\%} = 2t_{90\%}$, as required.

Quick Tip to Solve: Divide the disappearance rate by the reactant coefficient; for completion times use 10 percent and 1 percent remaining, giving logarithms of 10 and 100.

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

(b) $[\text{Ni}(\text{CO})_4]$ has tetrahedral geometry while $[\text{Ni}(\text{CN})_4]^{2-}$ has square planar yet both exhibit diamagnetism. Explain.

[Atomic number : Ni = 28]

[3 marks]

Solution:

Concept:

- In an octahedral crystal field, the three t_{2g} orbitals are lower in energy than the two e_g orbitals. Δ_o is their energy separation and P is the pairing energy.
- When $\Delta_o > P$, pairing in t_{2g} is preferred to occupation of e_g . Diamagnetism means that all electrons are paired.
- Four-coordinate complexes can use sp^3 hybridisation for tetrahedral geometry or dsp^2 hybridisation for square-planar geometry; the metal oxidation state determines its initial electron count.

Step 1: (a) Fill the lower-energy orbitals first The printed ion has five d electrons. Since promotion to an e_g orbital costs more than pairing in a t_{2g} orbital, the first three electrons occupy the three t_{2g} orbitals and the next two pair there. Thus its low-spin configuration is

$$(t_{2g})^5(e_g)^0.$$

The three t_{2g} orbitals contain two pairs and one unpaired electron; the e_g orbitals remain empty.

Step 2: (b) Explain tetrahedral nickel tetracarbonyl The CO ligands are neutral, so nickel has oxidation state zero in $[\text{Ni}(\text{CO})_4]$. Free nickel has configuration $[\text{Ar}]3d^84s^2$. In the valence-bond description of this complex, the two $4s$ electrons enter the $3d$ subshell, making it $3d^{10}$. The empty $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals that accept ligand lone pairs. This produces tetrahedral geometry. All ten $3d$ electrons are paired, so the complex is diamagnetic.

Step 3: (b) Explain square-planar tetracyanonickelate(II) Each CN^- ligand has charge -1 . Writing the oxidation state as x , $x - 4 = -2$ gives $x = +2$, so Ni^{2+} has configuration $[\text{Ar}]3d^8$. The strong-field CN^- ligands cause these eight electrons to pair in four $3d$ orbitals, leaving one $3d$ orbital vacant. This vacant orbital, the $4s$ orbital and two $4p$ orbitals form four dsp^2 hybrids directed in a square plane. No unpaired electrons remain, so this complex is also diamagnetic.

Step 4: Conclusion (a) The strong-field d^5 configuration is $(t_{2g})^5(e_g)^0$. (b) $[\text{Ni}(\text{CO})_4]$ is tetrahedral with sp^3 hybridisation and paired d^{10} electrons; $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar with dsp^2 hybridisation and paired d^8 electrons. Both have zero unpaired electrons.

Quick Tip to Solve: Find nickel's oxidation state before counting d electrons: neutral CO gives Ni(0), whereas four cyanide ions in a dianion give Ni(II).

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

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

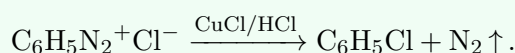
[3 marks]

Solution:

Concept:

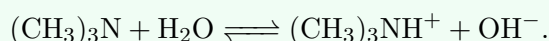
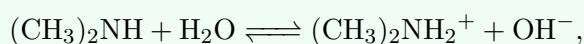
- Sandmeyer's reaction replaces the diazonium group of an aromatic diazonium salt by chloride, bromide or cyanide using the corresponding cuprous salt, with evolution of nitrogen.
- An amine acts as a base by accepting a proton through the lone pair on nitrogen. In water, its basicity depends on the alkyl group's inductive effect as well as the hydration of the protonated amine.

Step 1: (a) Write a Sandmeyer reaction Treat benzenediazonium chloride with cuprous chloride in hydrochloric acid. The diazonium group is replaced by chlorine, forming chlorobenzene and liberating nitrogen:



Cuprous chloride supplies the Sandmeyer reagent. Correspondingly, cuprous bromide gives bromobenzene and cuprous cyanide gives benzonitrile. Loss of the diazonium group as nitrogen is characteristic of these substitutions.

Step 2: (b) Compare electron donation and hydration The proton-acceptance equilibria are



Methyl groups exert a positive inductive effect, increasing electron density on nitrogen. Considered alone, three methyl groups would favour proton acceptance more than two. In aqueous solution, however, stabilisation of the conjugate acid by water must also be considered. The dimethylammonium ion has two N–H bonds and less crowding around its charged nitrogen than the trimethylammonium ion, which has only one N–H bond and three methyl groups. It is therefore hydrated more effectively through interactions with water. The greater hydration stabilisation of $(\text{CH}_3)_2\text{NH}_2^+$ outweighs the additional inductive advantage of the third methyl group in trimethylamine. Consequently, protonation of dimethylamine is more favourable in water.

Step 3: Conclusion (a) Benzenediazonium chloride gives chlorobenzene and nitrogen with CuCl/HCl , illustrating Sandmeyer's 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 stabilised.

Quick Tip to Solve: For aqueous methylamine basicity, compare hydration of the conjugate acids as well as the positive inductive effect; counting methyl groups alone gives the wrong order here.

29. 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]

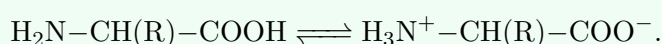
Solution:

Concept:

- Hydroxylamine forms an oxime with a free aldehyde or ketone carbonyl group. A carbonyl locked in an acetal form does not undergo this reaction.
- Amino acids contain both an acidic carboxyl group and a basic amino group, so internal proton transfer produces a zwitterion containing opposite charges.
- Water-soluble vitamins generally have little storage in the body. DNA strands follow specific base pairing: adenine with thymine, and guanine with cytosine.

Step 1: (a) Check for an available carbonyl group Penta-acetate of glucose is a cyclic derivative in which all five hydroxyl groups, including the anomeric hydroxyl group, have been acetylated. The anomeric centre is thereby locked in an acetal form, and a free aldehyde group is not available. Since hydroxylamine must react with a free carbonyl group to form an oxime, glucose penta-acetate does not react with hydroxylamine.

Step 2: (b) Show formation of the dipolar ion The carboxyl group donates a proton to the amino group of an amino acid:



The product is a zwitterion: it has a positively charged ammonium group and a negatively charged carboxylate group, although its overall charge is zero. Electrostatic attraction between these ionic centres in the solid gives salt-like properties, such as crystalline character and comparatively high melting points.

Step 3: (c) Explain the need for regular dietary intake Water-soluble vitamins, such as vitamin C and most B-group vitamins, are generally not stored in significant amounts in the body. Excess quantities are readily removed in urine. Their supply must therefore be replenished regularly through the diet to maintain the amounts required for normal metabolism and prevent deficiency. Vitamin B12 is an exception because appreciable reserves can be stored.

Step 4: (d) Apply specific base pairing in DNA Adenine on one DNA strand pairs specifically with thymine on the opposite strand through two hydrogen bonds. Guanine pairs with cytosine through three hydrogen bonds. Therefore, each base in one strand determines the matching base in the other: an A requires a T, and a G requires a C. This specific pairing makes their base sequences complementary and allows either strand to act as a template during replication.

Step 5: Conclusion The four observations follow respectively from absence of a free carbonyl group, zwitterion formation, limited storage and urinary loss of water-soluble vitamins, and specific A-T and G-C pairing. The question permits any three of these explanations.

Quick Tip to Solve: Match each observation to its molecular cause: carbonyl availability, opposite ionic groups, vitamin storage, and the A-T/G-C pairing rule.

30(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:

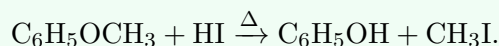
Concept:

- Resonance delocalisation of an oxygen lone pair into the aromatic ring gives the phenolic C – O bond partial double-bond character.
- For molecules of comparable size, stronger intermolecular attractions require more heat to separate molecules and therefore raise boiling point.
- Hydrogen iodide cleaves an aryl–alkyl ether at its alkyl–oxygen bond, leaving the aryl–oxygen bond intact.

Step 1: (i) Compare the carbon–oxygen bonds In phenol, a lone pair on oxygen overlaps with the conjugated π -system of the benzene ring. The resonance contributors give the bond joining the ring carbon to oxygen some double-bond character. This makes it shorter than the ordinary single C – O bond in methanol, where no aromatic resonance delocalisation is possible. Also, the bonded carbon in phenol is sp^2 -hybridised, whereas the carbon in methanol is sp^3 -hybridised.

Step 2: (ii) Compare intermolecular forces The four compounds have broadly comparable molecular sizes. Nonpolar n-butane has only London dispersion forces. Ethoxyethane also has dipole–dipole attractions, but cannot form hydrogen bonds with itself. Butanal has a more strongly polar carbonyl group and hence stronger dipole–dipole attractions than the ether. Butanol has an O – H group and forms intermolecular hydrogen bonds, giving the greatest attraction among these liquids.

Step 3: (iii) Cleave anisole with hydrogen iodide On heating anisole with HI, the ether oxygen is protonated and iodide attacks the methyl carbon. Cleavage therefore produces phenol and methyl iodide:

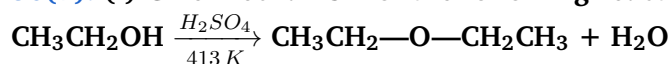


Attack at the aromatic sp^2 carbon is unfavourable; the resonance-stabilised aryl–oxygen bond is retained.

Step 4: Conclusion (i) Resonance gives the phenolic C – O bond partial double-bond character, shortening it. (ii) The increasing boiling-point order is n-butane < ethoxyethane < butanal < butanol. (iii) Heating anisole with HI gives phenol and CH_3I .

Quick Tip to Solve: Rank these boiling points by dispersion, ether dipole, carbonyl dipole, then hydrogen bonding; in anisole cleavage, iodide attacks the methyl group.

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



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

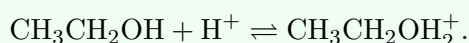
[3 marks]

Solution:

Concept:

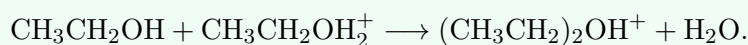
- Concentrated sulphuric acid catalyses intermolecular dehydration of ethanol at 413 K; protonation changes the poor leaving group OH into water.
- Ether formation involves nucleophilic attack by a second ethanol molecule, followed by loss of a proton to regenerate the acid catalyst.
- Hydroboration–oxidation converts an alkene into an alcohol with anti-Markovnikov orientation: the hydroxyl group goes to the less substituted carbon.

Step 1: (i) Protonate the ethanol oxygen An oxygen lone pair accepts a proton from the acid:

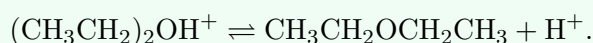


Water is a better leaving group than hydroxide.

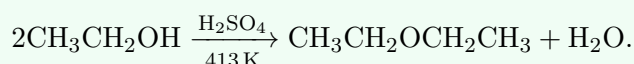
Step 2: Attack with a second ethanol molecule A second ethanol molecule uses its oxygen lone pair to attack the primary carbon of protonated ethanol. The carbon–oxygen bond to water breaks simultaneously in an S_N2 step, producing a protonated ether:



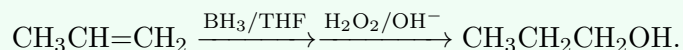
Step 3: Remove a proton and regenerate the catalyst The protonated ether loses a proton to give ethoxyethane:



The overall reaction is



Step 4: (ii) Illustrate hydroboration–oxidation with propene Treat propene with borane in tetrahydrofuran, then alkaline peroxide. Boron adds to the less substituted carbon; oxidation replaces it with OH:



The product is propan-1-ol. The process gives anti-Markovnikov hydration without a carbocation rearrangement.

Step 5: Conclusion (i) Ethoxyethane forms by protonation, attack of ethanol with water departure, and deprotonation. (ii) Hydroboration followed by alkaline peroxide oxidation converts propene into propan-1-ol.

Quick Tip to Solve: In ether formation, show the second ethanol attacking protonated ethanol; in hydroboration–oxidation place OH on propene's terminal carbon.

Section D (8 marks)

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

31. Nucleophilic Substitution

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

Influences of solvent polarity: In S_N1 reaction, the polarity of the system increases from the reactant to the transition state, because a polar solvent has a greater effect on the transition state than the reactant, thereby reducing activation energy and accelerating the reaction. In S_N2 reaction, the polarity of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and slow down the reaction rate. For example, the decomposition rate (S_N1) of tertiary chlorobutane at 25 °C in water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate (S_N2) of 2-Bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. Hence the level of solvent polarity has influence on both S_N1 and S_N2 reaction, but with different results. Generally speaking weak polar solvent is favourable for S_N2 reaction, while strong polar solvent is favourable for S_N1 . Generally speaking the substitution reaction of tertiary haloalkane is based on S_N1 mechanism in solvents with a strong polarity (for example ethanol containing water). [4 marks]

Answer the following questions:

31(a). Why racemisation occurs in S_N1 ?

[1 mark]

Solution:

Concept:

- An S_N1 reaction forms a carbocation intermediate when the leaving group departs.
- The positively charged carbon is sp^2 -hybridised and trigonal planar, so both faces are accessible to the nucleophile.

Step 1: Identify the planar intermediate For an optically active haloalkane, departure of the halide ion breaks the tetrahedral arrangement at the reacting chiral carbon. The resulting carbocation is planar and therefore no longer retains that centre's original spatial configuration.

Step 2: Consider attack from each face The nucleophile can attack from either face of this planar carbocation. One approach gives retention and the other inversion of configuration, producing both enantiomers. Their opposite optical rotations reduce or cancel the rotation of the product mixture.

Step 3: Conclusion Racemisation occurs in S_N1 because nucleophilic attack on either face of the planar carbocation gives both enantiomers.

Quick Tip to Solve: Link racemisation to a planar carbocation with two accessible faces, rather than to the two-step mechanism alone.

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

[1 mark]

Solution:

Concept:

- Water is a strongly polar solvent because its polar O–H bonds are arranged in a bent molecule with a net dipole.
- Ethanol contains a polar hydroxyl group attached to a relatively nonpolar ethyl group, reducing its overall solvent polarity.

Step 1: Compare the molecular structures Water, H_2O , has no hydrocarbon portion. Ethanol, $\text{C}_2\text{H}_5\text{OH}$, contains a polar –OH group but also a nonpolar C_2H_5 group. This hydrocarbon portion reduces the relative contribution of the polar group to the liquid's behaviour.

Step 2: Relate the structures to solvent polarity The nonpolar ethyl group makes ethanol less effective than water at screening electrostatic attraction and stabilising separated ions. Consistent with this, the passage gives a dielectric constant of 24 for ethanol and 79 for water; the lower dielectric constant indicates lower solvent polarity.

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

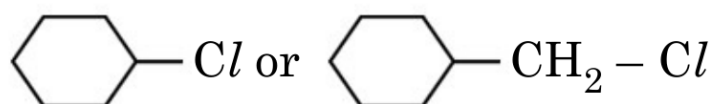
Quick Tip to Solve: Compare the nonpolar ethyl group in ethanol with its absence in water, and use the lower dielectric constant as supporting evidence.

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

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

(ii)

[2 marks]



Solution:

Concept:

- In an $\text{S}_{\text{N}}2$ substitution, the nucleophile attacks the carbon bearing the halogen from the side opposite to the leaving group in a single concerted step.
- Reactivity increases with better leaving-group ability and lower steric hindrance. For comparable alkyl groups, I^- leaves more readily than Cl^- ; primary substrates generally react faster than secondary substrates.

Step 1: (i) Compare the leaving groups Both $\text{CH}_3\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{Cl}$ have the same primary ethyl group, so their steric environments are essentially the same. The weaker carbon-iodine bond breaks more readily, and iodide is a better leaving group than chloride. Consequently ethyl iodide undergoes nucleophilic substitution faster under otherwise identical conditions.

Step 2: (ii) Compare the carbon bearing chlorine In chlorocyclohexane, chlorine is directly bonded to

Quick Tip to Solve: Compare leaving groups only when the alkyl groups match; otherwise first count the carbon neighbours of the carbon directly bonded to the halogen.

a ring carbon attached to two other carbons: the reacting centre is secondary and backside attack is hindered by the ring. In $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, chlorine is on the exocyclic CH_2 carbon, which is primary. Both compounds have the same leaving group, so the less hindered primary centre in cyclohexylmethyl chloride favours the $\text{S}_{\text{N}}2$ pathway.

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

Quick Tip to Solve: Compare leaving groups only when the alkyl groups match; otherwise first count the carbon neighbours of the carbon directly bonded to the halogen.

OR

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

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

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

[2 marks]

Solution:

Concept:

- The slow step of an $\text{S}_{\text{N}}1$ reaction is ionisation of the carbon-halogen bond to form a carbocation; the nucleophile attacks subsequently.
- For comparable alkyl bromides, a more stable carbocation forms more readily. Alkyl groups stabilise carbocations through their electron-releasing inductive effect and hyperconjugation, giving the usual order primary < secondary < tertiary.

Step 1: (i) Identify each reacting carbon 1-Bromopentane has bromine on a terminal CH_2 carbon and initially gives a primary carbocation. 2-Bromopentane has bromine on a carbon bonded to two other carbons and gives a secondary carbocation. In 2-bromo-2-methylbutane, the carbon bearing bromine is bonded to three alkyl groups and gives a tertiary carbocation. Since bromide is the leaving group in all three, the increasing reactivity follows their increasing carbocation stability.

Step 2: (ii) Classify before considering remote branching 1-Bromo-3-methylbutane has a primary carbon bearing bromine; branching at carbon 3 does not make that reacting centre tertiary. 2-Bromo-3-methylbutane has a secondary reacting centre. 2-Bromo-2-methylbutane has a tertiary reacting centre. Thus the primary compound is least reactive, the secondary compound is intermediate, and the tertiary compound is most reactive. Possible rearrangement after ionisation does not replace the classification of the initial rate-determining ionisation step.

Step 3: Conclusion Increasing $\text{S}_{\text{N}}1$ reactivity:

(i) 1-Bromopentane < 2-Bromopentane < 2-Bromo-2-methylbutane.

(ii) 1-Bromo-3-methylbutane < 2-Bromo-3-methylbutane < 2-Bromo-2-methylbutane.

Quick Tip to Solve: For an $\text{S}_{\text{N}}1$ order, locate the carbon bearing bromine and count its carbon neighbours; branching elsewhere does not change its primary or secondary classification.

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

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

Answer the following questions:

[4 marks]

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

[1 mark]

Solution:

Concept:

- Conductivity κ measures the ability of a unit volume of solution to conduct electric current and depends on the number of ions present per unit volume and their mobility.
- Dilution increases the solution volume and lowers the concentration of charge-carrying ions, even if their mobility increases slightly.

Step 1: Follow the ion concentration on dilution Adding water spreads the dissolved K^+ and Cl^- ions through a larger volume. Thus a given unit volume contains fewer ions available to carry current through the solution.

Step 2: Distinguish conductivity from molar conductivity The reduction in the number of ions per unit volume outweighs the mobility increase caused by weaker interionic interactions. Therefore conductivity falls on dilution, although molar conductivity, which refers to one mole of electrolyte, rises. The table illustrates this fall in κ as concentration decreases.

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

Quick Tip to Solve: Link conductivity to ions per unit volume; do not confuse its dilution trend with that of molar conductivity.

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

Solution:

Concept:

- The conductivity ratio used to calculate degree of dissociation is $\alpha = \Lambda_m / \Lambda_m^\circ$, where Λ_m is the molar conductivity at the stated concentration and Λ_m° is its limiting value.
- Degree of dissociation is dimensionless; multiplying its fractional value by 100 gives the percentage.

Step 1: Select the reading at the required concentration The table gives $\Lambda_m = 141.0 \text{ S cm}^2 \text{ mol}^{-1}$ at 0.01 M. The supplied limiting molar conductivity is $150.0 \text{ S cm}^2 \text{ mol}^{-1}$. Use the third row, rather than

Quick Tip to Solve: Read molar conductivity from the row for 0.01 M and divide by the limiting molar conductivity; do not divide the conductivity itself by 150.

the value for a more concentrated solution.

Step 2: Calculate the conductivity ratio Substituting the two values with identical units gives

$$\alpha = \frac{141.0}{150.0} = 0.940, \quad 100\alpha = 94.0\%.$$

This is the degree obtained by the requested conductivity-ratio calculation. KCl is a strong electrolyte; its finite-concentration molar conductivity is also affected by interionic interactions, so the ratio should not be taken as proof that the remaining fraction of KCl molecules is unionised.

Step 3: Conclusion The calculated degree of dissociation is $\alpha = 0.94$, or 94% .

Quick Tip to Solve: Read molar conductivity from the row for 0.01 M and divide by the limiting molar conductivity; do not divide the conductivity itself by 150.

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

Solution:

Concept:

- Molar conductivity, Λ_m , measures the conductance contributed by one mole of an electrolyte in solution; it depends on the mobilities of its constituent ions.
- Both HCl and KCl are strong electrolytes in water. At infinite dilution, Kohlrausch's law gives $\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$, where λ_i° is an ion's limiting molar conductivity.

Step 1: Identify the ions to be compared Aqueous HCl supplies H^+ and Cl^- , whereas KCl supplies K^+ and Cl^- . Each is essentially fully ionised. At a given concentration, their comparison therefore depends chiefly on the different cations, since the chloride ion is common to both.

Step 2: Compare the cation mobilities The hydrogen ion has exceptionally high mobility in water because charge can be transferred rapidly through the hydrogen-bonded water network by proton transfer. Its ionic molar conductivity is much greater than that of K^+ . Consequently, HCl has a larger molar conductivity at the same concentration; the difference is not due to HCl producing a greater number of ions per formula unit.

Step 3: Conclusion Rahul would obtain $\Lambda_m(HCl) > \Lambda_m(KCl)$ at the same concentration because H^+ is much more mobile than K^+ .

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

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

Solution:

Concept:

- Dilution increases the molar conductivity Λ_m of both strong and weak electrolytes, though the reasons and magnitude of the increase differ.
- KCl is a strong electrolyte and is essentially fully dissociated. Ethanoic acid is weak: $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$. Its degree of ionisation increases substantially on dilution.

Step 1: State one similar observation For both KCl and CH_3COOH , the molar conductivity increases as the concentration decreases. Thus Amit, like Rahul, would observe larger Λ_m values for the more dilute solutions. Molar conductivity refers to one mole of electrolyte and should not be confused with conductivity per unit volume, which decreases on dilution.

Step 2: State one different observation and explain it The rise in Λ_m on dilution would be much more pronounced for ethanoic acid than for KCl . Dilution increases the ionisation of the weak acid, producing more mobile ions per mole of acid. KCl already supplies nearly all its ions, so its smaller increase is mainly due to reduced interionic interactions and greater ionic mobility. The weak acid therefore shows a sharp, nonlinear rise towards its limiting molar conductivity, unlike the relatively gradual rise for KCl .

Step 3: Conclusion Similarity: Λ_m increases on dilution in both solutions. Difference: the increase is much steeper for CH_3COOH , owing to increased ionisation of the weak electrolyte.

Quick Tip to Solve: Compare the trend of molar conductivity first, then distinguish increased ionisation of a weak acid from improved mobility in KCl .

Section E (15 marks)

- 33(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:

- Elevation of boiling point is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent's ebullioscopic constant and m the solute molality in mol kg^{-1} .

Quick Tip to Solve: Convert 90 percent remaining vapour pressure into 10 percent lowering, retain the total-moles denominator, and use $i = 3$ for fully dissociated MgCl_2 .

- For a non-volatile solute in an ideal solution, Raoult's law gives $p = x_1 p^\circ$. Thus the relative lowering of vapour pressure is $(p^\circ - p)/p^\circ = x_2 = n_2/(n_1 + n_2)$, where subscripts 1 and 2 denote solvent and solute respectively.
- Complete dissociation into ν ions per formula unit gives $i = \nu$. An undissociated molecular solute such as glucose has $i = 1$.

Step 1: (i) Compare the number of dissolved particles NaCl dissociates according to $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$, giving approximately two particles per formula unit, whereas glucose remains molecular. In the usual comparison of these solutions, NaCl therefore contributes more dissolved particles and causes a greater lowering of the solvent's vapour pressure. Its solution must be heated to a higher temperature before its vapour pressure reaches atmospheric pressure, so its boiling point is higher. The relevant factors are approximately $i = 2$ for NaCl and $i = 1$ for glucose; equal molarity should not be substituted directly for molality in a numerical boiling-point calculation.

Step 2: (ii) Translate the vapour pressure into mole fractions The final pressure is $p = 0.90p^\circ$, so the relative lowering is 0.10. Using the molar mass of benzene, 78 g mol^{-1} , gives

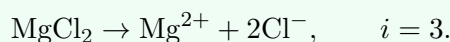
$$n_1 = \frac{78}{78} = 1.00 \text{ mol}, \quad \frac{n_2}{1 + n_2} = 0.10.$$

Rearrangement yields $n_2 = 0.10(1 + n_2)$, and hence $0.90n_2 = 0.10$, or $n_2 = 1/9 \text{ mol}$. The dissolved mass is

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

The full mole-fraction expression is used because the specified lowering is ten percent; replacing its denominator with solvent moles would introduce an unnecessary dilute-solution approximation.

Step 3: (iii) Calculate molality and account for dissociation Complete dissociation follows



The solute amount is $10/95 = 0.10526 \text{ mol}$, and the solvent mass is $200 \text{ g} = 0.200 \text{ kg}$. Therefore

$$\begin{aligned} m &= \frac{10/95}{0.200} = 0.52632 \text{ mol kg}^{-1}, \\ \Delta T_b &= 3 \times 0.512 \times 0.52632 \\ &= 0.80842 \text{ K}. \end{aligned}$$

Here i accounts for the three ions, so molality is calculated from formula units of MgCl_2 and is not multiplied by three a second time.

Step 4: Conclusion (i) NaCl produces more solute particles than glucose, giving the higher boiling point. (ii) The mass of X is 5.56 g. (iii) The boiling-point elevation is 0.808 K.

Quick Tip to Solve: Convert 90 percent remaining vapour pressure into 10 percent lowering, retain the total-moles denominator, and use $i = 3$ for fully dissociated MgCl_2 .

33(b). (i) Why is the value of Van't Hoff factor for ethanoic acid in benzene close to 0.5 ?

(ii) Determine the osmotic pressure of a solution prepared by dissolving 2.32×10^{-2} g of K_2SO_4 in 2 L of solution at $25^\circ C$, assuming that K_2SO_4 is completely dissociated.

($R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$, Molar mass $K_2SO_4 = 174 \text{ g mol}^{-1}$)

(iii) When 25.6 g of Sulphur was dissolved in 1000 g of benzene, the freezing point lowered by 0.512 K. Calculate the formula of Sulphur (S_x).

(K_f for benzene = $5.12 \text{ K kg mol}^{-1}$, Atomic mass of Sulphur = 32 g mol^{-1})

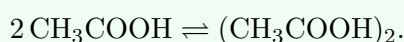
[5 marks]

Solution:

Concept:

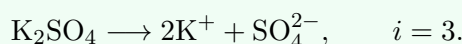
- The van't Hoff factor i is the actual number of solute particles divided by the number expected without association or dissociation. Association reduces i , whereas dissociation increases it.
- Osmotic pressure is $\pi = iCRT = i(n/V)RT$, where C is the molar concentration, V the solution volume in litres and T the absolute temperature.
- Freezing-point depression is $\Delta T_f = K_f m$, where m is moles of solute per kilogram of solvent. The molecular mass divided by the atomic mass gives the number of atoms per molecule.

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



Two acid molecules therefore behave as one dissolved particle. If association is nearly complete, the number of particles is nearly halved, giving $i \approx 1/2$. More generally, if α is the fraction of acid molecules that dimerise, an initial mole leaves $1 - \alpha$ mole of monomers and $\alpha/2$ mole of dimers; hence $i = 1 - \alpha/2$. A value close to 0.5 indicates α close to unity.

Step 2: (ii) Count ions and calculate osmotic pressure Complete dissociation gives three ions per formula unit:



Use the volume of the solution and convert the temperature to kelvin:

$$\begin{aligned} n &= \frac{2.32 \times 10^{-2}}{174} = 1.333 \times 10^{-4} \text{ mol}, \\ C &= \frac{1.333 \times 10^{-4}}{2} = 6.667 \times 10^{-5} \text{ mol L}^{-1}, \\ T &= 25 + 273 = 298 \text{ K}, \\ \pi &= 3(6.667 \times 10^{-5})(0.082)(298) \\ &= 4.8872 \times 10^{-3} \text{ atm}. \end{aligned}$$

The factor three accounts for the dissolved ions; using CRT alone would underestimate the pressure by a factor of three.

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

Quick Tip to Solve: Count particles before using a colligative-property equation: acid dimers halve the count, whereas each fully dissociated potassium sulphate unit gives three ions.

Treat the dissolved sulphur molecules as nondissociating solute particles. Thus:

$$m = \frac{\Delta T_f}{K_f} = \frac{0.512}{5.12} = 0.100 \text{ mol kg}^{-1},$$
$$n = 0.100 \times 1.000 = 0.100 \text{ mol},$$
$$M = \frac{25.6}{0.100} = 256 \text{ g mol}^{-1},$$
$$x = \frac{M}{32} = \frac{256}{32} = 8.$$

This calculation determines the molecular mass of the solute particles actually present in benzene; it must be compared with sulphur's atomic mass to obtain the molecular formula.

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

Quick Tip to Solve: Count particles before using a colligative-property equation: acid dimers halve the count, whereas each fully dissociated potassium sulphate unit gives three ions.

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

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

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

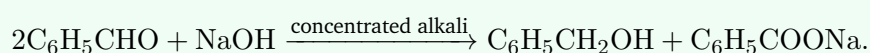
[5 marks]

Solution:

Concept:

- Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised to carboxylate and another is reduced to an alcohol.
- Carboxylic acids form strong intermolecular hydrogen bonds, often as dimers. Aldehydes and ketones have dipole interactions but cannot hydrogen-bond to each other because they lack an O – H bond.
- Wolff-Kishner reduction converts each carbonyl group to a methylene group. Hydroxylamine forms one oxime per carbonyl group; Tollens' reagent detects an aldehyde and the iodoform test detects a $\text{CH}_3\text{CO}-$ group.

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



This is disproportionation of the aldehyde: oxidation and reduction occur simultaneously in different

Quick Tip to Solve: Combine the tests before choosing a structure: a dioxime means two carbonyl groups, and simultaneous Tollens and iodoform positives require an aldehyde and a methyl ketone on the straight five-carbon chain.

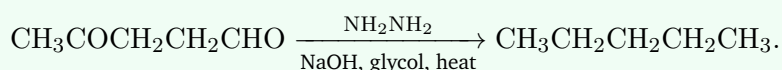
molecules of the same reactant.

Step 2: (ii) Explain the boiling-point difference Corresponding carboxylic acid molecules associate by intermolecular hydrogen bonding between their carboxyl groups, commonly forming cyclic dimers. More energy is needed to overcome these strong attractions during vaporisation. Aldehydes and ketones lack a hydrogen bonded directly to oxygen and therefore cannot form comparable hydrogen bonds among their own molecules. Their dipole–dipole attractions are weaker, so their boiling points are lower than those of corresponding carboxylic acids.

Step 3: (iii) Use all four observations to identify A Formation of a dioxime requires two carbonyl groups. The positive Tollens' test requires an aldehyde group, while the iodoform test requires a methyl ketone group. Reduction to *n*-pentane fixes an unbranched five-carbon skeleton. Combining these facts gives the structure

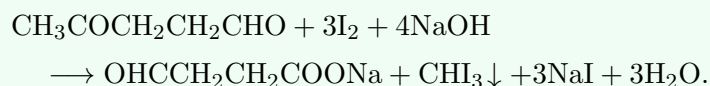


Its formula is $\text{C}_5\text{H}_8\text{O}_2$. Both carbonyl oxygens are removed in Wolff–Kishner reduction, preserving the carbon skeleton:

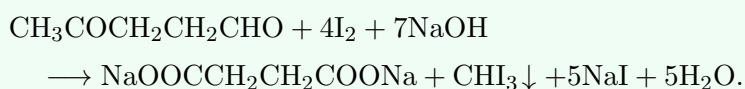


The dioxime has structure $\text{CH}_3\text{C}(=\text{NOH})\text{CH}_2\text{CH}_2\text{CH}=\text{NOH}$. Thus neither a simple ketone nor a simple aldehyde can satisfy all the observations.

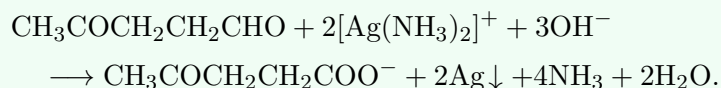
Step 4: Write the iodoform and Tollens' test reactions In the iodoform test the methyl ketone group produces a yellow precipitate of iodoform. The group-specific haloform equation is:



This equation shows cleavage at the methyl ketone. With excess alkaline iodine, the aldehyde end can also be oxidised to carboxylate; the complete equation then is:



Tollens' reagent oxidises the aldehyde end while leaving the ketone group intact. Metallic silver forms a silver mirror:



The carboxylate product is appropriate because Tollens' reagent is alkaline; acidification would give 4-oxopentanoic acid.

Step 5: Conclusion Cannizzaro reaction gives an alcohol and a carboxylate from a non-enolisable aldehyde. Strong hydrogen bonding raises the boiling points of carboxylic acids.

$A = \text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO}$, 4-oxopentanal, gives yellow CHI_3 in the iodoform test and a silver

Quick Tip to Solve: Combine the tests before choosing a structure: a dioxime means two carbonyl groups, and simultaneous Tollens and iodoform positives require an aldehyde and a methyl ketone on the straight five-carbon chain.

mirror with Tollens' reagent.

Quick Tip to Solve: Combine the tests before choosing a structure: a dioxime means two carbonyl groups, and simultaneous Tollens and iodoform positives require an aldehyde and a methyl ketone on the straight five-carbon chain.

OR

34(b). (i) Give a chemical test to distinguish between ethanal acid and ethanoic acid.

(ii) Why is the α -hydrogens of aldehydes and ketones are acidic in nature ?

(iii) An organic compound 'A' with molecular formula $C_4H_8O_2$ undergoes acid hydrolysis to form two compounds 'B' and 'C'. Oxidation of 'C' with acidified potassium permanganate also produces 'B'. Sodium salt of 'B' on heating with soda lime gives methane.

(1) Identify 'A', 'B' and 'C'.

(2) Out of 'B' and 'C', which will have higher boiling point ? Give reason.

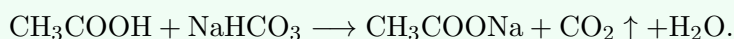
[5 marks]

Solution:

Concept:

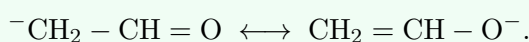
- Carboxylic acids react with sodium hydrogen carbonate to release carbon dioxide; aldehydes do not give this acid-base test.
- An α -hydrogen is attached to the carbon adjacent to a carbonyl group. Its removal forms a resonance-stabilised enolate ion.
- Acid hydrolysis of an ester yields a carboxylic acid and an alcohol. A primary alcohol can be oxidised to the corresponding carboxylic acid.
- Soda-lime decarboxylation converts $RCOONa$ to RH , removing the carboxyl carbon. Intermolecular hydrogen bonding affects boiling points.

Step 1: (i) Distinguish ethanal and ethanoic acid Add aqueous sodium hydrogen carbonate separately to the two samples. Ethanoic acid gives brisk effervescence of carbon dioxide, whereas ethanal gives no effervescence:



The evolved gas turns limewater milky. The aldehyde group in ethanal does not supply the acidic proton needed to liberate carbon dioxide from hydrogen carbonate, so this observation distinguishes the samples.

Step 2: (ii) Explain the acidity of alpha-hydrogens The electron-withdrawing carbonyl group facilitates removal of an adjacent hydrogen as a proton. More importantly, the conjugate base is stabilised because its negative charge is delocalised between the α -carbon and oxygen. For ethanal, the two resonance contributors are

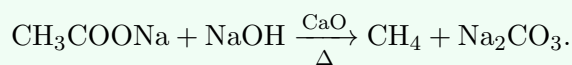


These represent one enolate ion, not two separate substances. Stabilisation of the conjugate base

Quick Tip to Solve: Start the identification with methane from soda lime: restore one carboxyl carbon to obtain ethanoic acid, then use oxidation to identify ethanol.

makes loss of an α -proton easier than loss of an ordinary alkane hydrogen; the same reasoning applies to ketones with α -hydrogens.

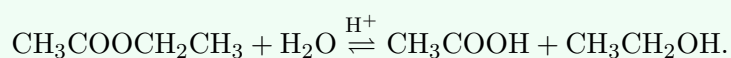
Step 3: (iii)(1) Identify the acid B and alcohol C The sodium salt of B gives methane on soda-lime decarboxylation. Since the product has one fewer carbon atom than the salt, B must be ethanoic acid, CH_3COOH :



C oxidises to ethanoic acid and is the alcohol obtained by ester hydrolysis. Hence C is ethanol, $\text{CH}_3\text{CH}_2\text{OH}$:



Step 4: (iii)(1) Identify and verify the ester A Combining the ethanoic acid residue with the ethyl group of ethanol gives ethyl ethanoate, $\text{CH}_3\text{COOCH}_2\text{CH}_3$. It has the required molecular formula $\text{C}_4\text{H}_8\text{O}_2$. Its acid-catalysed hydrolysis accounts for both identified products:



Thus the hydrolysis, oxidation and decarboxylation observations consistently identify the same three compounds.

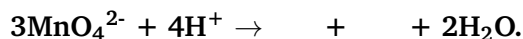
Step 5: (iii)(2) Compare the boiling points B, ethanoic acid, has the higher boiling point. Although ethanol also forms intermolecular hydrogen bonds, carboxylic acid molecules associate strongly as dimers, with two hydrogen bonds between a pair of molecules. This stronger association requires more energy to separate the molecules into the vapour phase. Consequently, ethanoic acid boils at about 118°C , compared with about 78°C for ethanol.

Step 6: Conclusion Ethanoic acid gives the sodium hydrogen carbonate test; ethanal does not. Alpha-hydrogens are acidic because the resulting enolate is resonance-stabilised. $\text{A} = \text{CH}_3\text{COOCH}_2\text{CH}_3$ (ethyl ethanoate), $\text{B} = \text{CH}_3\text{COOH}$ (ethanoic acid) and $\text{C} = \text{CH}_3\text{CH}_2\text{OH}$ (ethanol). B has the higher boiling point because of strong hydrogen-bonded association.

Quick Tip to Solve: Start the identification with methane from soda lime: restore one carboxyl carbon to obtain ethanoic acid, then use oxidation to identify ethanol.

35. (a) Why is chemistry of actinoids complicated as compared to lanthanoids ?

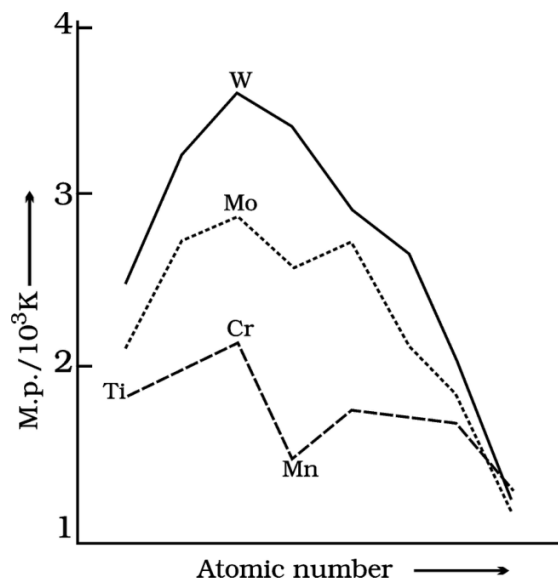
(b) Complete the following reaction and justify that it is a disproportionation reaction:



(c) The given graph shows the trends in melting points of transition metals:

Explain the reason why Cr has highest melting point and manganese (Mn) a lower melting point.

[5 marks]



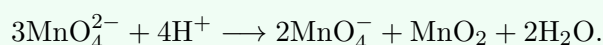
Solution:

Concept:

- Actinoids fill $5f$ orbitals and lanthanoids fill $4f$ orbitals. The relative energies of available valence orbitals influence the range of oxidation states.
- Disproportionation is a reaction in which the same species is simultaneously oxidised and reduced; identify it by changes in the oxidation number of one element.
- Stronger metallic bonding generally raises melting point. In transition metals, participation of valence s and d electrons contributes to the strength of metallic bonding.

Step 1: (a) Explain the more complicated chemistry of actinoids The $5f$, $6d$ and $7s$ orbitals of actinoids have comparable energies, so varying numbers of these electrons can participate in bonding. Actinoids therefore exhibit a wider range of oxidation states and more varied chemical behaviour. In lanthanoids, the $4f$ electrons are more deeply buried and the $+3$ oxidation state predominates. The greater variability of actinoid oxidation states makes their chemistry more complicated. Their radioactivity also makes experimental study more difficult.

Step 2: (b) Complete and check the reaction Manganate(VI) ions form permanganate ions and manganese dioxide in acidic solution:



There are three manganese atoms, twelve oxygen atoms and four hydrogen atoms on each side. The total charge on the left is $3(-2) + 4 = -2$; the two permanganate ions on the right also give a total

Quick Tip to Solve: For disproportionation, write the starting and both final oxidation numbers: a rise from $+6$ to $+7$ and a fall from $+6$ to $+4$ prove both processes occur.

charge of -2 . Thus both atoms and charge are balanced.

Step 3: (b) Justify disproportionation using oxidation numbers Taking oxygen as -2 , the oxidation number of manganese in MnO_4^{2-} is $+6$. In MnO_4^- , it is $+7$, whereas in MnO_2 , it is $+4$. Hence two manganese atoms each undergo oxidation from $+6$ to $+7$, releasing two electrons in total. One manganese atom undergoes reduction from $+6$ to $+4$, accepting those two electrons. Because the same starting species undergoes both oxidation and reduction, the reaction is a disproportionation reaction.

Step 4: (c) Explain the high melting point of chromium The chromium maximum shown is in the first transition series. Chromium has the configuration $[\text{Ar}] 3d^5 4s^1$, with five unpaired d electrons and one unpaired s electron. The large number of unpaired valence electrons available for metallic bonding produces strong cohesion and a high enthalpy of atomisation. Considerable energy is therefore required to overcome its metallic bonding on melting, giving chromium a high melting point in this series.

Step 5: (c) Explain the lower melting point of manganese Manganese has the configuration $[\text{Ar}] 3d^5 4s^2$. Its $4s$ electrons are paired, and its half-filled $3d^5$ subshell has extra stability. The d electrons are relatively less available for metallic bonding, making the metallic bonding weaker than the trend near chromium would suggest. Manganese consequently has a relatively low enthalpy of atomisation and an anomalously lower melting point. Merely counting its five unpaired d electrons does not explain the dip; the stability of its half-filled subshell must also be considered.

Step 6: Conclusion Actinoid chemistry is more varied because several valence orbitals of similar energy support many oxidation states. The reaction is $3\text{MnO}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{MnO}_4^- + \text{MnO}_2 + 2\text{H}_2\text{O}$, with Mn(VI) both oxidised to Mn(VII) and reduced to Mn(IV) . Strong metallic bonding accounts for chromium's high melting point in the first transition series; weaker bonding associated with manganese's stable half-filled $3d^5$ configuration explains its lower value.

Quick Tip to Solve: For disproportionation, write the starting and both final oxidation numbers: a rise from $+6$ to $+7$ and a fall from $+6$ to $+4$ prove both processes occur.