

CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-6-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **33** questions. **All questions are compulsory.**
- (ii) This question paper is divided into **five** sections – **Section A, B, C, D and E.**
- (iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1** mark.
- (iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2** marks.
- (v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3** marks.
- (vi) **Section D** – questions number **29 and 30** are case-based questions. Each question carries **4** marks.
- (vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5** marks.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculator is not allowed.

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

1. Which by-product is obtained in the manufacture of phenol from cumene ?

[1 mark]

- (A) Acetaldehyde
- (B) Acetone
- (C) Anisole
- (D) o-Cresol

Correct Answer: (B) Acetone

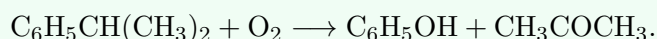
Solution:

Concept:

- Cumene is isopropylbenzene, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$, the industrial starting material for this process.
- Oxidation produces cumene hydroperoxide; acid-catalysed cleavage gives phenol and a carbonyl compound.

Step 1: Identify the process Cumene is first oxidised by air to its hydroperoxide. Cleavage of this intermediate in an acidic medium converts the aromatic portion into phenol and the three-carbon side-chain portion into a ketone.

Step 2: Identify the co-product and reject alternatives The net product relation is



The carbonyl co-product is acetone. Acetaldehyde has only two carbon atoms, while anisole and o-cresol are aromatic compounds and are not the co-products of this cleavage.

Step 3: Conclusion The by-product is acetone, CH_3COCH_3 . Hence, the correct option is (B).

Quick Tip to Solve: Remember that the three-carbon side chain of cumene gives the three-carbon ketone acetone.

2. Which reagents are required for one step conversion of chlorobenzene to toluene ?

[1 mark]

- (A) $\text{NaNO}_2 + \text{HCl}$
- (B) $\text{CH}_3\text{Cl}/\text{Anhydrous AlCl}_3$
- (C) $\text{CH}_3\text{Cl}/\text{Fe}$, Dark
- (D) CH_3Cl , Na, Dry ether

Correct Answer: (D) CH_3Cl , Na, Dry ether

Solution:

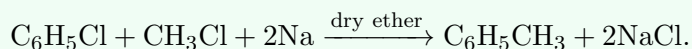
Concept:

- The Wurtz-Fittig reaction couples an aryl halide with an alkyl halide using sodium in dry ether.
- Replacing the chlorine of chlorobenzene by a methyl group produces toluene, $\text{C}_6\text{H}_5\text{CH}_3$.

Quick Tip to Solve: An aryl halide plus an alkyl halide with sodium in dry ether signals Wurtz-Fittig coupling.

Step 1: Choose the coupling partner The aryl halide is chlorobenzene, $\text{C}_6\text{H}_5\text{Cl}$. The required alkyl partner is methyl chloride, CH_3Cl , because the product must contain one methyl group attached to the benzene ring.

Step 2: Apply Wurtz-Fittig conditions and check the other choices Use sodium metal in dry ether:



Sodium nitrite and hydrochloric acid are used for diazotisation of a primary aromatic amine, not this conversion. Methyl chloride with anhydrous aluminium chloride would be a Friedel-Crafts reagent; halobenzenes do not undergo the usual Friedel-Crafts alkylation under these conditions. Iron in the dark does not supply the sodium coupling conditions.

Step 3: Conclusion The required reagents are CH_3Cl , sodium and dry ether. Hence, the correct option is (D).

Quick Tip to Solve: An aryl halide plus an alkyl halide with sodium in dry ether signals Wurtz-Fittig coupling.

3. Coordination number of Fe in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is :

[1 mark]

- (A) 6
- (B) 3
- (C) 4
- (D) 5

Correct Answer: (A) 6

Solution:

Concept:

- Coordination number counts donor atoms directly bonded to the central metal, not simply the number of ligand molecules.
- Oxalate, $\text{C}_2\text{O}_4^{2-}$, is a bidentate ligand: each oxalate coordinates through two oxygen donor atoms.

Step 1: Count the ligands and their denticity The complex $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ contains three oxalate ligands. Each oxalate contributes two donor oxygen atoms to iron, forming a chelate ring.

Step 2: Calculate the total number of donor atoms The coordination number is

$$3 \times 2 = 6.$$

Option (B), 3, counts ligand molecules rather than donor atoms. Neither 4 nor 5 accounts for all three bidentate oxalate ligands. The overall charge -3 is not the coordination number.

Step 3: Conclusion The coordination number of Fe is 6. Hence, the correct option is (A).

Quick Tip to Solve: For a chelating ligand, multiply the number of ligands by their denticity before selecting the option.

4. Which of the following complexes shows geometrical isomerism ?

[1 mark]

- (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (B) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
- (C) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
- (D) $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

Correct Answer: (C) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$

Solution:

Concept:

- Geometrical isomers have the same bonding but different relative positions of ligands around the central metal.
- An octahedral complex of type $[\text{MA}_4\text{B}_2]$ can have cis and trans forms: the two B ligands are adjacent or opposite.

Step 1: Examine the complex with two chlorido ligands In $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, the two chlorido ligands can occupy adjacent positions, with a 90° angle, or opposite positions, with a 180° angle. These are distinct cis and trans geometrical isomers.

Step 2: Compare the remaining complexes In $[\text{Co}(\text{NH}_3)_6]^{3+}$, all six ligands are identical. Both $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ have five identical ammine ligands and one different ligand, so no distinct cis/trans arrangement exists. The nitrito ligand in the last complex may give linkage isomerism with nitro coordination; that is a different type of isomerism.

Step 3: Conclusion $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ shows geometrical isomerism. Hence, the correct option is (C).

Quick Tip to Solve: For octahedral complexes, look for two identical minority ligands that can be adjacent or opposite.

5. Which of the following does not show variable oxidation state ?

[1 mark]

- (A) Sc
- (B) Mn
- (C) Cr
- (D) Cu

Correct Answer: (A) Sc

Solution:

Concept:

- Variable oxidation states occur when different numbers of nearby-energy ns and $(n-1)d$ electrons participate in bonding.
- Scandium has configuration $[\text{Ar}]3d^14s^2$; its usual oxidation state in compounds is +3.

Step 1: Consider scandium Loss of its two $4s$ electrons and one $3d$ electron gives Sc^{3+} with the stable $[\text{Ar}]$ configuration. In the standard chemistry of these elements, scandium does not show the range of oxidation states characteristic of many other transition elements.

Quick Tip to Solve: At the start of the transition series, Sc loses all three valence electrons to give its usual +3 state.

Step 2: Check the other elements Manganese shows several oxidation states, including +2, +4 and +7. Chromium commonly shows +2, +3 and +6. Copper shows +1 and +2. Thus each of these three alternatives exhibits variable oxidation states.

Step 3: Conclusion Scandium (Sc) does not show variable oxidation state in the standard CBSE context. Hence, the correct option is (A).

Quick Tip to Solve: At the start of the transition series, Sc loses all three valence electrons to give its usual +3 state.

6. The reagent that can be used to convert benzenediazonium chloride to benzene is : [1 mark]

- (A) Cu/HCl
- (B) H₂O
- (C) CH₃CH₂OH
- (D) CuCN

Correct Answer: (C) CH₃CH₂OH

Solution:

Concept:

- Reduction of an aromatic diazonium salt replaces the diazonium group by hydrogen, with nitrogen gas released.
- Ethanol reduces benzenediazonium chloride to benzene and is itself oxidised to ethanal.

Step 1: Recognise replacement by hydrogen The required change is from C₆H₅N₂⁺Cl⁻ to C₆H₆. The diazonium group must therefore be replaced by hydrogen rather than by hydroxyl, chloride or cyanide.

Step 2: Use ethanol and compare the other reagents The reaction is



Copper with hydrochloric acid replaces the diazonium group by chlorine. Water on warming produces phenol, while cuprous cyanide produces benzonitrile. Only ethanol among the listed reagents gives benzene.

Step 3: Conclusion The reagent is ethanol, CH₃CH₂OH. Hence, the correct option is (C).

Quick Tip to Solve: When the diazonium group must become hydrogen, select a reducing reagent such as ethanol or hypophosphorous acid.

7. The gas evolved when methylamine reacts with HNO_2 is :

[1 mark]

- (A) NO
- (B) N_2
- (C) NH_3
- (D) NO_2

Correct Answer: (B) N_2

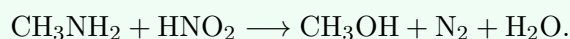
Solution:

Concept:

- Primary aliphatic amines react with nitrous acid to form unstable aliphatic diazonium intermediates.
- These intermediates decompose with loss of nitrogen gas; aqueous reaction conditions give the corresponding alcohol.

Step 1: Identify methylamine as a primary aliphatic amine Methylamine, CH_3NH_2 , contains an amino group attached to a methyl group. Unlike aromatic diazonium salts at low temperature, its diazonium intermediate is unstable and decomposes readily.

Step 2: Write the reaction and identify the gas The overall reaction is



The two nitrogen atoms, one from the amine and one from nitrous acid, leave as N_2 . Nitric oxide and nitrogen dioxide are not the gas identified in this deamination reaction, and ammonia is not released because the amino group undergoes diazotisation and decomposition.

Step 3: Conclusion The evolved gas is nitrogen, N_2 . Hence, the correct option is (B).

Quick Tip to Solve: Primary aliphatic amine plus nitrous acid indicates alcohol formation accompanied by brisk nitrogen evolution.

8. A solution of acetone in chloroform :

[1 mark]

- (A) obeys Raoult's law.
- (B) forms azeotrope.
- (C) shows a positive deviation from Raoult's law.
- (D) shows a negative deviation from Raoult's law.

Correct Answer: (D) shows a negative deviation from Raoult's law.

Solution:

Concept:

- Negative deviation occurs when unlike intermolecular attractions exceed the attractions between like molecules.
- For an ideal solution, Raoult's law gives $p_i = x_i p_i^\circ$; stronger attractions reduce the actual vapour pressure below this value.

Quick Tip to Solve: Look for stronger hydrogen bonding between unlike molecules: it lowers vapour pressure and gives negative deviation.

Step 1: Identify the intermolecular interaction The oxygen of the carbonyl group in acetone forms a hydrogen bond with the hydrogen of chloroform. The acetone–chloroform attraction is stronger than the attractions present in the separate liquids.

Step 2: Compare the options The molecules consequently escape less readily into the vapour phase, giving negative deviation. Thus (A), ideal behaviour, and (C), positive deviation, do not describe this mixture. Such a mixture can also form a maximum-boiling azeotrope at a particular composition, so (B) is a possible consequence; (D) directly states its characteristic departure from Raoult's law.

Step 3: Conclusion The solution shows negative deviation from Raoult's law. The expected option is (D).

Quick Tip to Solve: Look for stronger hydrogen bonding between unlike molecules: it lowers vapour pressure and gives negative deviation.

9. The freezing point of one molal KCl solution, assuming KCl to be completely dissociated in water, is :

(K_f for water = $1.86 \text{ K kg mol}^{-1}$)

[1 mark]

- (A) -3.72°C
- (B) $+3.72^\circ\text{C}$
- (C) -1.86°C
- (D) $+2.72^\circ\text{C}$

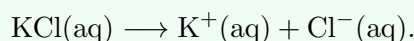
Correct Answer: (A) -3.72°C

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_fm$, where i is the van't Hoff factor and m is molality.
- Complete dissociation of one formula unit of KCl gives two ions, so $i = 2$.

Step 1: Count the dissolved particles



Since dissociation is complete, the effective particle concentration is twice the stated molality.

Step 2: Calculate the freezing temperature

$$\Delta T_f = 2 \times 1.86 \times 1 = 3.72 \text{ K}.$$

Pure water freezes at 0°C , so the solution freezes at $0 - 3.72 = -3.72^\circ\text{C}$. Option (C) ignores dissociation; (B) and (D) have the wrong positive sign for a freezing-point depression.

Step 3: Conclusion The freezing point is -3.72°C . Hence the correct option is (A).

Quick Tip to Solve: Count ions first, then subtract the depression from the freezing point of the pure solvent.

10. A galvanic cell can behave like an electrolytic cell when :

[1 mark]

- (A) $E_{\text{cell}} = E_{\text{ext}}$
- (B) $E_{\text{ext}} > E_{\text{cell}}$
- (C) $E_{\text{cell}} > E_{\text{ext}}$
- (D) $E_{\text{cell}} = 0$

Correct Answer: (B) $E_{\text{ext}} > E_{\text{cell}}$

Solution:

Concept:

- A galvanic cell drives a spontaneous reaction using its own emf E_{cell} .
- An opposing external voltage E_{ext} reverses the reaction only when it exceeds the cell emf.

Step 1: Compare the opposing voltages Connect the external source so that it opposes the spontaneous cell current. If $E_{\text{ext}} < E_{\text{cell}}$, the cell still supplies current. At equality, the opposing driving forces cancel and no net current flows.

Step 2: Identify the electrolytic condition When $E_{\text{ext}} > E_{\text{cell}}$, the external source forces current in the reverse direction and drives the non-spontaneous reverse reaction. This is electrolytic operation. Thus (A) describes zero net current, (C) describes continued galvanic operation, and (D) alone does not provide a reverse driving source.

Step 3: Conclusion The required condition is $E_{\text{ext}} > E_{\text{cell}}$. Hence the correct option is (B).

Quick Tip to Solve: An opposing voltage equal to the emf stops the current; a larger opposing voltage reverses it.

11. The value of rate constant for a pseudo first order reaction :

[1 mark]

- (A) depends only on temperature.
- (B) depends on the concentration of reactants present in small amount.
- (C) depends on the concentration of reactants present in large excess.
- (D) is not dependent on the concentration of reactants.

Correct Answer: (C) depends on the concentration of reactants present in large excess.

Solution:

Concept:

- In a pseudo first order reaction, an excess reactant has practically constant concentration during a run.
- For $r = k[A][B]$ with B in large excess, $r = k_{\text{obs}}[A]$, where $k_{\text{obs}} = k[B]$.

Step 1: Absorb the excess concentration into the constant The concentration of the reactant present in large excess changes negligibly as the small amount of the other reactant is consumed. It can therefore be included in the observed first order rate constant.

Step 2: Distinguish observed and intrinsic constants The pseudo first order constant depends on the chosen excess concentration through $k_{\text{obs}} = k[B]$. It also changes with temperature through k ,

Quick Tip to Solve: Write the actual rate law and absorb only the effectively constant excess concentration into the observed constant.

but does not depend only on temperature as (A) claims. The concentration of the limiting reactant remains explicitly in the rate law, excluding (B). Option (D) confuses the observed constant with the intrinsic rate constant.

Step 3: Conclusion It depends on the concentration of the reactant present in large excess. Hence the correct option is (C).

Quick Tip to Solve: Write the actual rate law and absorb only the effectively constant excess concentration into the observed constant.

12. Furanose ring of fructose is formed due to reaction between :

[1 mark]

- (A) C_1 and C_5
- (B) C_2 and C_5
- (C) C_1 and C_4
- (D) C_1 and C_2

Correct Answer: (B) C_2 and C_5

Solution:

Concept:

- Fructose is a ketohexose with its carbonyl group at C_2 .
- Intramolecular addition of an alcohol group to a ketone forms a cyclic hemiketal; a furanose ring has five ring atoms.

Step 1: Identify the reacting functional groups The hydroxyl group attached to C_5 reacts with the carbonyl group at C_2 . The hydroxyl oxygen becomes the ring oxygen and C_2 becomes the anomeric carbon.

Step 2: Count the ring members and reject alternatives The ring contains the oxygen atom and carbons C_2, C_3, C_4, C_5 : five atoms in total. Thus the participating carbon positions are C_2 and C_5 . Options (A), (C), and (D) use C_1 , which is not the carbonyl carbon of open-chain fructose and cannot give this hemiketal closure.

Step 3: Conclusion The furanose ring forms through reaction between C_2 and C_5 . Hence the correct option is (B).

Quick Tip to Solve: For fructose, start at the ketone carbon C_2 and count four carbons plus one oxygen for the furanose ring.

13. Assertion (A) : Actinoids show wide range of oxidation states.

Reason (R) : This is due to comparable energies of 5f, 6d and 7s orbitals.

[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:

- Variable oxidation states arise when electrons from several subshells can participate in bonding.
- The 5f, 6d, and 7s subshells of actinoids have comparable energies.

Step 1: Judge the assertion Actinoids exhibit a wide range of oxidation states because different numbers of their valence electrons can be involved in bonding. The assertion is true.

Step 2: Judge the reason The energy separations between the 5f, 6d, and 7s subshells are relatively small, particularly in the earlier actinoids. The reason is therefore true.

Step 3: Check the explanatory link Comparable orbital energies allow electrons from all these subshells to participate, producing multiple oxidation states. Hence the reason directly explains the assertion. Option (B) incorrectly denies this causal link, while (C) and (D) incorrectly declare one of the true statements false.

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

Quick Tip to Solve: Link comparable subshell energies to participation of different numbers of electrons in bonding.

14. Assertion (A) : Order of the reaction can be zero or fractional.

Reason (R) : We cannot determine order from balanced chemical equation.

[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:

- For $r = k[A]^a[B]^b$, reaction order is $a + b$; the exponents are determined experimentally.
- Overall balanced equations express stoichiometry, whereas rate laws depend on the reaction mechanism.

Step 1: Judge the assertion Rate-law exponents need not be positive integers. For example, a concentration-independent rate has order zero, and an experimental rate law can have a fractional exponent. Therefore the assertion is true.

Step 2: Judge the reason For a general reaction, the balanced overall chemical equation does not determine the rate-law exponents. Order must be established from kinetic measurements. Therefore the reason is true.

Step 3: Check whether the reason explains the assertion The reason describes how order is determined; it does not itself explain why a rate can be independent of concentration or exhibit fractional concentration dependence. Those behaviours arise from the kinetics and mechanism. Thus the two true statements lack the direct explanatory link required by (A). Options (C) and (D) incorrectly call a true statement false.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence the correct option is (B).

Quick Tip to Solve: For assertion–reason questions, test the causal link separately after establishing that both statements are true.

15. Assertion (A): Boiling point of $(C_2H_5)_2NH$ is lower than that of $n-C_4H_9NH_2$.

Reason (R): Hydrogen bonding is much more extensive in $n-C_4H_9NH_2$ as compared to $(C_2H_5)_2NH$.

[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:

- Intermolecular hydrogen bonding raises the boiling point of an amine.
- Primary amines have two N–H bonds per molecule, while secondary amines have one; compare compounds of similar molar mass.

Step 1: Judge the assertion Diethylamine, $(C_2H_5)_2NH$, and butan-1-amine, $n-C_4H_9NH_2$, are isomeric amines with the same molecular formula $C_4H_{11}N$. The primary amine forms a more extensive intermolecular hydrogen-bond network, so its boiling point is higher. Thus the assertion is true.

Step 2: Judge the reason Butan-1-amine has two N–H bonds available for hydrogen-bond donation per molecule, whereas diethylamine has only one. Both have a nitrogen lone pair for accepting hydrogen bonds. Hence hydrogen bonding is more extensive in the primary amine, making the reason true.

Step 3: Connect the reason to the assertion More extensive hydrogen bonding requires more energy to separate the molecules during boiling. This directly explains the higher boiling point of butan-1-amine. Options (B), (C) and (D) incorrectly deny either this causal connection or the truth of one of the statements.

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

Quick Tip to Solve: For isomeric amines, first count N–H bonds before comparing intermolecular hydrogen bonding.

16. Assertion (A) : Phenol is less acidic than alcohol.

Reason (R) : Phenoxide ion is more stable than alkoxide ion.

[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:

- Acidity increases when the conjugate base formed by loss of H^+ is more stable.
- The negative charge in phenoxide is delocalised by resonance; in an alkoxide it is localised on oxygen.

Step 1: Judge the assertion Phenol is more acidic than an ordinary alcohol because it loses a proton to form a resonance-stabilised phenoxide ion. Therefore the statement that phenol is less acidic than alcohol is false.

Step 2: Judge the reason In phenoxide, the negative charge is delocalised between oxygen and the ortho and para positions of the aromatic ring. An alkoxide lacks this resonance stabilisation; its alkyl group also has an electron-releasing inductive effect. Thus phenoxide is more stable than alkoxide and the reason is true.

Step 3: Assess the relationship The reason explains why phenol is more acidic, which is opposite to the assertion. Options (A) and (B) require a true assertion, and option (C) requires a false reason; none matches these truth values.

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

Quick Tip to Solve: Compare conjugate-base stability: resonance stabilisation of phenoxide favours loss of a proton.

Section B (10 marks)

17. State Raoult's law for a solution containing volatile components. Why is the vapour pressure of an aqueous solution of glucose lower than that of water ?

[2 marks]

Solution:

Concept:

- For an ideal solution, Raoult's law is $p_i = x_i p_i^0$, where p_i is the partial vapour pressure, x_i the liquid mole fraction and p_i^0 the pure-component vapour pressure at the same temperature.
- Glucose is non-volatile, so only water contributes appreciably to the vapour pressure of its aqueous solution.

Quick Tip to Solve: For a non-volatile solute, apply Raoult's law only to the solvent and check that its mole fraction is below one.

Step 1: State the law for volatile components The partial vapour pressure of each volatile component is directly proportional to its mole fraction in the solution. For two volatile components A and B,

$$p_A = x_A p_A^0, \quad p_B = x_B p_B^0, \quad p_{\text{total}} = x_A p_A^0 + x_B p_B^0.$$

Here $x_A + x_B = 1$, and the pure-component pressures are measured at the temperature of the solution.

Step 2: Apply the law to aqueous glucose Dissolving glucose reduces the mole fraction of water below unity: $x_w = n_w / (n_w + n_g) < 1$, where n_w and n_g are the amounts of water and glucose. Since glucose has negligible vapour pressure,

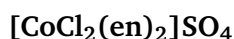
$$p_{\text{solution}} = x_w p_w^0 < p_w^0.$$

Thus fewer water molecules escape into the vapour at equilibrium. The lowering is $p_w^0 - p_{\text{solution}} = (1 - x_w)p_w^0$.

Step 3: Conclusion Raoult's law gives $p_i = x_i p_i^0$. Aqueous glucose has lower vapour pressure than pure water because glucose is non-volatile and lowers the mole fraction of water.

Quick Tip to Solve: For a non-volatile solute, apply Raoult's law only to the solvent and check that its mole fraction is below one.

18(a)(i). Write IUPAC names of the following coordination compounds :



[1 mark]

Solution:

Concept:

- For naming a coordination compound, name the cation before the anion and list ligand names alphabetically.
- Ethane-1,2-diamine (en) is neutral, chlorido has charge -1 , and sulphate has charge -2 .

Step 1: Determine the cobalt oxidation state The sulphate counter-ion is SO_4^{2-} , so the complex cation has charge $+2$. Let the oxidation state of cobalt be x . The two chlorido ligands contribute -2 , while the two en ligands are neutral:

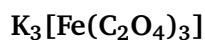
$$x + 2(-1) + 2(0) = +2 \Rightarrow x = +4.$$

Step 2: Name the complex and counter-ion The chlorido ligands are named before ethane-1,2-diamine alphabetically. Use dichlorido for two chlorido ligands and bis(ethane-1,2-diamine) for two ligands whose names already contain numerical terms. The cationic complex retains the metal name cobalt and includes its oxidation state (IV); sulphate is named last.

Step 3: Conclusion The IUPAC name is dichloridobis(ethane-1,2-diamine)cobalt(IV) sulphate.

Quick Tip to Solve: Find the charge of the complex from its counter-ion before calculating the metal oxidation state.

18(a)(ii). Write IUPAC names of the following coordination compounds :



[1 mark]

Solution:

Concept:

- Potassium is the cation and the complex is an anion, so the metal is named ferrate.
- Oxalato, $C_2O_4^{2-}$, is a bidentate ligand with charge -2 .

Step 1: Calculate the oxidation state of iron Three potassium ions each have charge $+1$, so the complex ion has charge -3 . If iron has oxidation state x , the three oxalato ligands contribute a total charge of -6 :

$$x + 3(-2) = -3 \Rightarrow x = +3.$$

Step 2: Construct the IUPAC name Name potassium first. Three oxalato ligands are indicated by tris(oxalato), using the multiplicative prefix suitable for a complex ligand. Because the coordination entity is negatively charged, use ferrate rather than iron; append (III) to state the metal oxidation state.

Step 3: Conclusion The IUPAC name is potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: Use the three potassium ions to infer a 3-minus complex charge, then subtract the ligand charges.

OR

18(b)(i). Differentiate between :

Double salt and Complex compound

[1 mark]

Solution:

Concept:

- A double salt contains two simple salts crystallised together and dissociates into all its constituent ions in water.
- A complex compound retains its coordination entity in solution under ordinary conditions.

Step 1: Explain double salts A double salt loses its identity on dissolution and gives the ions of both constituent salts. For example, Mohr's salt, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$, gives NH_4^+ , Fe^{2+} and SO_4^{2-} ions in water. These ions can give their usual characteristic tests.

Step 2: Explain complex compounds A complex compound dissociates to give counter-ions and an intact complex ion, rather than all the ions within its coordination sphere. For example, $K_4[Fe(CN)_6]$ gives $4K^+$ and $[Fe(CN)_6]^{4-}$, but does not ordinarily give free Fe^{2+} and CN^- ions. Its coordinated ions therefore do not give the usual tests for those free ions.

Step 3: Conclusion A double salt dissociates completely into its constituent simple ions; a complex compound retains its complex ion in aqueous solution.

Quick Tip to Solve: Distinguish the two by writing the species present after dissolution and checking whether the complex ion survives.

18(b)(ii). Differentiate between :

Didentate ligand and Ambidentate ligand

[1 mark]

Solution:

Concept:

- A donor atom supplies a lone pair to form a coordinate bond with a metal ion.
- Denticity counts donor atoms attached simultaneously to the same metal centre.

Step 1: Didentate ligand A didentate ligand binds to the same metal ion simultaneously through two donor atoms. For example, ethane-1,2-diamine, $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, attaches through both nitrogen atoms, generally forming a chelate ring.

Step 2: Ambidentate ligand An ambidentate ligand has two possible donor atoms but attaches through only one of them in a particular coordination bond. For example, NO_2^- can bind through nitrogen (nitro) or oxygen (nitrito). It does not bind through both atoms simultaneously as a didentate ligand does.

Step 3: Conclusion Didentate: two donor atoms bind simultaneously; ambidentate: either of two alternative donor atoms binds at a time.

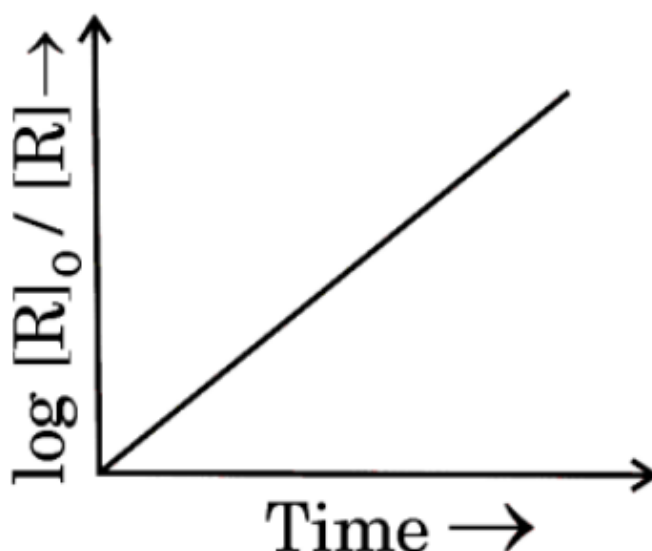
Quick Tip to Solve: Count simultaneous metal attachments, not merely the number of possible donor atoms.

19. Observe the graph in the given figure and answer the following questions :

(a) Predict the order of reaction.

(b) What is the slope of the curve ?

[2 marks]



Solution:

Concept:

- For a first-order reaction, $-d[R]/dt = k[R]$, where $[R]$ is reactant concentration and k is the rate constant.

Quick Tip to Solve: Read the logarithm axis carefully: common logarithms give slope $k/2.303$, while natural logarithms give k .

- Its integrated equation is $\log_{10}([R]_0/[R]) = kt/2.303$, with $[R]_0$ the initial concentration and t the elapsed time.

Step 1: (a) Identify the plotted quantity The vertical axis shows $\log([R]_0/[R])$, and the horizontal axis shows time. The straight line through the origin therefore represents the integrated first-order equation. At $t = 0$, $[R] = [R]_0$, so the logarithmic ratio is zero, consistent with the graph. A zero-order reaction would instead give a straight line when concentration itself is plotted against time.

Step 2: (b) Compare with the straight-line equation Writing the integrated equation as $y = mt + c$, we identify $y = \log_{10}([R]_0/[R])$, $m = k/2.303$ and $c = 0$. Hence

$$\text{slope} = \frac{\Delta \log_{10}([R]_0/[R])}{\Delta t} = \frac{k}{2.303}.$$

It is positive, since reactant concentration falls with time and the ratio increases. Its units are inverse time, matching those of k .

Step 3: Conclusion (a) First-order reaction. (b) Slope = $k/2.303$.

Quick Tip to Solve: Read the logarithm axis carefully: common logarithms give slope $k/2.303$, while natural logarithms give k .

20. How do you explain the following ?

(a) Presence of an aldehydic group in glucose.

(b) Presence of five -OH groups in glucose.

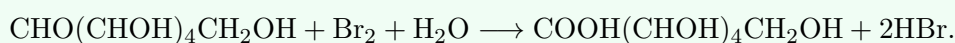
[2 marks]

Solution:

Concept:

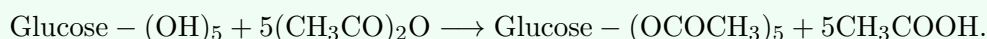
- Mild oxidation distinguishes an aldehydic group because $-\text{CHO}$ is converted to $-\text{COOH}$.
- Acetylation replaces the hydrogen of each alcohol $-\text{OH}$ group by an acetyl group, $-\text{COCH}_3$.

Step 1: (a) Evidence for the aldehydic group Glucose is oxidised by the mild oxidising agent bromine water to gluconic acid, containing the same six-carbon skeleton. This conversion of the terminal aldehyde into a carboxylic acid establishes an aldehydic group in the open-chain form of glucose:



Mild oxidation is more specific than merely showing that glucose forms a carbonyl derivative, since both aldehydes and ketones can form such derivatives.

Step 2: (b) Evidence for five hydroxyl groups Glucose reacts with acetic anhydride to form glucose pentaacetate. Each hydroxyl group produces one acetate ester group, so incorporation of five acetyl groups establishes the presence of five $-\text{OH}$ groups. In symbolic form,



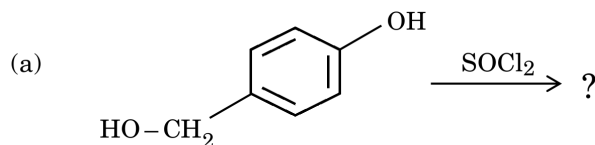
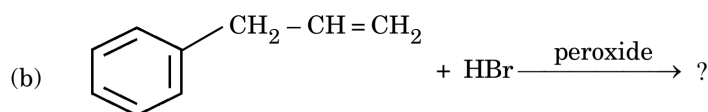
Here the notation indicates the five hydroxyl sites and their conversion into acetate groups.

Quick Tip to Solve: Use bromine water for the aldehyde and count the five acetyl groups in glucose pentaacetate for hydroxyls.

Step 3: Conclusion (a) Oxidation by bromine water to gluconic acid proves the aldehydic group. (b) Formation of glucose pentaacetate proves five hydroxyl groups.

Quick Tip to Solve: Use bromine water for the aldehyde and count the five acetyl groups in glucose pentaacetate for hydroxyls.

21. Draw the structures of the major monohalo products in each of the following reactions : [2 marks]

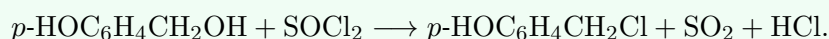


Solution:

Concept:

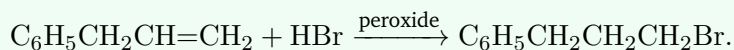
- Thionyl chloride, SOCl_2 , replaces the hydroxyl group of an alcohol by chlorine.
- In the presence of peroxide, HBr adds to an unsymmetrical alkene by the free-radical mechanism with anti-Markovnikov orientation.

Step 1: (a) Replace the benzylic alcohol group The starting compound contains both a phenolic $-\text{OH}$ group and a benzylic $-\text{CH}_2\text{OH}$ group at para positions. Thionyl chloride converts the benzylic alcohol to $-\text{CH}_2\text{Cl}$; the phenolic hydroxyl remains unchanged because its aryl carbon-oxygen bond is resistant to this substitution. The reaction is



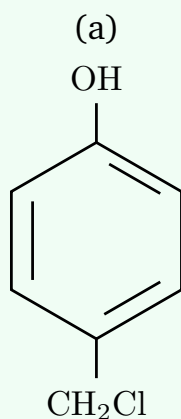
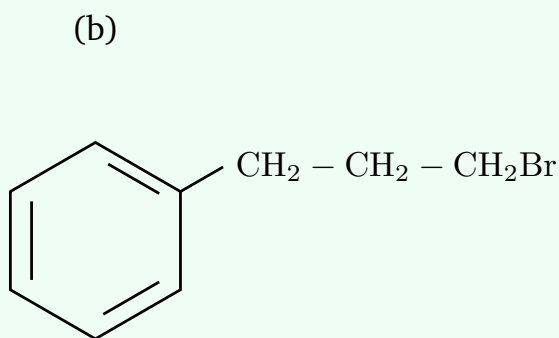
The product is 4-(chloromethyl)phenol.

Step 2: (b) Apply the peroxide effect The alkene is $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$. A bromine radical attaches to the terminal carbon so that the intermediate radical lies on the more substituted carbon; it then abstracts hydrogen from HBr. Thus bromine goes to the terminal carbon and hydrogen to the internal alkene carbon:



Only the side-chain double bond reacts; the benzene ring retains its aromatic structure.

Quick Tip to Solve: For SOCl_2 distinguish phenolic OH from benzylic OH; with HBr/peroxide place Br on the terminal alkene carbon.



Structures of the major monohalo products

Step 3: Conclusion The major products are (a) $p\text{-HOC}_6\text{H}_4\text{CH}_2\text{Cl}$ and (b) $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, as drawn.

Quick Tip to Solve: For SOCl_2 distinguish phenolic OH from benzylic OH; with HBr /peroxide place Br on the terminal alkene carbon.

Section C (21 marks)

22. How can you obtain the following from aniline ? Give only chemical equation.

(a) p-nitroaniline

(b) Chlorobenzene

(c) Phenol

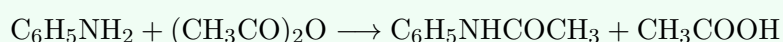
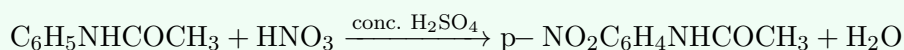
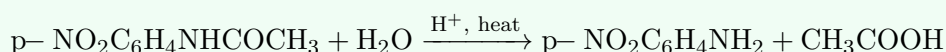
[3 marks]

Solution:

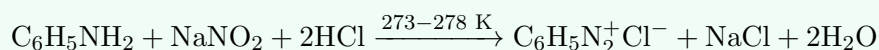
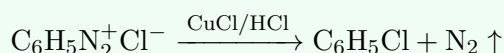
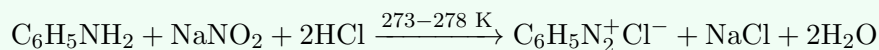
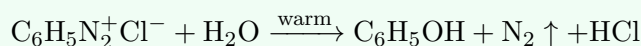
Concept:

- Acetylation protects the amino group as $-\text{NHCOCH}_3$. Nitration then gives mainly the para product; hydrolysis restores $-\text{NH}_2$. Direct nitration of aniline is avoided because the strongly acidic medium protonates its amino group.
- Diazotisation uses NaNO_2/HCl at 273–278 K. The resulting benzenediazonium chloride gives chlorobenzene with cuprous chloride and phenol on warming with water, liberating nitrogen in both substitutions.

Step 1: (a) p-Nitroaniline



Quick Tip to Solve: Protect aniline before nitration; prepare the cold diazonium salt for both chlorine and hydroxyl replacement.

Step 2: (b) Chlorobenzene**Step 3: (c) Phenol**

Step 4: Conclusion These reaction sequences produce *p*-nitroaniline, chlorobenzene and phenol, respectively.

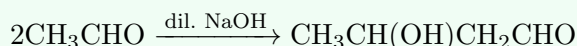
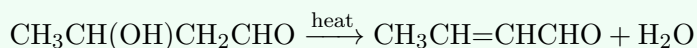
Quick Tip to Solve: Protect aniline before nitration; prepare the cold diazonium salt for both chlorine and hydroxyl replacement.

23. A compound (A) with molecular formula $\text{C}_4\text{H}_5\text{N}$ on reduction with DIBAL-H followed by hydrolysis, gives a compound (B). Compound (B) gives positive Tollens' test but does not give iodoform test. Compound (B) can also be obtained when ethanal is treated with dilute NaOH followed by heating. Identify (A) and (B). Write the reactions of (A) with DIBAL-H followed by hydrolysis. [3 marks]

Solution:**Concept:**

- DIBAL-H partially reduces a nitrile, $\text{R}-\text{C}\equiv\text{N}$, and hydrolysis gives the aldehyde $\text{R}-\text{CHO}$. The nitrile carbon becomes the aldehyde carbon, so the carbon skeleton is retained.
- Ethanal undergoes aldol addition with dilute NaOH. Heating the aldol removes water and forms an α, β -unsaturated aldehyde. Tollens' reagent detects the aldehyde group; the iodoform test requires a $\text{CH}_3\text{CO}-$ group or a group readily oxidised to it.

Step 1: Identify B from the ethanal reaction Ethanal first forms 3-hydroxybutanal and then loses water on heating:

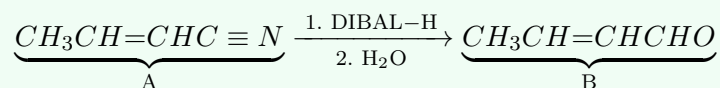


Thus B is but-2-enal (crotonaldehyde). Its aldehyde group reduces Tollens' reagent to metallic silver. It contains no methyl ketone group, and unlike ethanal it is not CH_3CHO ; therefore it gives no iodoform test.

Step 2: Identify A and write its reduction Replace the aldehyde group of B by a nitrile group while retaining its carbon atom. This gives A as $\text{CH}_3\text{CH}=\text{CHC}\equiv\text{N}$, but-2-enenitrile (crotononitrile). Its formula is $\text{C}_4\text{H}_5\text{N}$, matching the given composition. Controlled DIBAL-H reduction followed by

Quick Tip to Solve: Identify the heated aldol product first, then replace its CHO group with CN to recover the nitrile precursor.

hydrolysis converts the nitrile group to $-\text{CHO}$:

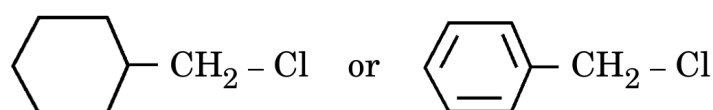


The carbon-carbon double bond is retained in this partial reduction.

Step 3: Conclusion A is but-2-enenitrile, $\text{CH}_3\text{CH}=\text{CHCN}$. B is but-2-enal, $\text{CH}_3\text{CH}=\text{CHCHO}$.

Quick Tip to Solve: Identify the heated aldol product first, then replace its CHO group with CN to recover the nitrile precursor.

24. Write any two differences between $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions. Which of the following compounds would undergo $\text{S}_{\text{N}}1$ reaction faster and why ? [3 marks]

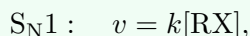
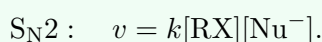


Solution:

Concept:

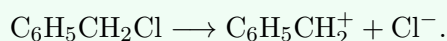
- In an $\text{S}_{\text{N}}1$ reaction the slow step is ionisation to a carbocation. Its rate is $v = k[\text{RX}]$, where RX is the halo compound; increasing carbocation stability favours this pathway.
- An $\text{S}_{\text{N}}2$ reaction involves simultaneous nucleophilic attack and departure of the leaving group. Its rate is $v = k[\text{RX}][\text{Nu}^-]$, where Nu^- is the nucleophile.

Step 1: State two differences between the mechanisms (i) Molecularity and rate: $\text{S}_{\text{N}}1$ is unimolecular in its rate-determining step and first order overall, depending only on halo compound concentration. $\text{S}_{\text{N}}2$ is bimolecular and second order overall, depending on both halo compound and nucleophile concentrations.



(ii) Steps and intermediate: $\text{S}_{\text{N}}1$ proceeds by slow C-X bond cleavage followed by nucleophilic attack, through a carbocation intermediate. $\text{S}_{\text{N}}2$ proceeds in a single concerted step through a transition state, with no carbocation intermediate.

Step 2: Compare the two printed compounds The compounds are cyclohexylmethyl chloride, $\text{C}_6\text{H}_{11}\text{CH}_2\text{Cl}$, and benzyl chloride, $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$. Loss of chloride from benzyl chloride gives the benzyl carbocation:



Its positive charge is delocalised by resonance over the benzylic carbon and the ortho and para positions of the benzene ring. Cyclohexylmethyl chloride initially gives a primary $\text{C}_6\text{H}_{11}\text{CH}_2^+$ carbocation without this aromatic resonance stabilisation. Consequently, the slow ionisation step is easier for benzyl chloride.

Quick Tip to Solve: Compare the carbocations formed immediately after chloride leaves; a benzene ring directly next to the positive carbon supplies resonance stabilisation.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, benzyl chloride, undergoes $\text{S}_{\text{N}}1$ faster because its initially formed benzyl carbocation is resonance stabilised.

Quick Tip to Solve: Compare the carbocations formed immediately after chloride leaves; a benzene ring directly next to the positive carbon supplies resonance stabilisation.

25. Vapour pressure of pure water at 298 K is 24.8 mm Hg. Calculate the lowering in vapour pressure of an aqueous solution which freezes at -0.3°C . (K_f of water = $1.86 \text{ K kg mol}^{-1}$) [3 marks]

Solution:

Concept:

- Freezing-point depression is a colligative property: $\Delta T_f = K_f m$, where m is the effective molality of dissolved solute particles.
- For a non-volatile solute, Raoult's law gives $\Delta p = p^\circ - p = p^\circ x_2$, where x_2 is the solute mole fraction. For a dilute aqueous solution, $x_2 \simeq n_2/n_1$.

Step 1: Find the molality from the freezing point Pure water freezes at 0°C , whereas the solution freezes at -0.3°C . Thus the depression, taken as a positive quantity, is $\Delta T_f = 0 - (-0.3) = 0.3 \text{ K}$. Using the given cryoscopic constant,

$$m = \frac{\Delta T_f}{K_f} = \frac{0.3}{1.86} = 0.16129 \text{ mol kg}^{-1}.$$

This is the number of effective solute particles per kilogram of water; a separate molar mass of the solute is therefore unnecessary.

Step 2: Convert to mole fraction and apply Raoult's law Take 1 kg of water as the basis. Its molar mass is 18 g mol^{-1} , so $n_1 = 1000/18 = 55.56 \text{ mol}$ and $n_2 = 0.16129 \text{ mol}$. Since $n_2 \ll n_1$, the dilute-solution expression gives

$$\frac{\Delta p}{p^\circ} \simeq \frac{n_2}{n_1} = \frac{0.16129}{55.56} = 0.002903.$$

Therefore

$$\Delta p = 24.8 \times 0.002903 = 0.0720 \text{ mm Hg}.$$

Retaining $n_1 + n_2$ in the mole-fraction denominator gives 0.07179 mm Hg , which rounds to the same 0.072 mm Hg . The required quantity is the decrease in pressure, not the remaining solution vapour pressure.

Step 3: Conclusion The lowering in vapour pressure is $\Delta p \approx 0.072 \text{ mm Hg}$.

Quick Tip to Solve: Use a 1 kg water basis: $n_2 = \Delta T_f / K_f$ and $n_1 = 1000/18$; multiply their dilute mole ratio by 24.8.

26(a)(i). Answer the following about the complexes $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$:

Write the hybridization involved in each case.

[Atomic number : Fe = 26]

[1 mark]

Solution:

Concept:

- The oxidation state is obtained using F^- and CN^- as singly negative ligands: iron is +3 in $[\text{FeF}_6]^{3-}$ and +2 in $[\text{Fe}(\text{CN})_6]^{4-}$.
- Fe^{3+} is $3d^5$ and Fe^{2+} is $3d^6$. Fluoride is a weak-field ligand, whereas cyanide is a strong-field ligand.

Step 1: Hybridisation of the fluoride complex For $[\text{FeF}_6]^{3-}$, $x - 6 = -3$, giving $x = +3$. Weak-field F^- does not cause pairing of the five $3d$ electrons. All five $3d$ orbitals remain singly occupied, so two vacant inner $3d$ orbitals are unavailable. Six octahedral bond orbitals instead use one $4s$, three $4p$, and two $4d$ orbitals: sp^3d^2 .

Step 2: Hybridisation of the cyanide complex For $[\text{Fe}(\text{CN})_6]^{4-}$, $x - 6 = -4$, giving $x = +2$ and $3d^6$. Strong-field CN^- pairs the six electrons in three $3d$ orbitals. The two empty $3d$ orbitals combine with one $4s$ and three $4p$ orbitals, giving d^2sp^3 hybridisation.

Step 3: Conclusion $[\text{FeF}_6]^{3-}$: sp^3d^2 ; $[\text{Fe}(\text{CN})_6]^{4-}$: d^2sp^3 .

Quick Tip to Solve: Determine Fe oxidation state before counting d electrons: weak-field fluoride uses outer d orbitals; strong-field cyanide permits inner d orbitals.

26(a)(ii). Answer the following about the complexes $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$:

Which of them is the outer orbital complex and which one is the inner orbital complex ?

[Atomic number : Fe = 26]

[1 mark]

Solution:

Concept:

- The oxidation state is obtained using F^- and CN^- as singly negative ligands: iron is +3 in $[\text{FeF}_6]^{3-}$ and +2 in $[\text{Fe}(\text{CN})_6]^{4-}$.
- Fe^{3+} is $3d^5$ and Fe^{2+} is $3d^6$. Fluoride is a weak-field ligand, whereas cyanide is a strong-field ligand.

Step 1: Identify the d orbitals used by the fluoride complex Weak-field F^- leaves the $3d^5$ electrons of Fe^{3+} unpaired. No two inner $3d$ orbitals are vacant. Its sp^3d^2 hybridisation therefore uses $4s$, $4p$ and $4d$ orbitals. The d orbitals belong to the outer principal shell, making this an outer orbital complex.

Step 2: Identify the d orbitals used by the cyanide complex Strong-field CN^- pairs the $3d^6$ electrons of Fe^{2+} in three orbitals, leaving two $3d$ orbitals empty. Its d^2sp^3 hybridisation uses these inner $3d$ orbitals along with $4s$ and $4p$. Thus this is an inner orbital complex; both complexes are octahedral despite using different d shells.

Step 3: Conclusion $[\text{FeF}_6]^{3-}$ is outer orbital and $[\text{Fe}(\text{CN})_6]^{4-}$ is inner orbital.

Quick Tip to Solve: Read the shell of the d orbitals: 4d means outer orbital for Fe, while 3d means inner orbital.

26(a)(iii). Answer the following about the complexes $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$:

Compare their magnetic behaviour.

[Atomic number : Fe = 26]

[1 mark]

Solution:

Concept:

- The oxidation state is obtained using F^- and CN^- as singly negative ligands: iron is +3 in $[\text{FeF}_6]^{3-}$ and +2 in $[\text{Fe}(\text{CN})_6]^{4-}$.
- Fe^{3+} is $3d^5$ and Fe^{2+} is $3d^6$. Fluoride is a weak-field ligand, whereas cyanide is a strong-field ligand.

Step 1: Count unpaired electrons in the fluoride complex In $[\text{FeF}_6]^{3-}$, iron is Fe^{3+} , with $3d^5$. The weak fluoride field gives the high-spin octahedral configuration $t_{2g}^3 e_g^2$. Each of the five d orbitals contains one electron, so there are five unpaired electrons. The complex is therefore strongly paramagnetic and is attracted by a magnetic field.

Step 2: Count unpaired electrons in the cyanide complex In $[\text{Fe}(\text{CN})_6]^{4-}$, iron is Fe^{2+} , with $3d^6$. The strong cyanide field gives the low-spin configuration $t_{2g}^6 e_g^0$. All six d electrons are paired in the three lower orbitals. With no unpaired electrons, this complex is diamagnetic and is weakly repelled by a magnetic field.

Step 3: Conclusion $[\text{FeF}_6]^{3-}$ is paramagnetic with five unpaired electrons; $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic with no unpaired electrons.

Quick Tip to Solve: Do not assign both complexes the same d count: fluoride contains Fe(III), while the cyanide complex contains Fe(II).

OR

26(b). (i) What happens to the colour of complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ when heated gradually ?

(ii) Write the electronic configuration for d^5 ion if $\Delta_o < P$.

(iii) Write the hybridization and magnetic behaviour of the complex $[\text{Ni}(\text{CO})_4]$.

[Atomic number : Ni = 28]

[3 marks]

Solution:

Concept:

- Visible colour can arise from a $d-d$ transition between ligand-field-split orbitals. Coordinated ligands provide the field responsible for splitting.
- For an octahedral ion, Δ_o is the splitting energy and P is the electron-pairing energy. If $\Delta_o < P$, occupying an upper orbital costs less energy than pairing.
- The magnetic behaviour follows the number of unpaired electrons: their presence gives paramagnetism, while complete pairing gives diamagnetism.

Step 1: (i) Effect of gradual heating on the titanium complex Water is neutral, so titanium in

Quick Tip to Solve: For $\text{Ni}(\text{CO})_4$, CO is neutral: start with Ni(0), use the paired d10 arrangement, then assign tetrahedral sp^3 hybridisation.

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is Ti^{3+} , with configuration $3d^1$. Its violet colour arises when the d electron absorbs visible light and moves from a lower t_{2g} orbital to a higher e_g orbital. On gradual heating, coordinated water ligands are lost. The ligand environment responsible for this characteristic splitting changes, so the violet colour fades and ultimately disappears.

Step 2: (ii) Configuration of a d5 ion when the splitting is small When $\Delta_o < P$, the five electrons occupy all five d orbitals singly before any pairing occurs. The first three enter the three t_{2g} orbitals and the next two enter the two e_g orbitals. Thus the octahedral electronic configuration is



This is the high-spin arrangement with five unpaired electrons; pairing in t_{2g} would have the greater energy cost.

Step 3: (iii) Hybridisation and magnetism of nickel tetracarbonyl CO is a neutral ligand, so nickel in $[\text{Ni}(\text{CO})_4]$ has oxidation state zero. Free Ni has configuration $[\text{Ar}]3d^8 4s^2$; in the carbonyl complex its valence electrons adopt the paired $3d^{10}$ arrangement. One empty $4s$ and three empty $4p$ orbitals form four sp^3 hybrid orbitals for ligand bonding. Consequently the complex is tetrahedral. All the d electrons are paired, so it is diamagnetic, not paramagnetic.

Step 4: Conclusion (i) The violet colour fades and disappears on gradual heating. (ii) The configuration is $t_{2g}^3 e_g^2$. (iii) $[\text{Ni}(\text{CO})_4]$ has sp^3 hybridisation and is diamagnetic.

Quick Tip to Solve: For $\text{Ni}(\text{CO})_4$, CO is neutral: start with $\text{Ni}(0)$, use the paired d10 arrangement, then assign tetrahedral sp^3 hybridisation.

27. Give reasons for the following :

- The pH of aqueous NaCl increases when it is electrolysed.
- Unlike dry cell, mercury cell has a constant cell potential through its lifetime.
- Conductivity of solution decreases with dilution.

[3 marks]

Solution:

Concept:

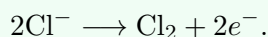
- In aqueous electrolysis, reduction occurs at the cathode and oxidation occurs at the anode. The electrolyte can change composition during the process.
- Cell potential depends on the reaction quotient. A constant composition of the reacting species gives a nearly constant cell potential.
- Conductivity, κ , measures conduction through unit dimensions of solution and depends on the number of mobile ions per unit volume.

Step 1: (a) Increase in pH At the cathode, water is reduced in preference to sodium ions:



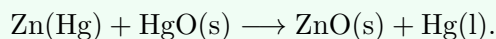
Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole.

Chloride ions are oxidised at the anode:



Thus hydroxide ions accumulate in the solution along with sodium ions, giving NaOH. The increase in OH^- concentration makes the solution alkaline and raises its pH.

Step 2: (b) Constant potential of the mercury cell The overall cell reaction is



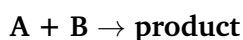
The hydroxide ions involved in the electrode reactions cancel in the net reaction. No ion in solution appears in this overall reaction, so the electrolyte concentration does not change appreciably during discharge. Consequently the reaction quotient and hence the cell potential remain essentially constant, unlike those of a dry cell.

Step 3: (c) Conductivity on dilution Dilution reduces the number of ions per unit volume of solution. Hence fewer charge carriers are available in a given volume and conductivity decreases. This must be distinguished from molar conductivity: the conductivity per mole of electrolyte generally increases on dilution because ionic mobility, and for weak electrolytes ionisation, increases.

Step 4: Conclusion (a) Electrolysis generates OH^- , raising pH. (b) The mercury-cell net reaction does not change electrolyte concentration. (c) Dilution decreases the number of ions per unit volume.

Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole.

28. The rate of a reaction :



is given below as a function of different initial concentrations of A and B.

Experiment	[A] / mol L ⁻¹	[B] / mol L ⁻¹	Initial Rate / mol L ⁻¹ min ⁻¹
1	0.01	0.01	5×10^{-3}
2	0.02	0.01	1×10^{-2}
3	0.01	0.02	5×10^{-3}

Calculate the order of the reaction with respect to A and B. Determine the rate constant of the reaction.

[3 marks]

Solution:

Concept:

- Use the experimental rate law $r = k[\text{A}]^m[\text{B}]^n$, where m and n are the orders in A and B; stoichiometric coefficients do not determine these orders.
- Compare experiments in which only one reactant concentration changes, so the other concentration and the rate constant cancel in the ratio.

Step 1: Order with respect to A Compare experiments 2 and 1: $[\text{B}] = 0.01 \text{ mol L}^{-1}$ in both, while $[\text{A}]$

Quick Tip to Solve: Choose pairs with one concentration fixed before taking rate ratios; retain minutes in the units of k .

doubles from 0.01 to 0.02 mol L⁻¹. The rate also doubles. Therefore

$$\frac{r_2}{r_1} = \frac{1 \times 10^{-2}}{5 \times 10^{-3}} = 2 = \left(\frac{0.02}{0.01}\right)^m = 2^m.$$

It follows that $m = 1$; the reaction is first order in A.

Step 2: Order with respect to B Compare experiments 3 and 1. Here $[A]$ is unchanged, while $[B]$ doubles. The initial rate remains 5×10^{-3} mol L⁻¹ min⁻¹. Thus

$$\frac{r_3}{r_1} = 1 = \left(\frac{0.02}{0.01}\right)^n = 2^n,$$

giving $n = 0$. The rate is independent of the concentration of B over these experimental conditions; the overall order is $m + n = 1$.

Step 3: Rate constant and units The rate law reduces to $r = k[A]$, since $[B]^0 = 1$. Using experiment 1,

$$k = \frac{r}{[A]} = \frac{5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}}{0.01 \text{ mol L}^{-1}} = 0.50 \text{ min}^{-1}.$$

Experiment 2 gives $0.01/0.02 = 0.50 \text{ min}^{-1}$ as well, confirming consistency. The concentration units cancel, as expected for an overall first-order rate constant.

Step 4: Conclusion Order in A: 1; order in B: 0; overall order: 1. The rate constant is $k = 0.50 \text{ min}^{-1}$.

Quick Tip to Solve: Choose pairs with one concentration fixed before taking rate ratios; retain minutes in the units of k .

Section D (8 marks)

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

29(a). Case-based: The α -amino acids are the building blocks of proteins. All α -amino acids exist as zwitter ion due to which they show amphoteric behaviour. All amino acids are joined through peptide bond. Proteins are broadly classified as globular proteins and fibrous proteins. Globular proteins are water soluble, whereas fibrous proteins are not. The complete structure of protein is discussed at four different levels i.e. primary, secondary, tertiary and quaternary structures. Protein loses its biological activity in denatured form.

Define the following :

(i) Peptide linkage (ii) Denatured protein

[2 marks]

Solution:

Concept:

- Proteins consist of amino-acid residues linked through amide bonds formed by condensation.
- The biological activity of a protein depends on its native three-dimensional conformation as well as its amino-acid sequence.

Quick Tip to Solve: Define denaturation using loss of conformation and activity; do not describe it as peptide-bond hydrolysis.

Step 1: (i) Peptide linkage A peptide linkage is the amide linkage $-\text{CO}-\text{NH}-$ formed when the carboxyl group of one amino acid reacts with the amino group of another amino acid, with elimination of a water molecule. The bond joins the carbonyl carbon of one residue to the nitrogen of the next. Repetition of this condensation connects many amino-acid residues to form a polypeptide chain.

Step 2: (ii) Denatured protein A denatured protein is a protein that has lost its native conformation and consequently its biological activity under the action of heat, a change in pH, or other denaturing agents. The interactions maintaining its secondary and tertiary structures are disrupted, while its primary structure, that is, the sequence of amino acids and the peptide linkages, remains intact. Coagulation of egg albumin on heating is an example.

Step 3: Conclusion Peptide linkage: $-\text{CO}-\text{NH}-$, formed by condensation of two amino acids. Denatured protein: a protein whose native conformation and biological activity are lost without cleavage of its primary peptide chain.

Quick Tip to Solve: Define denaturation using loss of conformation and activity; do not describe it as peptide-bond hydrolysis.

29(b). Why do amino acids show amphoteric behaviour ?

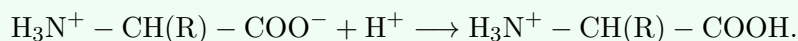
[1 mark]

Solution:

Concept:

- Amphoteric substances can react with both acids and bases.
- An amino acid contains an acidic carboxyl group and a basic amino group; in its zwitterion these appear as $-\text{COO}^-$ and $-\text{NH}_3^+$.

Step 1: Reaction with an acid The carboxylate end of the zwitterion accepts a proton:



The amino acid therefore behaves as a base in an acidic medium.

Step 2: Reaction with a base The ammonium end donates a proton to hydroxide:



It therefore behaves as an acid in a basic medium. The simultaneous presence of these proton-accepting and proton-donating groups accounts for the behaviour.

Step 3: Conclusion Amino acids show amphoteric behaviour because they contain both acidic and basic groups and can therefore react with both bases and acids.

Quick Tip to Solve: In the zwitterion, identify COO^- as the proton acceptor and NH_3^+ as the proton donor.

29(c). How can you differentiate between Fibrous protein and Globular protein ?

[1 mark]

Solution:

Concept:

- Protein shape depends on the arrangement and folding of its polypeptide chains.
- Water solubility is a useful distinguishing property of fibrous and globular proteins.

Step 1: Compare the shapes Fibrous proteins have polypeptide chains arranged into long, thread-like fibres. Globular proteins have polypeptide chains folded into compact, approximately spherical structures.

Step 2: Compare solubility and examples Fibrous proteins are generally insoluble in water; keratin in hair and wool is an example. Globular proteins are generally soluble in water; albumin is an example. Thus shape and water solubility together distinguish the two classes.

Step 3: Conclusion Fibrous proteins are elongated and generally water-insoluble; globular proteins are compact, spherical and generally water-soluble.

Quick Tip to Solve: Recall keratin as the fibrous example and albumin as the globular example.

OR

29(c). Write the names of two different secondary structures of proteins.

[1 mark]

Solution:

Concept:

- Secondary structure describes the regular local folding of a polypeptide backbone.
- Hydrogen bonds involving backbone carbonyl and amide groups stabilise these structures.

Step 1: Identify the coiled arrangement In the α -helix, the polypeptide chain coils into a regular helix. Hydrogen bonding within the same chain helps maintain this coiled arrangement.

Step 2: Identify the sheet arrangement In the β -pleated sheet, extended polypeptide segments lie alongside one another. Hydrogen bonding between neighbouring segments stabilises the sheet, whose backbone has a pleated appearance. These are secondary structures, rather than the amino-acid sequence or overall three-dimensional folding.

Step 3: Conclusion The two secondary structures are the α -helix and the β -pleated sheet.

Quick Tip to Solve: For secondary structure, name helix and sheet; do not give primary sequence or tertiary folding.

30(a). Case-based: Alcohols undergo a number of reactions involving the cleavage of C - OH bond. However, phenols do not undergo reactions involving the cleavage of C - OH bond. Alcohols are weaker acids than water. Alcohols react with halogen acids to form the corresponding haloalkanes. Phenols are stronger acids than alcohols. A characteristic feature of phenols is that they undergo electrophilic substitution reactions such as halogenation, nitration, etc. Since -OH group is a strong activating group, phenol gives trisubstituted products during halogenation, nitration, etc.

What happens when phenol is treated with the following ?

(i) Br₂ water (ii) Conc. HNO₃

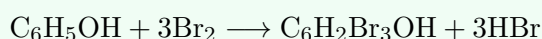
[2 marks]

Solution:

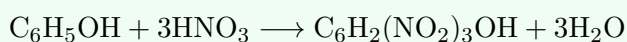
Concept:

- The -OH group activates the benzene ring of phenol and directs electrophilic substitution to ortho and para positions.
- With bromine water or concentrated nitric acid, substitution occurs at both ortho positions and the para position.

Step 1: Reaction with bromine water Phenol decolourises bromine water and gives a white precipitate of 2,4,6-tribromophenol. The three bromine atoms replace ring hydrogens at positions 2, 4 and 6; the hydroxyl group remains attached to the ring.



Step 2: Reaction with concentrated nitric acid Concentrated nitric acid nitrates the activated ring to form 2,4,6-trinitrophenol, also called picric acid, a yellow compound. Three nitro groups occupy the two ortho sites and the para site relative to the hydroxyl group.



Step 3: Conclusion Bromine water gives a white precipitate of 2,4,6-tribromophenol; concentrated nitric acid gives 2,4,6-trinitrophenol (picric acid).

Quick Tip to Solve: With these strong phenol substitution conditions, fill all three activated sites: 2, 4 and 6.

30(b). Write the mechanism of alcohol reacting as nucleophile in a reaction with CH₃⁺.

[1 mark]

Solution:

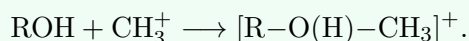
Concept:

- The oxygen atom of an alcohol ROH has lone pairs and can act as a nucleophile.
- The methyl carbocation CH₃⁺ is electron-deficient and accepts an electron pair.

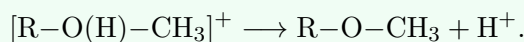
Step 1: Nucleophilic attack by oxygen A lone pair on the alcohol oxygen is donated to the positively charged carbon of CH₃⁺, forming a new oxygen-carbon bond. Electron flow is from oxygen to carbon.

Quick Tip to Solve: Draw electron donation from the oxygen lone pair towards the positively charged methyl carbon.

Oxygen now has three bonds and carries a positive charge:



Step 2: Deprotonation of the oxonium ion The oxonium intermediate loses a proton to a base in the medium. The electrons of the oxygen-hydrogen bond return to oxygen, giving the neutral ether:



Step 3: Conclusion Alcohol attacks through its oxygen lone pair, forming an oxonium ion; deprotonation gives the ether ROCH_3 .

Quick Tip to Solve: Draw electron donation from the oxygen lone pair towards the positively charged methyl carbon.

OR

30(b). Why do phenols not undergo reactions involving cleavage of C - OH bond ?

[1 mark]

Solution:

Concept:

- In phenol, an oxygen lone pair is conjugated with the benzene ring.
- Resonance gives the aryl C–O bond partial double-bond character.

Step 1: Explain the effect of resonance Delocalisation of the oxygen lone pair into the aromatic ring gives the carbon-oxygen bond partial double-bond character. Consequently, this bond is shorter and stronger than the corresponding carbon-oxygen single bond in an alcohol.

Step 2: Relate bond strength to cleavage The stronger aryl carbon-oxygen bond is difficult to break in the usual reactions that replace the hydroxyl group of an alcohol. The carbon bonded to oxygen is also sp^2 -hybridised, which strengthens this bond. Phenols therefore resist the usual cleavage of the C–OH bond, even though their oxygen-hydrogen bond can undergo acidic dissociation.

Step 3: Conclusion Phenols resist C–OH cleavage because resonance gives the aryl carbon-oxygen bond partial double-bond character and makes it stronger.

Quick Tip to Solve: Distinguish the resistant carbon-oxygen bond from the oxygen-hydrogen bond responsible for acidity.

30(c). How can you distinguish between Butan-1-ol and 2-Methylpropan-2-ol by using HCl in the presence of anhydrous ZnCl_2 ? [1 mark]

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous ZnCl_2 .
- Formation of an insoluble alkyl chloride produces turbidity; tertiary alcohols react much faster than primary alcohols at room temperature.

Step 1: Test the tertiary alcohol Add Lucas reagent separately to the two alcohol samples at room temperature. 2-Methylpropan-2-ol is a tertiary alcohol and gives immediate turbidity due to formation of insoluble 2-chloro-2-methylpropane.

Step 2: Test the primary alcohol Butan-1-ol is a primary alcohol and shows no turbidity at room temperature during the ordinary test period. Conversion to its alkyl chloride is very slow under these conditions and requires heating. Compare the immediate observations under identical conditions to identify the samples.

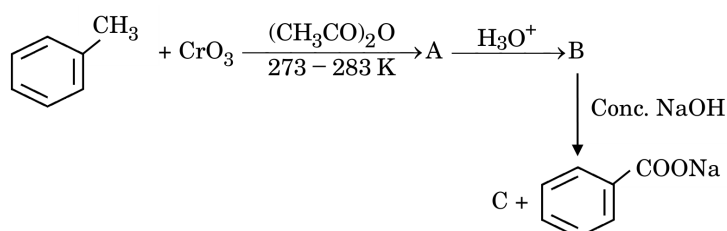
Step 3: Conclusion Immediate turbidity identifies 2-methylpropan-2-ol; no turbidity at room temperature identifies butan-1-ol.

Quick Tip to Solve: Use Lucas reagent at room temperature and compare the time taken for turbidity to appear.

Section E (15 marks)

31(a)(i). Identify A, B and C in the following reactions :

[3 marks]



Solution:

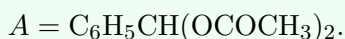
Concept:

- Chromium trioxide in acetic anhydride oxidises a benzylic methyl group to the aldehyde level, trapping it as a geminal diacetate.
- Acidic hydrolysis converts the geminal diacetate into the corresponding aldehyde.
- An aldehyde without an α -hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one molecule is oxidised and another reduced.

Step 1: Identify the protected oxidation product A The initial aromatic compound is toluene, $\text{C}_6\text{H}_5\text{CH}_3$. Under the printed conditions, CrO_3 in acetic anhydride at 273–283 K, oxidation of the

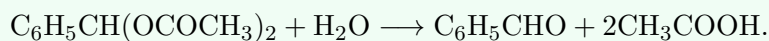
Quick Tip to Solve: Recognise concentrated NaOH plus benzaldehyde as Cannizzaro: the companion to benzoate is benzyl alcohol.

methyl side chain gives benzylidene diacetate. Thus



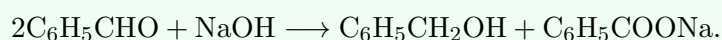
Both acetate groups are attached through oxygen to the same benzylic carbon. This is the protected aldehyde product, not benzoic acid or benzyl acetate.

Step 2: Hydrolyse A to obtain B Aqueous acid hydrolyses the two acetate groups, regenerating the aldehyde:



Therefore B is benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$.

Step 3: Apply the Cannizzaro reaction to find C Benzaldehyde has no α -hydrogen because the carbon adjacent to its carbonyl group is the substituted aromatic ring carbon. With concentrated sodium hydroxide it therefore undergoes the Cannizzaro reaction:



The paper already shows sodium benzoate as one product. The other product, C, must be the alcohol formed by reduction of the second benzaldehyde molecule.

Step 4: Conclusion $A = \text{C}_6\text{H}_5\text{CH}(\text{OCOCH}_3)_2$, benzylidene diacetate; $B = \text{C}_6\text{H}_5\text{CHO}$, benzaldehyde; $C = \text{C}_6\text{H}_5\text{CH}_2\text{OH}$, benzyl alcohol.

Quick Tip to Solve: Recognise concentrated NaOH plus benzaldehyde as Cannizzaro: the companion to benzoate is benzyl alcohol.

31(a)(ii). Give reasons for the following :

(I) Carboxylic acids do not give the characteristic reactions of carbonyl group.

(II) Ethanoic acid is a stronger acid than ethanol.

[2 marks]

Solution:

Concept:

- Resonance donation from the hydroxyl oxygen reduces the electrophilicity of the carbonyl carbon in a carboxylic acid.
- Acid strength increases when the conjugate base is more stable; equivalent resonance structures stabilise a carboxylate ion.

Step 1: Explain the behaviour of the carbonyl group In RCOOH , a lone pair on the hydroxyl oxygen participates in resonance with the carbonyl group. Electron donation towards the carbonyl carbon reduces its positive character compared with the carbonyl carbon in aldehydes and ketones. Consequently nucleophilic addition, responsible for the characteristic carbonyl reactions of aldehydes and ketones, is less favourable. Carboxylic acids generally undergo reactions involving replacement of the hydroxyl group instead.

Step 2: Compare the conjugate bases Ethanoic acid loses a proton to form the ethanoate ion,

Quick Tip to Solve: For acidity comparisons, remove the acidic hydrogen first and compare the stability of the resulting anions.

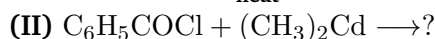
CH_3COO^- . Its negative charge is delocalised equally over two oxygen atoms through two equivalent resonance structures. Ethanol forms ethoxide, $\text{CH}_3\text{CH}_2\text{O}^-$, whose negative charge remains localised on one oxygen and lacks this resonance stabilisation. The more stable ethanoate ion makes proton loss from ethanoic acid easier than from ethanol.

Step 3: Conclusion Carboxylic acids show reduced carbonyl electrophilicity due to resonance. Ethanoic acid is stronger than ethanol because its conjugate base is resonance-stabilised.

Quick Tip to Solve: For acidity comparisons, remove the acidic hydrogen first and compare the stability of the resulting anions.

OR

31(b)(i). Write the product(s) in the following reactions :



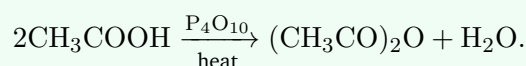
[3 marks]

Solution:

Concept:

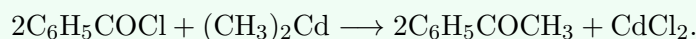
- Phosphorus pentoxide is a dehydrating agent: two carboxylic acid molecules form an acid anhydride.
- Dialkylcadmium reacts with an acid chloride to give a ketone without further addition to the ketone.
- An ortho-dicarboxamide forms a cyclic imide on strong heating with loss of ammonia.

Step 1: Form the acid anhydride in reaction I P_4O_{10} removes water from two molecules of ethanoic acid on heating. The organic product is ethanoic anhydride (acetic anhydride):



The equation shows the formal dehydration; the dehydrating reagent takes up the water. The anhydride has the linkage $-\text{CO} - \text{O} - \text{CO}-$.

Step 2: Replace chloride with methyl in reaction II The reactant is benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$. Dimethylcadmium transfers a methyl group to the acyl carbon, replacing chloride and producing acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$. A balanced equation is

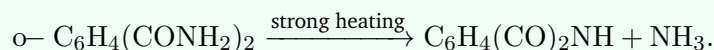


The carbonyl group remains in the product; this reagent does not give the tertiary alcohol obtained with excess Grignard reagent.

Step 3: Close the imide ring in reaction III The printed substrate is phthalamide: two $-\text{CONH}_2$ groups occupy adjacent positions on a benzene ring. On strong heating these adjacent amide groups

Quick Tip to Solve: Keep track of the reagent: dehydrating agent gives anhydride, dialkylcadmium gives ketone, and adjacent amides cyclise to an imide.

cyclise with elimination of ammonia:



The organic product is phthalimide, with the group $-\text{CO}-\text{NH}-\text{CO}-$ joining the two adjacent ring carbons to form a five-membered imide ring.

Step 4: Conclusion (I) Ethanoic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$; (II) acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$; (III) phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$, and ammonia.

Quick Tip to Solve: Keep track of the reagent: dehydrating agent gives anhydride, dialkylcadmium gives ketone, and adjacent amides cyclise to an imide.

31(b)(ii). Write the reaction involved in the following reactions :

(I) Wolff-Kishner Reduction

(II) Decarboxylation Reaction

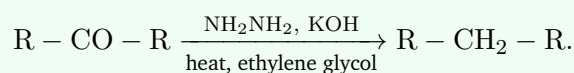
[2 marks]

Solution:

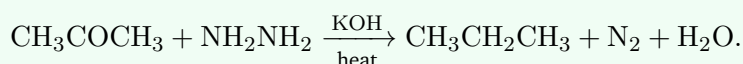
Concept:

- Wolff-Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and strong base on heating.
- Soda-lime decarboxylation removes the carboxyl carbon from a sodium carboxylate, giving an alkane with one fewer carbon atom.

Step 1: Write Wolff-Kishner reduction An aldehyde or ketone first reacts with hydrazine, NH_2NH_2 , to form a hydrazone. Heating with KOH in a high-boiling solvent such as ethylene glycol then reduces the carbonyl group completely:

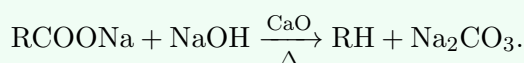


For example, propanone gives propane:

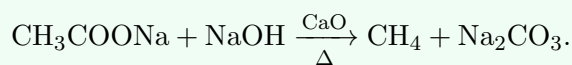


The carbon skeleton is retained.

Step 2: Write soda-lime decarboxylation A sodium salt of a carboxylic acid is heated with soda lime, a mixture of NaOH and CaO :



For example, sodium ethanoate produces methane:



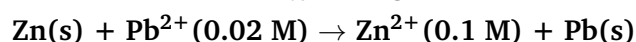
Quick Tip to Solve: Count carbon atoms: Wolff-Kishner retains all carbons, whereas soda-lime decarboxylation removes the carboxyl carbon.

The carboxyl carbon passes into sodium carbonate, so the alkane contains one fewer carbon atom than the original acid salt.

Step 3: Conclusion Wolff-Kishner reduction: $R_2CO \rightarrow R_2CH_2$ using hydrazine and hot alkali. Decarboxylation: $RCOONa + NaOH \rightarrow RH + Na_2CO_3$ on heating with soda lime.

Quick Tip to Solve: Count carbon atoms: Wolff-Kishner retains all carbons, whereas soda-lime decarboxylation removes the carboxyl carbon.

32(a)(i). Calculate E_{cell} of a galvanic cell in which the following reaction takes place at 25°C :



[Given : $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$, $E^\circ_{\text{Pb}^{2+}/\text{Pb}} = -0.13 \text{ V}$; $\log 2 = 0.3010$, $\log 4 = 0.6021$, $\log 5 = 0.6990$]

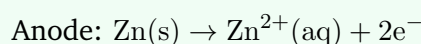
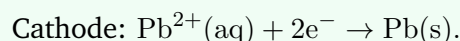
[3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 25°C , the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify the electrode reactions Zinc loses electrons and is the anode, while lead ions gain electrons at the cathode:



Thus, two electrons are transferred per balanced cell reaction, so $n = 2$. The potentials supplied are reduction potentials, even though zinc undergoes oxidation in this cell.

Step 2: Calculate the standard cell potential Using the lead electrode as cathode and the zinc electrode as anode,

$$E^\circ_{\text{cell}} = (-0.13) - (-0.76) = 0.63 \text{ V}.$$

Subtracting the negative zinc reduction potential increases the cell potential. The positive value agrees with the direction of the given galvanic reaction.

Step 3: Apply the concentration correction The solids do not enter the reaction quotient. For the printed concentrations,

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Pb}^{2+}]} = \frac{0.10}{0.02} = 5.$$

Substitution with $\log 5 = 0.6990$ gives

$$\begin{aligned} E_{\text{cell}} &= 0.63 - \frac{0.0591}{2} \log 5 \\ &= 0.63 - 0.02955(0.6990) \\ &= 0.63 - 0.02065545 \text{ V}. \end{aligned}$$

Since $Q > 1$, the concentration correction reduces the cell potential below its standard value.

Quick Tip to Solve: For this Zn–Pb reaction, place zinc-ion concentration above lead-ion concentration in Q ; $Q = 5$ must lower the standard 0.63 V value.

Step 4: Conclusion The cell potential is $E_{\text{cell}} = 0.6093 \text{ V} \approx 0.61 \text{ V}$.

Quick Tip to Solve: For this Zn–Pb reaction, place zinc-ion concentration above lead-ion concentration in Q; Q = 5 must lower the standard 0.63 V value.

32(a)(ii). State Faraday's first law of electrolysis. How much electricity, in terms of Faraday, is required to reduce one mol of MnO_4^- to Mn^{2+} ion ? [2 marks]

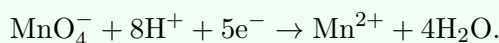
Solution:

Concept:

- Faraday's first law states that the mass m of a substance deposited or liberated at an electrode is directly proportional to the charge Q passed through the electrolyte: $m = ZQ = ZIt$, where Z is its electrochemical equivalent.
- One Faraday F is the charge carried by one mole of electrons, approximately 96485 C mol^{-1} . The charge needed follows from the electron stoichiometry.

Step 1: State the law and its mathematical form For a given substance, passing twice the charge deposits or liberates twice the mass at the electrode, provided the same electrode reaction occurs. Thus $m \propto Q$, or $m = ZIt$, where I is current and t is the duration of electrolysis. The proportionality constant Z is the mass produced per unit charge.

Step 2: Find the electron requirement for manganese In MnO_4^- , four oxygen atoms contribute -8 ; therefore manganese has oxidation state $+7$. Reduction to Mn^{2+} changes it to $+2$, so each manganese gains five electrons. The balanced acidic half-reaction confirms this:



Hence, one mole of permanganate requires five moles of electrons. Since one mole of electrons carries one Faraday of charge, multiply the electron amount by F .

Step 3: Conclusion The required quantity of electricity is 5 Faraday , approximately $4.82 \times 10^5 \text{ C}$.

Quick Tip to Solve: Find manganese oxidation states first: the drop from $+7$ to $+2$ directly gives five electrons and therefore 5 Faraday per mole.

32(b)(i). The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1000 ohm. What is the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.125 \times 10^{-3} \text{ S cm}^{-1}$? [2 marks]

Solution:

Concept:

- Conductance is $G = 1/R$, where R is the measured resistance. Conductivity κ and conductance obey $\kappa = G(l/A)$.
- The cell constant l/A is the electrode separation l divided by electrode area A . Therefore $l/A = \kappa R$; with conductivity in S cm^{-1} , its unit is cm^{-1} .

Step 1: Express the given conductivity and conductance The printed conductivity is

$$\kappa = 0.125 \times 10^{-3} \text{ S cm}^{-1} = 1.25 \times 10^{-4} \text{ S cm}^{-1}.$$

For the measured resistance $R = 1000 \Omega = 10^3 \Omega$, the conductance is

$$G = \frac{1}{1000} = 10^{-3} \text{ S}.$$

The concentration identifies the calibration solution; no additional concentration factor is used when its conductivity is already given.

Step 2: Calculate the cell constant Rearrange $\kappa = G(l/A)$ and substitute:

$$\begin{aligned} \frac{l}{A} &= \frac{\kappa}{G} = \kappa R \\ &= (0.125 \times 10^{-3})(1000) \\ &= 0.125 \text{ cm}^{-1}. \end{aligned}$$

The siemens and ohm cancel because $\text{S} = \Omega^{-1}$, leaving inverse centimetres. The cell constant describes the cell geometry, rather than the concentration of KCl.

Step 3: Conclusion The conductivity cell has cell constant $\boxed{l/A = 0.125 \text{ cm}^{-1}}$.

Quick Tip to Solve: Multiply the printed conductivity by resistance: the factor 10 to the power -3 cancels 1000, leaving 0.125 inverse centimetres.

32(b)(ii). Calculate the $E_{\text{Mg}^{2+}/\text{Mg}}$ potential for the following half cell at 25°C :

$\text{Mg}/\text{Mg}^{2+}(1 \times 10^{-4} \text{ M}); E^\circ_{\text{Mg}^{2+}/\text{Mg}} = +2.36 \text{ V}$

[Given : $\log 10 = 1$]

[2 marks]

Solution:

Concept:

- For the reduction half-reaction $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$, the electron number is $n = 2$; the pure solid has unit activity.
- At 25°C , $E = E^\circ - (0.0591/n) \log Q$. For this reduction, $Q = 1/[\text{Mg}^{2+}]$, so $E = E^\circ + (0.0591/2) \log[\text{Mg}^{2+}]$, with the concentration relative to its standard value.

Step 1: Form the reduction reaction quotient The requested potential is $E_{\text{Mg}^{2+}/\text{Mg}}$, corresponding to reduction of magnesium ions. For $[\text{Mg}^{2+}] = 1 \times 10^{-4} \text{ M}$,

$$Q = \frac{1}{1 \times 10^{-4}} = 10^4.$$

Consequently $\log Q = 4 \log 10 = 4$. A dilute cation solution lowers the reduction potential compared with its standard value.

Step 2: Substitute the supplied standard potential Using the standard potential $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = +2.36 \text{ V}$ supplied in the question,

$$\begin{aligned} E_{\text{Mg}^{2+}/\text{Mg}} &= 2.36 - \frac{0.0591}{2}(4) \\ &= 2.36 - 0.1182 \\ &= 2.2418 \text{ V}. \end{aligned}$$

Equivalently, the concentration form uses $\log(10^{-4}) = -4$ and produces the same negative correction. Retain the positive sign of the given standard potential throughout the substitution.

Step 3: Conclusion With the supplied standard potential, $E_{\text{Mg}^{2+}/\text{Mg}} = +2.2418 \text{ V} \approx +2.24 \text{ V}$.

Quick Tip to Solve: Use the sign of the standard potential printed here; a magnesium-ion concentration of 10 to the power -4 subtracts 0.1182 V from it.

32(b)(iii). What is the effect of temperature on the electrical conductance of metallic conductor ?

[1 mark]

Solution:

Concept:

- Electrical conductance is $G = 1/R$, where R is the resistance of the conductor.
- Metallic conduction occurs through mobile electrons; lattice vibrations hinder their motion.

Step 1: Identify the charge carriers In a metallic conductor, free electrons carry current through the lattice. Raising the temperature increases the thermal vibrations of the metal ions.

Step 2: Explain the effect on conductance The vibrating ions scatter the moving electrons more

Quick Tip to Solve: Remember the chain: higher temperature, more lattice vibration, greater resistance, lower conductance.

frequently, reducing their mobility. Thus the resistance R increases; since $G = 1/R$, the electrical conductance decreases as temperature increases.

Step 3: Conclusion The electrical conductance of a metallic conductor decreases with increase in temperature.

Quick Tip to Solve: Remember the chain: higher temperature, more lattice vibration, greater resistance, lower conductance.

33(a)(i). Account for the following :

(I) Orange colour of $\text{Cr}_2\text{O}_7^{2-}$ ion changes to yellow when treated with an alkali.

(II) Zn, Cd and Hg are non-transition elements.

(III) E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is highly positive (+1.57 V) as compared to $\text{Cr}^{3+}/\text{Cr}^{2+}$. [3 marks]

Solution:

Concept:

- Chromate CrO_4^{2-} is yellow and dichromate $\text{Cr}_2\text{O}_7^{2-}$ is orange; their equilibrium depends on pH.
- A transition element has an incompletely filled d subshell in its atom or at least one of its usual ions.
- A positive standard reduction potential indicates a favourable reduction; electronic configurations help explain relative stability.

Step 1: (I) Explain the orange-to-yellow change Alkali converts orange dichromate ions into yellow chromate ions. Hydroxide removes the acidity and shifts the chromate-dichromate equilibrium towards chromate:



The oxidation state of chromium remains +6; the colour change is an acid-base equilibrium change, not a redox reaction.

Step 2: (II) Explain why Zn, Cd and Hg are non-transition elements Their atomic configurations have completely filled d^{10} subshells: Zn has $3d^{10}4s^2$, Cd has $4d^{10}5s^2$, and Hg has $5d^{10}6s^2$. Their usual +2 ions also retain d^{10} configurations. Consequently they do not meet the definition of transition elements, even though they belong to the d block.

Step 3: (III) Compare the two standard reduction potentials Reduction of Mn^{3+} gives Mn^{2+} : $3d^4 \rightarrow 3d^5$. The product has an especially stable half-filled d subshell, so this reduction is strongly favoured and its E° is highly positive, +1.57 V. In contrast, reduction of Cr^{3+} gives Cr^{2+} : $3d^3 \rightarrow 3d^4$. It converts the relatively stable Cr^{3+} configuration into a less stable ion, so the reduction is less favourable and its potential is much lower.

Step 4: Conclusion (I) Alkali forms yellow chromate. (II) Zn, Cd and Hg have filled d subshells in their atoms and usual ions. (III) Formation of stable $3d^5 \text{Mn}^{2+}$ makes the manganese reduction potential highly positive.

Quick Tip to Solve: For redox-potential explanations, write the d configurations of both ions and identify which side has the more stable configuration.

33(a)(ii). What happens when :

(I) Manganate ion undergoes disproportionation reaction in acidic medium ?

(II) KMnO_4 is heated ?

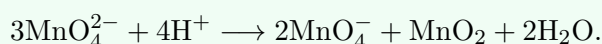
[2 marks]

Solution:

Concept:

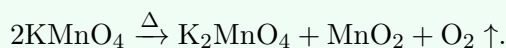
- Disproportionation is simultaneous oxidation and reduction of the same species.
- In manganate MnO_4^{2-} , manganese is +6; permanganate and manganese dioxide contain +7 and +4, respectively.

Step 1: (I) Disproportionation in acidic medium Green manganate ions form purple permanganate ions and brown manganese dioxide in acidic medium:



Two manganese atoms are oxidised from +6 to +7, while one is reduced from +6 to +4. Thus the same reactant undergoes oxidation and reduction.

Step 2: (II) Heating potassium permanganate On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen gas:



The solid products are green potassium manganate and brown manganese dioxide. The equation conserves two potassium atoms, two manganese atoms and eight oxygen atoms on each side.

Step 3: Conclusion (I) Acidic manganate gives permanganate and MnO_2 . (II) Heated KMnO_4 gives K_2MnO_4 , MnO_2 and O_2 .

Quick Tip to Solve: Distinguish the acidic reaction, which consumes hydrogen ions, from thermal decomposition, which releases oxygen gas.

OR

33(b)(i). What is 'Misch metal' ? Give its one use.

[1 mark]

Solution:

Concept:

- Misch metal is a commercial alloy containing predominantly lanthanoid metals.
- An alloy is a metallic mixture; misch metal is not a single element or a pure compound.

Step 1: State the composition Misch metal consists of about 95% lanthanoid metals and about 5% iron, with traces of S, C, Ca and Al. The lanthanoid portion mainly includes cerium and lanthanum together with other lanthanoids.

Step 2: Give one use Misch metal is used to make lighter flints. Its ability to produce sparks when struck makes it suitable for ignition in cigarette lighters.

Quick Tip to Solve: Recall misch metal as the lanthanoid-rich alloy associated with the spark-producing flint of a lighter.

Step 3: Conclusion Misch metal is an alloy of about 95% lanthanoid metals and 5% iron, with minor impurities; it is used in lighter flints.

Quick Tip to Solve: Recall misch metal as the lanthanoid-rich alloy associated with the spark-producing flint of a lighter.

33(b)(ii). Write the formula of an oxoanion of chromium in which it shows the oxidation state equal to its group number. [1 mark]

Solution:

Concept:

- Chromium belongs to group 6, so the required oxidation state is +6.
- In an oxoanion, oxygen normally has oxidation state -2 , and the sum of oxidation states equals the ionic charge.

Step 1: Choose a chromium oxoanion The chromate ion has formula CrO_4^{2-} . It contains one chromium atom and four oxygen atoms, with a total ionic charge of -2 .

Step 2: Verify the chromium oxidation state Let the oxidation state of chromium be x . Then

$$x + 4(-2) = -2 \Rightarrow x = +6.$$

Thus chromium in chromate has an oxidation state equal to its group number, 6. Dichromate $\text{Cr}_2\text{O}_7^{2-}$ is also a valid example, but one formula is sufficient.

Step 3: Conclusion The required formula is $\boxed{\text{CrO}_4^{2-}}$, in which chromium is in the +6 oxidation state.

Quick Tip to Solve: To check any oxoanion, set the sum of the metal and oxygen oxidation states equal to its overall ionic charge.

33(b)(iii). Why does Vanadium pentoxide (V_2O_5) act as a catalyst ? [1 mark]

Solution:

Concept:

- Transition-metal compounds can catalyse reactions because the metal can change its oxidation state and then return to its original state.
- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated during the overall process.

Step 1: Identify the variable oxidation states In V_2O_5 , vanadium has oxidation state +5. It can readily undergo reduction to a lower oxidation state, particularly +4, and subsequent oxidation back to +5. This reversible change allows the compound to take part in intermediate reactions.

Step 2: Explain regeneration in a catalytic cycle For example, in the oxidation of SO_2 to SO_3 , vanadium pentoxide supplies oxygen and is reduced; oxygen then reoxidises the reduced vanadium

Quick Tip to Solve: Link catalytic action to reversible changes in vanadium oxidation state, especially +5 and +4.

oxide. Thus, the catalyst participates in the reaction but is restored, facilitating the overall oxidation.

Step 3: Conclusion V_2O_5 acts as a catalyst because vanadium exhibits variable oxidation states, enabling intermediate reactions and regeneration of the catalyst.

Quick Tip to Solve: Link catalytic action to reversible changes in vanadium oxidation state, especially +5 and +4.

33(b)(iv). Why do transition elements have high enthalpies of atomisation ?

[1 mark]

Solution:

Concept:

- Enthalpy of atomisation is the enthalpy required to convert one mole of a metal into separate gaseous atoms.
- Strong metallic bonding requires more energy to separate the atoms; both valence s and d electrons can contribute to bonding in transition metals.

Step 1: Relate electronic structure to metallic bonding Transition elements generally have several unpaired electrons in their partially filled d subshells. Participation of these d electrons, together with the outer s electrons, produces strong interatomic metallic bonding in the solid.

Step 2: Relate bond strength to atomisation Atomisation separates the atoms completely, so the metallic interactions must be overcome. Because these interactions are strong, a large amount of energy is required. Consequently, transition elements generally have high enthalpies of atomisation; the values vary with their electronic configurations.

Step 3: Conclusion Transition elements generally have high enthalpies of atomisation because the participation of numerous unpaired d electrons in metallic bonding makes their interatomic bonds strong.

Quick Tip to Solve: Use the chain: unpaired d electrons, strong metallic bonding, then high energy needed for atomisation.

33(b)(v). How do you prepare $Na_2Cr_2O_7$ from Na_2CrO_4 ?

[1 mark]

Solution:

Concept:

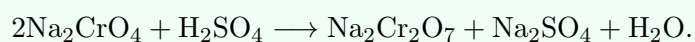
- Chromate and dichromate ions are interconverted by changing the acidity of the solution.
- Acidification favours dichromate: $2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$.

Step 1: Acidify the sodium chromate solution Treat an aqueous solution of sodium chromate with dilute sulphuric acid. The added H^+ ions shift the chromate–dichromate equilibrium towards dichromate, and the yellow solution becomes orange.

Step 2: Write the balanced preparation reaction The conversion is represented by the balanced

Quick Tip to Solve: Remember that acid converts yellow chromate into orange dichromate; two chromate ions give one dichromate ion.

equation:



Chromium remains in oxidation state +6 on both sides. This is an acid-dependent conversion of oxoanions, rather than an oxidation or reduction of chromium.

Step 3: Conclusion Sodium dichromate is prepared by acidifying sodium chromate solution with dilute sulphuric acid, as shown in the balanced equation above.

Quick Tip to Solve: Remember that acid converts yellow chromate into orange dichromate; two chromate ions give one dichromate ion.