

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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

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

You may use the following values of physical constants wherever necessary :

$$c = 3 \times 10^8 \text{ m/s}$$

$$h = 6.63 \times 10^{-34} \text{ J s}$$

$$e = 1.6 \times 10^{-19} \text{ C}$$

$$\mu_0 = 4\pi \times 10^{-7} \text{ T m A}^{-1}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$$

$$\frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \text{ N m}^2 \text{ C}^{-2}$$

$$\text{Mass of electron } (m_e) = 9.1 \times 10^{-31} \text{ kg}$$

$$\text{Mass of neutron} = 1.675 \times 10^{-27} \text{ kg}$$

$$\text{Mass of proton} = 1.673 \times 10^{-27} \text{ kg}$$

$$\text{Avogadro's number} = 6.023 \times 10^{23} \text{ per gram mole}$$

$$\text{Boltzmann's constant} = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Section A (16 marks)

Questions No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

1. In case of association, abnormal molar mass of solute will

[1 mark]

- (A) increase
- (B) decrease
- (C) remain same
- (D) first increase and then decrease

Correct Answer: (A) increase

Solution:

Concept:

- Colligative properties depend on the number of dissolved solute particles, rather than their chemical nature.
- The van't Hoff factor is $i = \frac{\text{observed colligative property}}{\text{calculated colligative property}} = \frac{M_{\text{normal}}}{M_{\text{observed}}}$, where M denotes molar mass. Association gives $i < 1$.

Step 1: Determine the effect of association In association, two or more solute molecules combine to form a larger species, for example $2A \rightleftharpoons A_2$. For a fixed mass of solute, the number of independent particles in solution decreases. Hence the observed colligative property is smaller than its value calculated without association.

Step 2: Relate particle number to the calculated molar mass Since $M_{\text{observed}} = M_{\text{normal}}/i$ and $i < 1$, the experimentally calculated, abnormal molar mass is greater than the normal molar mass. Option (B) describes the opposite trend, which occurs in dissociation. Option (C) would require no change in particle number, and option (D) does not follow from association.

Step 3: Conclusion The abnormal molar mass of the solute increases on association. Hence, the correct option is (A).

Quick Tip to Solve: Association reduces particle number: remember $i < 1$, so the observed molar mass is larger than the normal molar mass.

2. Standard electrode potential for $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple is +0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. The two couples in their standard states are connected to make a cell. The cell potential will be [1 mark]

- (A) +1.19 V
- (B) +0.89 V
- (C) +0.18 V
- (D) +1.83 V

Correct Answer: (B) +0.89 V

Solution:

Concept:

- The standard cell potential is $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$, using standard reduction potentials for both electrodes.
- The couple with the more positive reduction potential undergoes reduction at the cathode; the other undergoes oxidation at the anode. Electrode potential is intensive and is not multiplied when balancing electrons.

Step 1: Identify the electrodes The $\text{Sn}^{4+}/\text{Sn}^{2+}$ couple has the more positive potential, +0.15 V, so Sn^{4+} is reduced at the cathode. The Cr^{3+}/Cr couple has reduction potential -0.74 V, so chromium is oxidised at the anode.

Step 2: Calculate the potential difference Using the two reduction potentials directly,

$$E_{\text{cell}}^{\circ} = 0.15 - (-0.74) = 0.89 \text{ V.}$$

The electron coefficients used to balance the overall reaction do not change these potentials. The values in (A), (C) and (D) do not equal the cathode-minus-anode difference; multiplying either potential by a stoichiometric coefficient is incorrect.

Step 3: Conclusion The standard cell potential is +0.89 V. Hence, the correct option is (B).

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

3. The magnetic moment is associated with its spin angular momentum and orbital angular momentum. Spin only magnetic moment value of Cr^{3+} ion (Atomic no. : Cr = 24) is

[1 mark]

- (A) 2.87 B.M.
- (B) 3.87 B.M.
- (C) 3.47 B.M.
- (D) 3.57 B.M.

Correct Answer: (B) 3.87 B.M.

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ B.M., where n is the number of unpaired electrons and B.M. denotes Bohr magneton.
- When a transition-metal atom forms a cation, its outer $4s$ electrons are removed before its $3d$ electrons.

Step 1: Obtain the ionic configuration Chromium, with atomic number 24, has configuration $[\text{Ar}]3d^5 4s^1$. Forming Cr^{3+} removes the $4s$ electron and two $3d$ electrons, giving $[\text{Ar}]3d^3$. By Hund's rule the three d electrons are unpaired, so $n = 3$.

Step 2: Evaluate the spin-only moment Substituting the number of unpaired electrons,

$$\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$$

Option (A), 2.87 B.M., is not the value for three unpaired electrons; options (C) and (D) also do not equal $\sqrt{15}$. Orbital contributions are excluded because the question specifically asks for the spin-only value.

Step 3: Conclusion The spin-only magnetic moment of Cr^{3+} is 3.87 B.M.. Hence, the correct option is (B).

Quick Tip to Solve: Remove the chromium $4s$ electron first: the resulting $3d^3$ ion has three unpaired electrons, giving square root of 15 B.M.

4. Acidified KMnO_4 oxidises sulphite to

[1 mark]

- (A) $\text{S}_2\text{O}_3^{2-}$
- (B) $\text{S}_2\text{O}_8^{2-}$
- (C) $\text{SO}_2(\text{g})$
- (D) SO_4^{2-}

Correct Answer: (D) SO_4^{2-}

Solution:

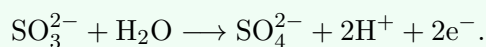
Concept:

- Acidified KMnO_4 is a strong oxidising agent: MnO_4^- is reduced to Mn^{2+} in acidic medium.

Quick Tip to Solve: Track sulphur: sulphite has S at +4, whereas its usual oxidation product sulphate has S at +6.

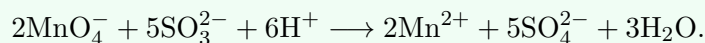
- Sulphite, SO_3^{2-} , contains sulphur in oxidation state +4; oxidation to sulphate raises its oxidation state to +6.

Step 1: Identify the oxidation product Oxidation increases the oxidation state of sulphur from +4 in sulphite to +6 in sulphate. The sulphite oxidation half-reaction in acidic solution is



Thus each sulphite ion loses two electrons.

Step 2: Check the competing options Combining this oxidation with permanganate reduction gives



Sulphur dioxide in (C) retains sulphur in oxidation state +4, so it is not the oxidation product. Neither thiosulphate in (A) nor peroxodisulphate in (B) is formed in this standard sulphite-permanganate reaction.

Step 3: Conclusion Acidified KMnO_4 oxidises sulphite to SO_4^{2-} . Hence, the correct option is (D).

Quick Tip to Solve: Track sulphur: sulphite has S at +4, whereas its usual oxidation product sulphate has S at +6.

5. The correct IUPAC name of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^{2+}$ is

[1 mark]

- (A) Diamminedichloridoplatinum(II)
- (B) Diamminedichloridoplatinum(IV)
- (C) Diamminedichloridoplatinum(O)
- (D) Diamminedichloridoplatinate(IV)

Correct Answer: (B) Diamminedichloridoplatinum(IV)

Solution:

Concept:

- In $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]^{2+}$, ammonia is a neutral ligand and each chlorido ligand has charge -1 . The sum of the metal oxidation state and ligand charges equals the complex charge.
- Ligands are named alphabetically, ignoring numerical prefixes: ammine precedes chlorido. A cationic complex retains the metal name platinum, followed by its oxidation state in Roman numerals.

Step 1: Determine the platinum oxidation state Let the oxidation state of platinum be x . Charge balance gives

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

The superscript 2+ is the charge of the whole complex, not the oxidation state of platinum, because the two chlorido ligands contribute a total charge of -2 .

Step 2: Construct and test the name Two ammonia ligands are named diammine and two chloride

Quick Tip to Solve: Calculate metal oxidation state from the total complex charge before choosing the Roman numeral or the metal-name ending.

ligands dichlorido. These precede platinum(IV), giving diamminedichloridoplatinum(IV). Option (A) assigns oxidation state II and option (C) assigns zero; both violate charge balance. Option (D) uses platinate, the metal-name form reserved for an anionic coordination entity, whereas the given complex is cationic.

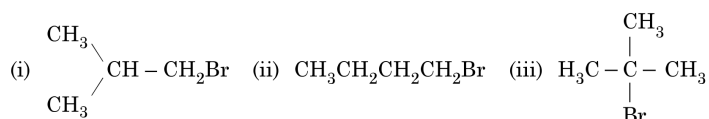
Step 3: Conclusion The correct IUPAC name is diamminedichloridoplatinum(IV). Hence, the correct option is (B).

Quick Tip to Solve: Calculate metal oxidation state from the total complex charge before choosing the Roman numeral or the metal-name ending.

6. Arrange the following compounds in increasing order of their boiling points :

The correct order is

[1 mark]



(A) (ii) < (i) < (iii)

(B) (i) < (ii) < (iii)

(C) (iii) < (i) < (ii)

(D) (iii) < (ii) < (i)

Correct Answer: (C) (iii) < (i) < (ii)

Solution:

Concept:

- For isomeric alkyl halides with the same molecular formula, increased branching reduces molecular surface area and weakens intermolecular dispersion forces.
- Weaker intermolecular attractions require less energy for vaporisation and therefore give a lower boiling point; a straight-chain isomer generally has the highest boiling point.

Step 1: Identify the three isomers in the figure Compound (i), $(\text{CH}_3)_2\text{CHCH}_2\text{Br}$, is 1-bromo-2-methylpropane. Compound (ii), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$, is straight-chain 1-bromobutane. Compound (iii), $(\text{CH}_3)_3\text{CBr}$, is the most compact, highly branched isomer, 2-bromo-2-methylpropane. All have molecular formula $\text{C}_4\text{H}_9\text{Br}$.

Step 2: Compare surface area and attractions The compact structure of (iii) gives the least effective intermolecular contact, so it boils first. Compound (i) is less compact and has intermediate boiling point. Straight-chain compound (ii) has the greatest surface contact and strongest dispersion forces, so it boils last. Options (A) and (B) incorrectly place (iii) highest, while (D) incorrectly places (ii) below (i).

Step 3: Conclusion The increasing order of boiling points is (iii) < (i) < (ii). Hence, the correct option is (C).

Quick Tip to Solve: For these same-formula bromides, identify the most compact isomer first and put the straight-chain isomer last in increasing boiling point.

7. Alkyl halides undergoing nucleophilic bimolecular substitution reaction involve

[1 mark]

- (A) retention of configuration
- (B) formation of racemic mixture
- (C) inversion of configuration
- (D) formation of carbocation

Correct Answer: (C) inversion of configuration

Solution:

Concept:

- A bimolecular nucleophilic substitution, S_N2 , is a concerted reaction with rate $k[RX][Nu^-]$, where RX is the alkyl halide and Nu is the nucleophile. Bond formation and bond cleavage occur in one step.
- The nucleophile attacks the carbon from the side opposite the leaving group. This backside attack reverses the spatial arrangement of the groups around a stereogenic carbon, called Walden inversion.

Step 1: Relate backside attack to stereochemistry The incoming nucleophile approaches opposite the carbon-halogen bond as the halide leaves. The three other groups move through a nearly planar arrangement in the transition state and emerge with the inverted arrangement. Consequently, an alkyl halide having a stereogenic reacting carbon undergoes inversion of configuration.

Step 2: Reject the alternative mechanisms Retention in option (A) does not describe the stereochemical result of a single backside substitution. Racemic-mixture formation in (B) is associated with attack on a planar carbocation in the S_N1 pathway. Option (D) is also incorrect because S_N2 forms no carbocation intermediate: it proceeds directly through one transition state.

Step 3: Conclusion Bimolecular nucleophilic substitution involves inversion of configuration. Hence, the correct option is (C).

Quick Tip to Solve: Link S_N2 with backside attack and inversion; a planar carbocation and possible racemisation belong to S_N1 .

8. Which is the correct order of acid strength from the following ?

[1 mark]

- (A) $C_6H_5OH > H_2O > ROH$
- (B) $C_6H_5OH > ROH > H_2O$
- (C) $ROH > C_6H_5OH > H_2O$
- (D) $H_2O > C_6H_5OH > ROH$

Correct Answer: (A) $C_6H_5OH > H_2O > ROH$

Solution:

Concept:

- Acid strength depends on the ease of donating H^+ and the stability of the conjugate base.
- Resonance stabilises phenoxide; an alkyl group has a positive inductive effect and destabilises

Quick Tip to Solve: Compare conjugate-base stability: resonance puts phenol first, while the alkyl group puts alcohol last.

alkoxide.

Step 1: Compare phenol with water Phenol loses a proton to give phenoxide, whose negative charge is delocalised over the aromatic system. Hydroxide has no comparable resonance stabilisation. Phenol therefore donates a proton more readily than water.

Step 2: Compare water with alcohol In RO^- , the electron-releasing alkyl group intensifies the negative charge on oxygen. Alkoxide is consequently less stable than hydroxide, so an ordinary alcohol is weaker as an acid than water. Option (B) reverses this last comparison; (C) incorrectly makes alcohol strongest; (D) puts water above phenol.

Step 3: Conclusion The order is $\text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{ROH}$. Hence, the correct option is (A).

Quick Tip to Solve: Compare conjugate-base stability: resonance puts phenol first, while the alkyl group puts alcohol last.

9. The acid formed when propyl magnesium bromide is treated with CO_2 followed by acid hydrolysis is : [1 mark]

- (A) $\text{C}_3\text{H}_7\text{COOH}$
- (B) $\text{C}_2\text{H}_5\text{COOH}$
- (C) CH_3COOH
- (D) $\text{C}_3\text{H}_7\text{OH}$

Correct Answer: (A) $\text{C}_3\text{H}_7\text{COOH}$

Solution:

Concept:

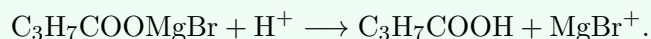
- A Grignard reagent RMgBr adds to carbon dioxide to form a magnesium carboxylate.
- Acid hydrolysis gives RCOOH ; the carbon of CO_2 adds one carbon to the original alkyl group.

Step 1: Form the carboxylate The propyl group contains three carbon atoms. Its carbon bonded to magnesium attacks the electrophilic carbon of carbon dioxide:



The new carboxyl carbon comes from carbon dioxide, not from shortening the propyl chain.

Step 2: Hydrolyse and compare the options Acid hydrolysis protonates the carboxylate:



The acid has four carbons. Option (B) has only three total carbons, and (C) has two; neither preserves the propyl group while adding a carbon. Option (D) is an alcohol rather than the carboxylic acid formed in this reaction.

Step 3: Conclusion The product is $\text{C}_3\text{H}_7\text{COOH}$, butanoic acid for n-propyl magnesium bromide. Hence, the correct option is (A).

Quick Tip to Solve: Count all carbons: reaction of an alkyl Grignard reagent with carbon dioxide increases the carbon count by one.

10. The best reagent for converting propanamide into propanamine is

[1 mark]

- (A) excess H_2
- (B) Br_2 in aqueous NaOH
- (C) iodine in the presence of red phosphorus
- (D) $LiAlH_4$ in ether

Correct Answer: (D) $LiAlH_4$ in ether

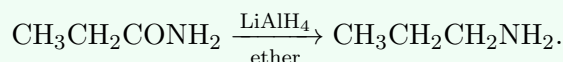
Solution:

Concept:

- Lithium aluminium hydride reduces an amide group $-CONH_2$ to $-CH_2NH_2$.
- This reduction retains the carbon skeleton; Hofmann bromamide degradation removes the carbonyl carbon.

Step 1: Identify the required change Propanamide is $CH_3CH_2CONH_2$, while propanamine is $CH_3CH_2CH_2NH_2$. Both compounds have three carbon atoms. The carbonyl oxygen must be removed and the carbonyl carbon converted to a methylene group without losing that carbon.

Step 2: Select the reducing reagent $LiAlH_4$ in dry ether, followed by work-up, achieves this conversion:



Bromine in aqueous sodium hydroxide instead gives ethanamine by Hofmann degradation. Excess hydrogen alone, with no suitable catalyst specified, is not the standard reagent here. Iodine with red phosphorus is not the appropriate selective amide-to-amine reagent.

Step 3: Conclusion The best reagent is $LiAlH_4$ in ether. Hence, the correct option is (D).

Quick Tip to Solve: For an amide-to-amine conversion, use $LiAlH_4$ when carbon count stays the same; Hofmann degradation loses one carbon.

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

[1 mark]

- (A) It is an aldohexose.
- (B) On heating with HI it forms n-hexane.
- (C) It exists in furanose form.
- (D) It does not give Schiff's test.

Correct Answer: (C) It exists in furanose form.

Solution:

Concept:

- Glucose is an aldohexose: its open-chain form has six carbons and an aldehyde group.
- Its usual cyclic forms are six-membered hemiacetal rings, called pyranose forms.

Step 1: Check the structural statements Statement (A) is true because glucose contains six carbon atoms and has an aldehyde group in its open-chain form. Statement (B) is also true: prolonged

Quick Tip to Solve: Distinguish total carbons from ring members: glucose has six carbons and its usual pyranose ring has six members.

heating with hydrogen iodide gives n-hexane, which supports an unbranched chain of six carbon atoms.

Step 2: Check the ring form and aldehyde test Glucose predominantly exists as the alpha and beta forms of glucopyranose, formed by intramolecular hemiacetal formation between C-1 and the hydroxyl group at C-5. The ring contains five carbon atoms and one oxygen atom. A furanose ring would have five ring members, so statement (C) is the incorrect description in this context. Statement (D) is true: glucose does not give Schiff's test despite the aldehyde structure of its open-chain form.

Step 3: Conclusion The statement that is not true is "It exists in furanose form." Hence, the correct option is (C).

Quick Tip to Solve: Distinguish total carbons from ring members: glucose has six carbons and its usual pyranose ring has six members.

12. An unripe mango placed in a concentrated salt solution to prepare pickle, shrivels because

[1 mark]

- (A) it gains water due to osmosis
- (B) it loses water due to reverse osmosis
- (C) it gains water due to reverse osmosis
- (D) it loses water due to osmosis

Correct Answer: (D) it loses water due to osmosis

Solution:

Concept:

- Osmosis is solvent movement through a semipermeable membrane from lower solute concentration to higher solute concentration.
- An external hypertonic solution draws water out of plant cells; pressure-driven reverse osmosis requires applied pressure.

Step 1: Compare the solutions The concentrated salt solution outside the mango cells has a higher solute concentration than their cell sap. The cell membrane permits water movement and acts as the semipermeable barrier. Water therefore passes from the cells into the external solution.

Step 2: Relate water loss to shrivelling As the cells lose water by exosmosis, their turgor decreases and the mango shrivels. No external pressure greater than the osmotic pressure is applied, so this is ordinary osmosis, not reverse osmosis. Options (A) and (C) predict water gain and hence cannot explain shrivelling. Option (B) has the right direction of water loss but names the wrong process.

Step 3: Conclusion The mango loses water due to osmosis. Hence, the correct option is (D).

Quick Tip to Solve: When a fruit shrivels in concentrated salt solution, track water moving out towards the higher solute concentration.

13. For this Assertion-Reason question, select the correct answer:

(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.

Assertion (A): $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$ are examples of homoleptic complexes.

Reason (R): All the ligands attached to the metal are the same.

[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:

- A homoleptic complex contains only one type of ligand attached to its central metal ion.
- The coordination sphere is inside square brackets; ions outside the brackets are counterions.

Step 1: Judge the assertion Each printed complex contains six water molecules coordinated to the metal: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$ and $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$. In each coordination sphere, water is the only ligand type. Both complexes are therefore homoleptic, so Assertion (A) is true.

Step 2: Judge the reason Reason (R) states that all ligands attached to the metal are the same. This is precisely the defining property of a homoleptic complex. The chloride ions lie outside the coordination brackets and are counterions; they do not create a second type of coordinated ligand. The reason is true.

Step 3: Check the explanatory connection The reason directly explains why these two coordination spheres are homoleptic: each metal has only water ligands. Thus (B) wrongly denies the explanatory link, while (C) and (D) wrongly deny one of the true statements.

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

Quick Tip to Solve: For homoleptic classification, count ligand types inside the brackets and ignore counterions outside them.

14. For this Assertion-Reason question, select the correct answer :

(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.

Assertion (A): The boiling points of alkyl halides decrease in the order : $RI > RBr > RCl > RF$.

Reason (R): The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass. [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 the same alkyl group, increasing halogen size and polarizability strengthens dispersion forces.
- Boiling point depends on the total intermolecular attractions; polar halides also have dipole-dipole interactions.

Step 1: Judge the assertion For a fixed alkyl group, the halogen becomes larger and more polarizable from fluorine to iodine. Stronger dispersion attractions generally raise the boiling point in the order $RF < RCl < RBr < RI$. Thus the stated decreasing order $RI > RBr > RCl > RF$ is correct, and Assertion (A) is true.

Step 2: Judge the reason Alkyl chlorides, bromides and iodides are polar molecules, whereas comparable hydrocarbons are nonpolar. Additional intermolecular attractions in these alkyl halides make their boiling points considerably higher than those of hydrocarbons of comparable molecular mass. Reason (R) is therefore true.

Step 3: Check whether the reason explains the order The reason compares alkyl halides with hydrocarbons; it does not compare the four halogens for the same alkyl group. The asserted order is explained by increasing size and polarizability, not by this separate hydrocarbon comparison. Therefore (A) incorrectly treats the reason as the explanation; (C) and (D) incorrectly classify a true statement as false.

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

Quick Tip to Solve: In assertion-reason questions, distinguish a true comparison with hydrocarbons from an explanation of a trend among halides.

15. Assertion (A): The boiling point of ethanol is higher than that of methoxymethane.

Reason (R): There is intramolecular hydrogen bonding in ethanol.

[1 mark]

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

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

Solution:

Concept:

- Hydrogen bonding arises when hydrogen bonded to oxygen interacts with a lone pair on another oxygen atom.
- Intermolecular forces act between molecules; stronger attractions require more thermal energy to separate molecules during boiling.

Step 1: Judge the assertion Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, contains an O – H group and its molecules form hydrogen bonds with one another. Methoxymethane, CH_3OCH_3 , has no hydrogen attached to oxygen, so its pure liquid cannot form this hydrogen-bonded network. Their molecular masses are equal, but ethanol has stronger intermolecular attractions and consequently a higher boiling point. Assertion (A) is true.

Step 2: Judge the reason The hydrogen bonding responsible for the boiling point of ethanol is intermolecular: it occurs between distinct ethanol molecules. The stated intramolecular hydrogen bonding, which would occur within a single molecule, is therefore incorrect. Reason (R) is false.

Step 3: Compare the two statements The correct explanation would refer to intermolecular hydrogen bonding in ethanol. Since the printed reason instead says intramolecular, neither code requiring both statements to be true applies. The code asserting a false assertion is also excluded.

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

Quick Tip to Solve: Check the prefix: ethanol has intermolecular hydrogen bonding, so the word intramolecular makes this reason false.

16. Assertion (A): All naturally occurring α -amino acids except glycine are optically active.

Reason (R): Most naturally occurring amino acids have L-configuration.

[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:

- A chiral α -carbon bears four different substituents and produces non-superimposable mirror-image forms.
- L-configuration specifies relative stereochemical arrangement; it does not itself explain the presence of optical activity.

Step 1: Judge the assertion For an α -amino acid, the central carbon generally carries $-\text{NH}_2$, $-\text{COOH}$, $-\text{H}$ and a side chain R . When $R \neq \text{H}$, these four substituents are different, making this carbon asymmetric and the amino acid optically active. Glycine has $R = \text{H}$, so it carries two identical hydrogen atoms and is achiral. Assertion (A) is true.

Step 2: Judge the reason Most naturally occurring amino acids belong to the L-series. This statement about their relative configuration is true. The designation L must not be confused with the sign of rotation of plane-polarised light.

Step 3: Check the explanation Optical activity follows from molecular chirality, specifically the four different groups on the asymmetric carbon in these amino acids. Membership of the L-series is a separate configuration statement and does not explain why glycine is the exception. Thus Reason (R), although true, is not the correct explanation of Assertion (A).

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

Quick Tip to Solve: For optical activity, count different groups on the alpha carbon; L-configuration alone is not the explanation.

Section B (10 marks)

17(A). Give reasons : (1+1=2)

(a) Cooking is faster in pressure cooker than in an open pan.

(b) On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution ? What change in temperature would you observe after mixing liquids X and Y ?

[2 marks]

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure; increasing external pressure raises its boiling point.
- Stronger unlike-molecule attractions than like-molecule attractions lower the escaping tendency and cause negative deviation from Raoult's law.

Step 1: Explain faster cooking in a pressure cooker Steam is retained inside a closed pressure cooker, raising the pressure above the water. Water must then reach a higher temperature before its vapour pressure equals this higher external pressure. Thus water boils above its normal boiling point and the food cooks at a higher temperature than in an open pan. This higher cooking temperature makes cooking faster.

Step 2: Infer the deviation and temperature change The decrease in volume on mixing shows that the unlike $X - Y$ attractions are stronger than the original $X - X$ and $Y - Y$ attractions. The molecules pack more closely and escape less readily into the vapour. Consequently, the vapour pressure is lower than predicted by Raoult's law: the solution shows negative deviation. Formation of stronger attractions releases heat, so $\Delta H_{\text{mix}} < 0$, and the temperature rises after mixing.

Step 3: Conclusion (a) The increased pressure raises the boiling point of water, so cooking occurs at a higher temperature. (b) The solution shows negative deviation from Raoult's law, and its temperature increases.

Quick Tip to Solve: Volume contraction suggests stronger unlike attractions: connect it with negative deviation and heat release.

OR

17(B). Define Azeotrope. What type of Azeotrope is formed by negative deviation from Raoult's law ? Give an example.

[2 marks]

Solution:

Concept:

- An azeotrope is a constant-boiling mixture whose liquid and vapour phases have the same composition at its azeotropic composition.
- A sufficiently large negative deviation from Raoult's law produces a vapour-pressure minimum and therefore a maximum-boiling azeotrope.

Quick Tip to Solve: Lower vapour pressure requires a higher boiling temperature: negative deviation pairs with maximum boiling.

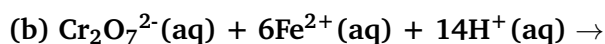
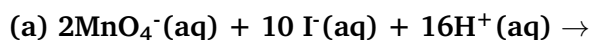
Step 1: Define an azeotrope An azeotrope is a mixture of liquids that boils at a constant temperature and has the same composition in its liquid and vapour phases. At the azeotropic composition, vaporisation does not change the proportion of the components. Hence the components cannot be completely separated by fractional distillation: the condensed vapour reproduces the liquid composition.

Step 2: Identify the type and give an example For a mixture with negative deviation from Raoult's law, unlike-molecule attractions are relatively strong and the vapour pressure is lower than the ideal prediction. When the deviation is sufficiently large to form an azeotrope, its vapour pressure has a minimum. A higher temperature is therefore needed to reach the external pressure, giving a maximum-boiling azeotrope. Nitric acid and water form such an azeotrope; at atmospheric pressure it contains about 68% nitric acid by mass.

Step 3: Conclusion An azeotrope is a constant-boiling mixture with identical liquid and vapour compositions. Negative deviation forms a maximum-boiling azeotrope; nitric acid and water are an example.

Quick Tip to Solve: Lower vapour pressure requires a higher boiling temperature: negative deviation pairs with maximum boiling.

18. Complete and balance the following chemical equations :



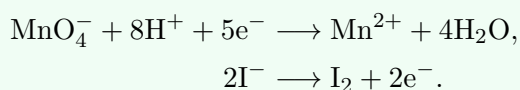
[2 marks]

Solution:

Concept:

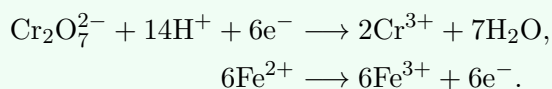
- In acidic medium, balance a redox equation by electron transfer, using H_2O for oxygen and H^+ for hydrogen.
- Permanganate is reduced to Mn^{2+} ; dichromate is reduced to Cr^{3+} . The electrons lost equal those gained.

Step 1: Balance permanganate with iodide Manganese changes from +7 to +2, gaining five electrons per manganese atom. Iodide is oxidised to iodine. The half-reactions are



Multiply the first equation by 2 and the second by 5, then add and cancel ten electrons. This gives 2Mn^{2+} , 5I_2 and $8\text{H}_2\text{O}$ as the products.

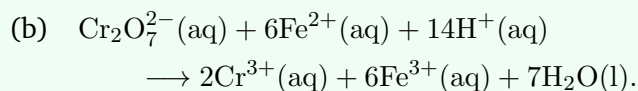
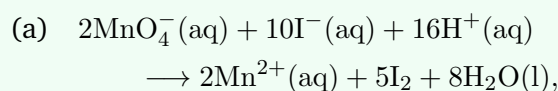
Step 2: Balance dichromate with iron(II) Each chromium changes from +6 to +3; two chromium atoms therefore gain six electrons. Each Fe^{2+} loses one electron to become Fe^{3+} . Thus



Quick Tip to Solve: In acid, remember five electrons per permanganate and six per dichromate; then check atoms and total charge.

Addition cancels six electrons. Oxygen and hydrogen balance through seven water molecules. The total charge on either side is +24, confirming charge conservation.

Step 3: Conclusion The completed balanced equations are



Quick Tip to Solve: In acid, remember five electrons per permanganate and six per dichromate; then check atoms and total charge.

19. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Justify your answer. [2 marks]

Solution:

Concept:

- In nucleophilic addition, a nucleophile attacks the electron-deficient carbon atom of the polar carbonyl group, $\text{C}=\text{O}$. Greater positive character on this carbon favours attack.
- Conjugation of a carbonyl group with a benzene ring delocalises electrons and decreases its electrophilicity; steric crowding also makes nucleophilic approach more difficult.

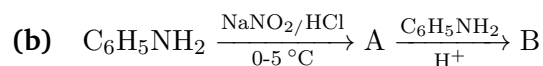
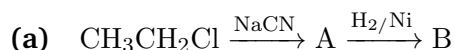
Step 1: Compare the electronic effects Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has its carbonyl group directly conjugated with the benzene ring. Resonance donation from the ring reduces the positive character of the carbonyl carbon. Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, has no such conjugation. Although its ethyl group has a positive inductive effect, the resonance effect in benzaldehyde makes its carbonyl carbon less susceptible to nucleophilic attack overall.

Step 2: Compare the accessibility of the carbonyl carbon The phenyl group in benzaldehyde is bulkier than the ethyl group in propanal. It causes greater steric hindrance to the incoming nucleophile. Thus both the reduced electrophilicity and the greater hindrance favour propanal in this comparison.

Step 3: Conclusion Benzaldehyde is less reactive than propanal towards nucleophilic addition because of resonance conjugation with its phenyl group and greater steric hindrance.

Quick Tip to Solve: For this comparison, check whether the aldehyde carbonyl is directly attached to a benzene ring; conjugation reduces nucleophilic addition reactivity.

20. Identify A and B in each of the following reaction sequences:



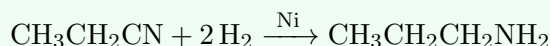
[2 marks]

Solution:

Concept:

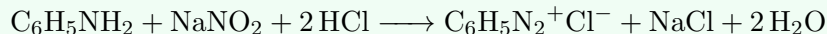
- Alkyl halides react with NaCN by substitution to give nitriles. Hydrogenation of a nitrile converts $-\text{C}\equiv\text{N}$ into $-\text{CH}_2\text{NH}_2$, retaining the nitrile carbon.
- Aniline undergoes diazotisation with NaNO_2/HCl at $0-5^\circ\text{C}$. The resulting diazonium salt couples with aniline predominantly at the para position to form an azo compound.

Step 1: Identify the compounds in sequence (a) Cyanide replaces chlorine in chloroethane, forming propanenitrile. Reduction then gives propan-1-amine:

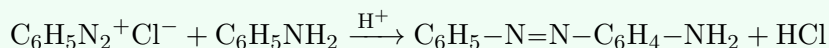


Therefore A is $\text{CH}_3\text{CH}_2\text{CN}$ and B is $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$. The product contains three carbon atoms because the carbon of cyanide is incorporated into the chain.

Step 2: Identify the compounds in sequence (b) Cold diazotisation gives benzenediazonium chloride, A:



This salt undergoes azo coupling with aniline in the indicated acidic medium:



In B, the $-\text{NH}_2$ group is para to the azo linkage on the second ring. Thus B is p-aminoazobenzene, also called 4-aminoazobenzene.

Step 3: Conclusion (a) A: propanenitrile; B: propan-1-amine. (b) A: benzenediazonium chloride; B: p-aminoazobenzene, $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$, with para substitution.

Quick Tip to Solve: Count the extra carbon introduced by NaCN in (a); in (b), retain the azo linkage and place the amino group para to it.

21. Write the reactions involved when D-glucose is treated with the following reagents : (1+1=2)

(a) HCN

(b) Br₂ water

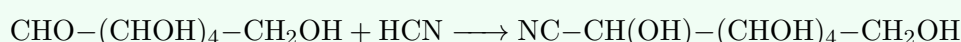
[2 marks]

Solution:

Concept:

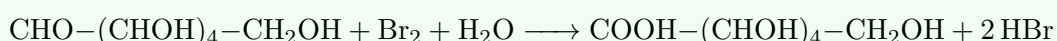
- The open-chain form of D-glucose is CHO-(CHOH)₄-CH₂OH. Its aldehyde group undergoes nucleophilic addition and mild oxidation.
- Hydrogen cyanide adds across the carbonyl group to form a cyanohydrin. Bromine water oxidises the aldehyde group to a carboxylic acid without oxidising the terminal primary alcohol group.

Step 1: Write the reaction with HCN Cyanide adds to the carbonyl carbon, and protonation of the oxygen gives glucose cyanohydrin:



The former aldehyde carbon now bears both -OH and -CN. Addition does not remove the terminal -CH₂OH group. This reaction demonstrates the carbonyl group present in the open-chain form of glucose.

Step 2: Write the reaction with bromine water Bromine water is a mild oxidising reagent. It converts the -CHO group into -COOH, producing D-gluconic acid:



The aldehyde end is oxidised, while the other end remains -CH₂OH. The formation of gluconic acid confirms that the carbonyl group in glucose is an aldehyde group, rather than a ketone group.

Step 3: Conclusion D-glucose gives glucose cyanohydrin with HCN and D-gluconic acid with bromine water, as shown by the balanced reactions above.

Quick Tip to Solve: Keep the four middle CHOH units unchanged: HCN changes CHO to CH(OH)CN, whereas bromine water changes only CHO to COOH.

Section C (21 marks)

22. A solution of glucose (molar mass = 180 g mol⁻¹) in water has a boiling point of 100.20 °C. Calculate the freezing point of the same solution. Molal constants for water K_f and K_b are 1.86 K kg mol⁻¹ and 0.512 K kg mol⁻¹ respectively.

[3 marks]

Solution:

Concept:

- Boiling-point elevation is $\Delta T_b = K_b m$, where m is the molality of the solution and K_b is the solvent's ebullioscopic constant.
- Freezing-point depression is $\Delta T_f = K_f m$, where K_f is the cryoscopic constant. Glucose is a

Quick Tip to Solve: For the same non-electrolyte solution, use $\Delta T_f = (K_f/K_b)\Delta T_b$, then subtract the depression from water's freezing point.

non-electrolyte, so the van't Hoff factor is $i = 1$ for both effects.

Step 1: Calculate the boiling-point elevation At the normal pressure implicit in the question, pure water boils at 100.00°C . The solution boils at 100.20°C , so the elevation is

$$\Delta T_b = 100.20 - 100.00 = 0.20 \text{ K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. Use this difference rather than the absolute boiling temperature in the colligative-property formula.

Step 2: Determine the solution molality Substituting into $\Delta T_b = K_b m$ gives

$$m = \frac{\Delta T_b}{K_b} = \frac{0.20 \text{ K}}{0.512 \text{ K kg mol}^{-1}} = 0.390625 \text{ mol kg}^{-1}.$$

The same solution has this molality for calculating its freezing-point depression. The glucose molar mass is not needed because neither its mass nor the solvent mass is required: the boiling-point elevation already determines the molality.

Step 3: Calculate the freezing-point depression and freezing point Use the given $K_f = 1.86 \text{ K kg mol}^{-1}$:

$$\Delta T_f = K_f m = 1.86 \times 0.390625 = 0.7265625 \text{ K}.$$

Since pure water freezes at 0°C , the solution freezes below this temperature:

$$T_f = 0 - 0.7265625 = -0.7265625^\circ\text{C} \simeq -0.73^\circ\text{C}.$$

Step 4: Conclusion The freezing point of the glucose solution is approximately -0.73°C .

Quick Tip to Solve: For the same non-electrolyte solution, use $\Delta T_f = (K_f/K_b)\Delta T_b$, then subtract the depression from water's freezing point.

23. (a) State the following:

(i) Kohlrausch law of independent migration of ions and

(ii) Faraday's first law of electrolysis.

(b) Using E° values of X and Y given below, predict which is better for coating the surface of iron to prevent corrosion and why?

Given $E^\circ_{\text{X}^{2+}/\text{X}} = -2.36 \text{ V}$, $E^\circ_{\text{Y}^{2+}/\text{Y}} = -0.14 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$.

[3 marks]

Solution:

Concept:

- At infinite dilution, ions migrate independently and their individual contributions add to the limiting molar conductivity of an electrolyte.
- Electrolysis transfers charge $Q = It$, where I is current and t is time. The mass deposited is proportional to this charge.

Quick Tip to Solve: Compare the coating's reduction potential with iron's: the more negative metal sacrifices itself even when the coating is scratched.

- A metal with a more negative standard reduction potential oxidises more readily. Such a coating can act as a sacrificial anode and protect iron.

Step 1: State Kohlrausch law for part (a)(i) Kohlrausch law of independent migration of ions states that at infinite dilution, each ion contributes a definite amount to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. Thus,

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ,$$

where λ_+° and λ_-° are limiting ionic molar conductivities and ν_+ , ν_- are the numbers of cations and anions per formula unit.

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

$$m = ZQ = Zit.$$

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

Step 3: Compare the coating metals for part (b) The printed reduction potentials satisfy

$$E_{X^{2+}/X}^\circ = -2.36 \text{ V} < -0.44 \text{ V} = E_{Fe^{2+}/Fe}^\circ.$$

Therefore X is oxidised preferentially and supplies electrons to the iron, which acts as the cathode. X protects iron even if the coating is scratched. In contrast, Y has $E_{Y^{2+}/Y}^\circ = -0.14 \text{ V}$, more positive than iron. If a Y coating is damaged, exposed iron becomes the anode and corrodes preferentially.

Step 4: Conclusion Kohlrausch law gives the sum of independent ionic contributions at infinite dilution; Faraday's first law gives $m = Zit$. X is the better coating metal because it provides sacrificial protection to iron.

Quick Tip to Solve: Compare the coating's reduction potential with iron's: the more negative metal sacrifices itself even when the coating is scratched.

24. A certain reaction is 50% complete in 20 minutes at 300 K and the same reaction is 50% complete in 5 minutes at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $\log 4 = 0.602$]

[3 marks]

Solution:

Concept:

- For a first order reaction, the half-life is $t_{1/2} = 0.693/k$, where k is the rate constant. Reaching 50% completion means one half-life has elapsed.
- The two-temperature Arrhenius equation is $\log(k_2/k_1) = E_a(T_2 - T_1)/(2.303RT_1T_2)$, where E_a is activation energy, R is the gas constant and temperatures are in kelvin.

Step 1: Relate the reaction times to the rate constants The reaction is 50% complete after 20 minutes

Quick Tip to Solve: For two first order half-lives, use $k_2/k_1 = t_{1/2,1}/t_{1/2,2}$; this avoids unnecessary time conversion before applying Arrhenius.

at $T_1 = 300\text{ K}$ and after 5 minutes at $T_2 = 350\text{ K}$. These times are the respective half-lives. Hence,

$$k_1 = \frac{0.693}{20} = 0.03465\text{ min}^{-1}, \quad k_2 = \frac{0.693}{5} = 0.1386\text{ min}^{-1}.$$

Since both times use the same unit, their ratio directly gives

$$\frac{k_2}{k_1} = \frac{20}{5} = 4.$$

Step 2: Rearrange the Arrhenius equation On subtracting the Arrhenius equations at the two temperatures, the pre-exponential factor cancels:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right).$$

Therefore,

$$E_a = \frac{2.303R \log(k_2/k_1) T_1 T_2}{T_2 - T_1}.$$

The logarithm is a common logarithm, so the factor 2.303 must be included.

Step 3: Substitute and calculate the activation energy Using the given $\log 4 = 0.602$ and $R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$,

$$\begin{aligned} E_a &= \frac{2.303 \times 8.314 \times 0.602 \times 300 \times 350}{350 - 300} \\ &= 2.4205 \times 10^4\text{ J mol}^{-1} \\ &\approx 24.2\text{ kJ mol}^{-1}. \end{aligned}$$

The positive value is consistent with the observed increase in rate constant when temperature rises.

Step 4: Conclusion The activation energy of the first order reaction is $E_a \approx 24.2\text{ kJ mol}^{-1}$.

Quick Tip to Solve: For two first order half-lives, use $k_2/k_1 = t_{1/2,1}/t_{1/2,2}$; this avoids unnecessary time conversion before applying Arrhenius.

25. The elements of 3d transition series are given as : (1+1+1=3)

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following :

- Copper has exceptionally positive $E^\circ_{\text{M}^{2+}/\text{M}}$ value, why ?
- Which element is a strong reducing agent in +2 oxidation state and why ?
- Zn^{2+} salts are colourless. Why ?

[3 marks]

Solution:

Concept:

- Standard electrode potentials depend on the balance of atomisation, ionisation and hydration enthalpies in converting a metal to its aqueous ion.
- A reducing agent donates electrons and is itself oxidised. An especially stable electronic configura-

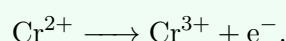
Quick Tip to Solve: For chromium(II), compare d^4 with the d^3 product after oxidation; for zinc(II), a filled d^{10} subshell rules out d-d colour.

tion in the higher oxidation state favours this oxidation.

- Coloured transition-metal ions generally have partially filled d orbitals that permit d–d transitions by absorption of visible light.

Step 1: Explain copper's positive potential in part (a) To convert solid copper into aqueous Cu^{2+} , energy is required for atomisation and for removal of two electrons. Copper has high atomisation enthalpy and high ionisation enthalpies; its second ionisation involves removing an electron from the stable $3d^{10}$ configuration of Cu^+ . The hydration enthalpy released on formation of aqueous Cu^{2+} does not compensate for these high energy requirements. Consequently oxidation of copper to Cu^{2+} is unfavourable relative to the standard hydrogen electrode, giving an exceptionally positive $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$.

Step 2: Identify the strong reducing agent in part (b) Chromium in the +2 oxidation state is a strong reducing agent. The Cr^{2+} ion has a $3d^4$ configuration and readily loses an electron:



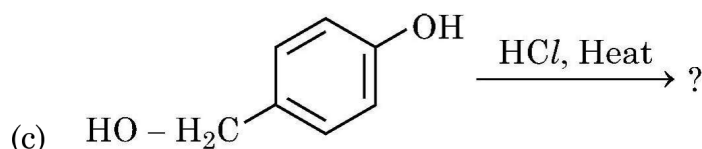
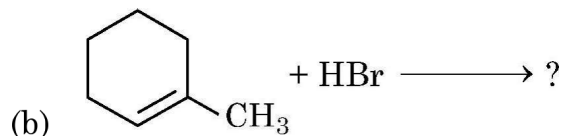
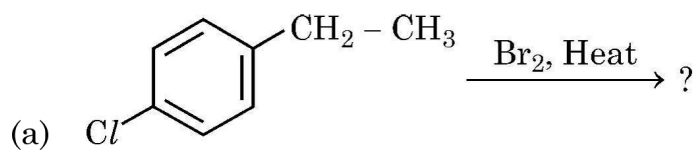
The resulting Cr^{3+} has the more stable $3d^3$ configuration. In an octahedral field this corresponds to the stable t_{2g}^3 arrangement. Thus chromium(II) readily reduces another species while it is oxidised to chromium(III).

Step 3: Explain the colour of zinc salts in part (c) Zinc loses its two 4s electrons to form Zn^{2+} , whose configuration is $[\text{Ar}]3d^{10}$. The d subshell is completely filled, so d–d transitions are not possible. Therefore ordinary Zn^{2+} salts have no colour arising from d–d absorption and are colourless.

Step 4: Conclusion (a) Copper's high atomisation and ionisation enthalpies are not compensated by hydration enthalpy. (b) Cr^{2+} is strongly reducing because it forms stable $3d^3$ Cr^{3+} . (c) Zn^{2+} is $3d^{10}$ and cannot undergo d–d transitions.

Quick Tip to Solve: For chromium(II), compare d^4 with the d^3 product after oxidation; for zinc(II), a filled d^{10} subshell rules out d–d colour.

26(A). Draw the structure of the major monohalo product for each of the following reactions :
(1+1+1=3) [3 marks]

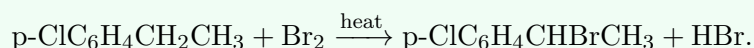


Solution:

Concept:

- Heat initiates free-radical bromination of an alkyl side chain attached to benzene. A benzylic hydrogen is replaced preferentially because the benzylic radical is resonance-stabilised.
- Addition of HBr without peroxide follows Markovnikov's rule: hydrogen attaches to the alkene carbon already bearing more hydrogens, and bromide attaches to the more substituted carbon.
- Hydrogen chloride converts a benzylic alcohol group $-\text{CH}_2\text{OH}$ into $-\text{CH}_2\text{Cl}$. The phenolic $-\text{OH}$ group is retained under these conditions.

Step 1: Brominate the benzylic position in (a) The ethyl side chain contains a benzylic CH_2 group directly attached to the aromatic ring. With Br_2 and heat, replacement occurs at this carbon, rather than on the ring or at the terminal methyl carbon. The chlorine already present on the ring remains in the para position:



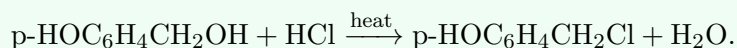
The product is 1-(1-bromoethyl)-4-chlorobenzene. The requested monohalogenation adds one bromine atom to the starting molecule.

Step 2: Apply Markovnikov addition in (b) In 1-methylcyclohexene, the double-bond carbon bearing the methyl group has no hydrogen, whereas the other double-bond carbon bears one hydrogen. Protonation at the latter gives the more stable tertiary carbocation at the methyl-substituted carbon. Bromide attacks this carbocation, giving 1-bromo-1-methylcyclohexane. Thus bromine and the methyl group are attached to the same ring carbon, and the original double bond becomes a single bond.

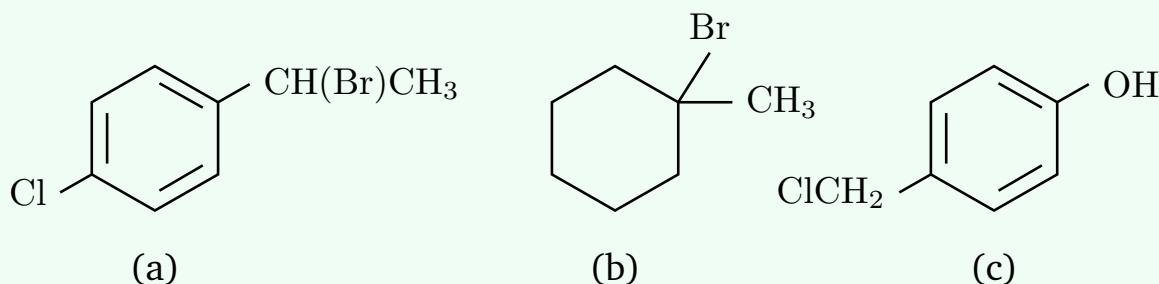
Step 3: Replace the benzylic hydroxyl group in (c) The substrate contains both a phenolic hydroxyl group and a benzylic alcohol group. On treatment with HCl and heat, substitution occurs at the $-\text{CH}_2\text{OH}$ side chain. The phenolic carbon-oxygen bond has partial double-bond character due to

Quick Tip to Solve: First classify the reagent: bromine plus heat targets a benzylic hydrogen, HBr targets the double bond, and HCl replaces the benzylic alcohol group while leaving phenolic OH intact.

resonance and is not replaced by chloride in this reaction:



The product is 4-(chloromethyl)phenol. The three product structures are drawn below.



Structures of the major products in (a), (b) and (c).

Step 4: Conclusion The major products are (a) $p\text{-ClC}_6\text{H}_4\text{CHBrCH}_3$, (b) 1-bromo-1-methylcyclohexane and (c) $p\text{-HOC}_6\text{H}_4\text{CH}_2\text{Cl}$, with the structures shown in the figure.

Quick Tip to Solve: First classify the reagent: bromine plus heat targets a benzylic hydrogen, HBr targets the double bond, and HCl replaces the benzylic alcohol group while leaving phenolic OH intact.

OR

26(B)(a). How do you convert :

Chlorobenzene to biphenyl

[1 mark]

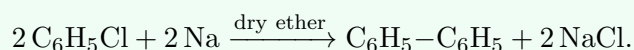
Solution:

Concept:

- The Fittig reaction couples two aryl halide molecules using sodium metal in dry ether.
- Biphenyl contains two benzene rings joined directly by a carbon-carbon single bond; the chlorine atoms must be replaced by this bond.

Step 1: Select the coupling reagent Treat chlorobenzene with sodium metal in dry ether. Use two molecules of the aryl halide so that coupling joins the two phenyl groups. The solvent must be dry because sodium reacts with water.

Step 2: Write the balanced Fittig reaction



Both chlorine atoms are removed as sodium chloride, while the two aromatic rings remain intact and become directly linked.

Step 3: Conclusion Chlorobenzene is converted to biphenyl by the Fittig reaction using sodium in dry ether.

Quick Tip to Solve: For two benzene rings joined directly, choose Fittig coupling of an aryl halide with sodium in dry ether.

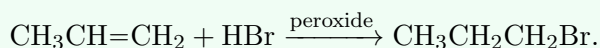
26(B)(b). How do you convert :**Propene to 1-Iodopropane**

[1 mark]

Solution:**Concept:**

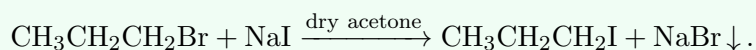
- In the presence of peroxide, addition of HBr to propene follows the anti-Markovnikov rule and forms 1-bromopropane.
- The Finkelstein reaction replaces bromide with iodide using NaI in dry acetone; precipitation of NaBr drives the exchange.

Step 1: Prepare the primary bromoalkane Add hydrogen bromide to propene in the presence of peroxide:



Bromine attaches to the terminal carbon, giving the primary halide required for the next step. Without peroxide, the major product would be 2-bromopropane.

Step 2: Replace bromine with iodine Treat the product with sodium iodide in dry acetone:



Direct addition of HI is unsuitable: the peroxide effect operates with HBr, not HI.

Step 3: Conclusion Propene is converted first to 1-bromopropane with HBr/peroxide, then to 1-iodopropane with NaI in dry acetone.

Quick Tip to Solve: To put iodine at the terminal carbon of propene, first use HBr/peroxide and then exchange Br for I with NaI in dry acetone.

26(B)(c). How do you convert :**2-bromobutane to but-2-ene.**

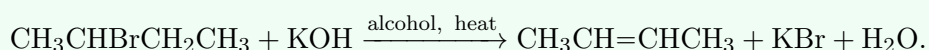
[1 mark]

Solution:**Concept:**

- Heating a haloalkane with alcoholic potassium hydroxide causes beta-elimination: a hydrogen from a neighbouring carbon and the halogen are removed.
- Saytzeff's rule favours the more substituted alkene as the major elimination product.

Step 1: Select elimination conditions Heat 2-bromobutane with alcoholic KOH. The base removes a beta-hydrogen from carbon 3 while bromide leaves carbon 2. A double bond then forms between these two carbons.

Step 2: Write the major-product reaction



But-2-ene is more substituted than but-1-ene and is therefore the major product. Aqueous KOH

Quick Tip to Solve: Use alcoholic KOH and heat for an alkene; apply Saytzeff's rule to choose but-2-ene over but-1-ene.

instead favours substitution to an alcohol.

Step 3: Conclusion Heat 2-bromobutane with alcoholic KOH to obtain but-2-ene as the major elimination product.

Quick Tip to Solve: Use alcoholic KOH and heat for an alkene; apply Saytzeff's rule to choose but-2-ene over but-1-ene.

27(a). Arrange the following compounds in increasing order of their boiling point :

$(\text{CH}_3)_2\text{NH}$, $\text{CH}_3\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{OH}$.

[1 mark]

Solution:

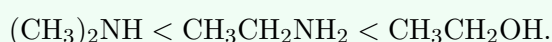
Concept:

- For compounds of similar molar mass, stronger intermolecular hydrogen bonding generally gives a higher boiling point.
- Primary amines form more extensive hydrogen-bonded associations than comparable secondary amines; alcohols form stronger hydrogen bonds because oxygen is more electronegative than nitrogen.

Step 1: Compare the two amines Ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, is a primary amine with two N–H bonds. Dimethylamine, $(\text{CH}_3)_2\text{NH}$, is secondary and has only one N–H bond. Their molar masses are equal, so the more extensive intermolecular hydrogen bonding of ethylamine places its boiling point above that of dimethylamine.

Step 2: Place ethanol above the amines Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, has a comparable molar mass but its O–H bond is more polar. Its intermolecular hydrogen bonds are stronger than those involving N–H in these amines, so it has the highest boiling point.

Step 3: Conclusion The increasing order of boiling point is



Quick Tip to Solve: With similar molecular masses, compare hydrogen bonding first: secondary amine below primary amine, then place ethanol above both.

27(b). Give plausible explanation for each of the following :

(i) Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis.

(ii) Amides are less basic than amines.

[2 marks]

Solution:

Concept:

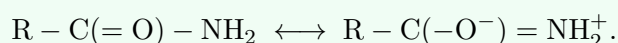
- Gabriel phthalimide synthesis introduces an alkyl group by nucleophilic substitution of an alkyl halide with the phthalimide anion, followed by hydrolysis to give a primary amine.

Quick Tip to Solve: For Gabriel synthesis, check whether the halide is alkyl or aryl; for amide basicity, locate the nitrogen lone pair next to the carbonyl group.

- A nitrogen base accepts a proton using its lone pair. Delocalisation of that lone pair makes it less available for protonation.

Step 1: Explain the limitation for aromatic primary amines To prepare an aromatic primary amine such as aniline by this route, the phthalimide anion would have to displace halide from an aryl halide. Aryl halides do not undergo the required nucleophilic substitution under the conditions of Gabriel synthesis. Their carbon-halogen bond has partial double-bond character through resonance, and the halogen is bonded to an sp^2 -hybridised carbon. Consequently, the required N-aryl phthalimide is not formed by this method.

Step 2: Compare the nitrogen lone pairs in amides and amines In an amide, the nitrogen lone pair is delocalised into the adjacent carbonyl group:



It is therefore less available to accept a proton. In an ordinary amine, there is no adjacent carbonyl group to produce this delocalisation, so the nitrogen lone pair is more available for protonation. The carbonyl group also withdraws electron density from nitrogen.

Step 3: Conclusion (i) Aryl halides do not undergo the substitution required for Gabriel synthesis, so aromatic primary amines cannot be prepared by it. (ii) Resonance with the carbonyl group reduces the availability of the amide nitrogen lone pair, making amides less basic than amines.

Quick Tip to Solve: For Gabriel synthesis, check whether the halide is alkyl or aryl; for amide basicity, locate the nitrogen lone pair next to the carbonyl group.

28. (a) What is the difference between native protein and denatured protein ? (1+1+1=3)

(b) Which one of the following is a disaccharide ?

Glucose, Lactose, Amylose, Fructose

(c) Which vitamin is responsible for the coagulation of blood ?

[3 marks]

Solution:

Concept:

- A protein's biological activity depends on its characteristic folded structure. Denaturation disrupts this organisation without breaking the peptide bonds of its primary structure.
- A disaccharide yields two monosaccharide units on hydrolysis, whereas a monosaccharide cannot be hydrolysed into simpler carbohydrates.
- Vitamins perform specific physiological functions; vitamin K is associated with normal blood coagulation.

Step 1: (a) Distinguish native and denatured proteins A native protein has its natural, specific three-dimensional conformation and possesses its normal biological activity. A denatured protein has lost this natural conformation and hence its biological activity due to agents such as heat or a change in pH. Denaturation disrupts the secondary and tertiary structures, while the primary sequence of amino acids remains unchanged because peptide bonds are not hydrolysed. For example, heating egg

Quick Tip to Solve: Link denaturation to loss of folding, lactose to glucose plus galactose, and vitamin K to blood clotting.

white denatures its proteins and causes coagulation.

Step 2: (b) Classify the listed carbohydrates Lactose is a disaccharide. On hydrolysis, each lactose molecule gives one molecule of glucose and one molecule of galactose:



Glucose and fructose are monosaccharides, so they do not satisfy the requirement. Amylose is a polysaccharide made of many glucose units, rather than just two monosaccharide units. Thus lactose alone belongs to the requested class among the four substances.

Step 3: (c) Identify the vitamin needed for clotting Vitamin K is responsible for normal coagulation of blood. It is required for the formation of functional clotting proteins, including prothrombin; deficiency can impair normal blood clotting. This function distinguishes it from vitamins associated mainly with other processes, such as vitamin C in collagen formation and vitamin D in calcium metabolism.

Step 4: Conclusion (a) A native protein retains its natural folded structure and biological activity; a denatured protein loses them while retaining its primary structure. (b) Lactose is the disaccharide. (c) Vitamin K is responsible for blood coagulation.

Quick Tip to Solve: Link denaturation to loss of folding, lactose to glucose plus galactose, and vitamin K to blood clotting.

Section D (8 marks)

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

29(a). The rate of a chemical reaction is expressed either in terms of decrease in the concentration of reactants or increase in the concentration of a product per unit time. Rate of the reaction depends upon the nature of reactants, concentration of reactants, temperature, presence of catalyst, surface area of the reactants and presence of light. Rate of reaction is directly related to the concentration of reactant. Rate law states that the rate of reaction depends upon the concentration terms on which the rate of reaction actually depends, as observed experimentally. The sum of powers of the concentration of the reactants in the Rate law expression is called order of reaction while the number of reacting species taking part in an elementary reaction which must collide simultaneously in order to bring about a chemical reaction is called molecularity of the reaction.

Answer the following questions :

(i) What is a rate determining step ? (1+1=2)

(ii) Define complex reaction.

[2 marks]

Solution:

Concept:

- An elementary reaction occurs in a single step. A reaction mechanism lists the elementary steps through which an overall reaction proceeds.

Quick Tip to Solve: Count the steps in the mechanism to identify a complex reaction, and locate its slowest step to identify the rate determining step.

- When one step of a multistep mechanism is much slower than the others, it limits the overall rate and is called the rate determining step.

Step 1: (i) Define the rate determining step The rate determining step is the slowest elementary step in the mechanism of a reaction, which controls the overall reaction rate. The faster steps cannot make the overall conversion proceed faster than this slow step permits. For a simple mechanism $A \rightarrow I$ (slow), followed by $I \rightarrow B$ (fast), formation of the intermediate I limits how rapidly product B can be formed, so the first step is rate determining.

Step 2: (ii) Define a complex reaction A complex reaction is a reaction that proceeds through two or more elementary steps rather than a single elementary event. Its overall chemical equation is obtained by adding the equations of these steps and cancelling any intermediates. In the example above, the overall conversion is $A \rightarrow B$, but it occurs through intermediate I . Thus a simple-looking overall equation does not by itself establish that the reaction is elementary; the actual mechanism determines this classification.

Step 3: Conclusion (i) The slowest elementary step that controls the overall reaction rate is the rate determining step. (ii) A complex reaction takes place through a sequence of two or more elementary steps.

Quick Tip to Solve: Count the steps in the mechanism to identify a complex reaction, and locate its slowest step to identify the rate determining step.

29(b). What is the effect of temperature on the rate constant of a reaction ? (1)

[1 mark]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- For ordinary reactions with positive activation energy, increasing temperature increases the fraction of molecules able to cross the activation-energy barrier.

Step 1: Apply the Arrhenius relation On increasing T , the exponent $-E_a/(RT)$ becomes less negative, assuming A and E_a remain approximately constant over the temperature interval. Consequently, the exponential factor and the rate constant increase.

Step 2: State the usual temperature effect For many reactions, the rate constant becomes approximately twice its value for every 10 K rise in temperature. This is a useful empirical estimate, while the Arrhenius equation gives the quantitative dependence for a specified activation energy.

Step 3: Conclusion The rate constant generally increases with temperature, often approximately doubling for a 10 K rise.

Quick Tip to Solve: In the Arrhenius exponent, a larger absolute temperature makes the negative exponent smaller in magnitude, so k increases.

29(b). Why is molecularity applicable only for elementary reactions whereas order is applicable for elementary as well as complex reactions ? (1) [1 mark]

Solution:

Concept:

- Molecularity counts the reacting species participating simultaneously in a single elementary step; it is a positive integer.
- Order is the sum of the powers of concentration terms in an experimentally determined rate law, for example $n = x + y$ in $r = k[A]^x[B]^y$.

Step 1: Explain why molecularity requires an elementary step An elementary reaction is a single event, so the number of species participating in that event is well defined. A complex reaction consists of several elementary steps with their own molecularities; its overall equation does not represent one simultaneous collision. Therefore, a single molecularity cannot be assigned to the overall complex reaction.

Step 2: Explain the wider applicability of order The rate law is established experimentally from how the reaction rate changes with concentration. This can be done for both an elementary reaction and the overall course of a complex reaction, so order is applicable to both. Order is determined by the measured rate law rather than by counting species in the overall balanced equation.

Step 3: Conclusion Molecularity applies only to a single elementary event, whereas order is an experimentally determined property of the rate law and thus applies to elementary as well as complex reactions.

Quick Tip to Solve: Associate molecularity with one elementary collision and order with the experimentally measured concentration powers.

29(c). The conversion of molecule X to Y follows second order kinetics. If concentration of X is increased 3 times, how will it affect the rate of formation of Y ? (1) [1 mark]

Solution:

Concept:

- For a second-order conversion of X into Y, the rate law is $r = k[X]^2$, where [X] is the reactant concentration and k is the rate constant.
- At unchanged temperature, k remains constant; the concentration multiplier is raised to the order of the reaction to obtain the rate multiplier.

Step 1: Write the original rate If the original concentration of X is C , the initial rate of formation of Y is $r_1 = kC^2$. The second-order dependence, rather than a direct proportionality, must be used.

Step 2: Substitute the increased concentration After the concentration becomes $3C$, the new rate is

$$r_2 = k(3C)^2 = 9kC^2, \quad \frac{r_2}{r_1} = \frac{9kC^2}{kC^2} = 9.$$

Quick Tip to Solve: For a concentration change by a factor of three in a second-order reaction, square the factor: $3^2 = 9$.

The factor of three is squared because the reaction is second order in X .

Step 3: Conclusion The rate of formation of Y becomes 9 times its original value at the same temperature.

Quick Tip to Solve: For a concentration change by a factor of three in a second-order reaction, square the factor: $3^2 = 9$.

30(a). Phenols undergo electrophilic substitution reactions readily due to the strong activating effect of OH group attached to the benzene ring. Since, the OH group increases the electron density more to o- and p- positions therefore OH group is ortho, para-directing. Reimer-Tiemann reaction is one of the examples of aldehyde group being introduced on the aromatic ring of phenol, ortho to the hydroxyl group. This is a general method used for the ortho-formylation of phenols.

Answer the following questions :

What happens when phenol reacts with

(i) Br_2/CS_2

(ii) Conc. HNO_3

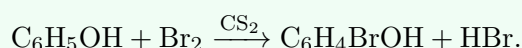
[2 marks]

Solution:

Concept:

- The hydroxyl group donates an oxygen lone pair into the benzene ring by resonance. It activates the ring towards electrophilic substitution and directs substitution to the ortho and para positions.
- Bromination in a non-polar solvent such as CS_2 gives monobromination; concentrated nitric acid introduces nitro groups at both ortho positions and the para position.

Step 1: (i) Reaction with bromine in carbon disulphide In CS_2 , phenol forms a mixture of 2-bromophenol and 4-bromophenol, with 4-bromophenol as the major product because substitution at the para position experiences less steric hindrance. For either positional isomer the balanced reaction is



These conditions give monobromophenols; bromine water instead produces 2,4,6-tribromophenol.

Step 2: (ii) Reaction with concentrated nitric acid Concentrated HNO_3 nitrates the activated ring at positions 2, 4 and 6 relative to the hydroxyl group. The product is 2,4,6-trinitrophenol, commonly called picric acid:



Dilute nitric acid would instead give a mixture of ortho- and para-nitrophenol, so the stated concentration is crucial.

Step 3: Conclusion Br_2/CS_2 gives 2-bromophenol and 4-bromophenol (para major); concentrated HNO_3 gives 2,4,6-trinitrophenol (picric acid).

Quick Tip to Solve: Read the medium: Br_2/CS_2 gives monobromination, whereas concentrated nitric acid gives three nitro groups at 2, 4 and 6.

30(b). Why phenol does not undergo protonation readily ? (1)

[1 mark]

Solution:

Concept:

- Protonation at oxygen requires an available lone pair to form a coordinate bond with H^+ . Greater lone-pair availability corresponds to greater basicity.
- In phenol, an oxygen lone pair is conjugated with the benzene ring and participates in resonance delocalisation.

Step 1: Identify the effect of conjugation The oxygen atom in phenol is directly attached to an aromatic carbon. Its lone pair overlaps with the ring's π -electron system and contributes to resonance structures with increased electron density at the ortho and para ring positions.

Step 2: Relate electron availability to protonation Because the oxygen lone pair is delocalised into the ring, it is less available for donation to H^+ . Thus phenol is a weaker oxygen base than an alcohol, whose oxygen lone pair is not conjugated with an aromatic ring. Protonation is correspondingly less favourable under comparable conditions.

Step 3: Conclusion Phenol does not undergo protonation readily because the oxygen lone pair is involved in resonance with the benzene ring and is less available to bind H^+ .

Quick Tip to Solve: For protonation, focus on the availability of oxygen's lone pair: conjugation with the benzene ring reduces phenol's basicity.

30(c). Which is a stronger acid - phenol or cresol ? Give reason. (1)

[1 mark]

Solution:

Concept:

- Acid strength depends on how readily the compound loses H^+ and on the stability of the resulting conjugate base.
- Cresol is methylphenol. Its methyl group has an electron-releasing inductive ($+I$) effect, unlike the hydrogen at the corresponding position in phenol.

Step 1: Compare the conjugate bases Loss of the hydroxyl proton gives phenoxide from phenol and methyl-substituted phenoxide (cresoxide) from cresol. Both anions delocalise the negative charge through resonance, so the additional substituent must be considered when comparing their stability.

Step 2: Apply the effect of the methyl group The methyl group in cresol releases electron density into the aromatic system. Its $+I$ effect increases electron density in the conjugate base and makes accommodation of the negative charge less favourable relative to phenoxide. Hence cresol loses its hydroxyl proton less readily than phenol.

Step 3: Conclusion Phenol is the stronger acid. The electron-releasing $+I$ effect of the methyl group in cresol destabilises its conjugate base relative to phenoxide and reduces acidity.

Quick Tip to Solve: Compare conjugate-base stability: adding an electron-releasing methyl group to phenol reduces its acidity.

30(c). Write the IUPAC name of the product formed in the Reimer-Tiemann reaction. (1)

[1 mark]

Solution:

Concept:

- The Reimer-Tiemann reaction introduces a formyl group, $-\text{CHO}$, into the phenol ring, mainly at the ortho position relative to $-\text{OH}$.
- In IUPAC naming, the aldehyde has priority over the hydroxyl group. The parent is benzaldehyde and the hydroxyl group is named as a hydroxy substituent.

Step 1: Identify the principal product Phenol reacts with chloroform and aqueous alkali, followed by acidification, to give chiefly the ortho-formylated product. Its condensed structure is $o\text{-HOC}_6\text{H}_4\text{CHO}$; the common name is salicylaldehyde.

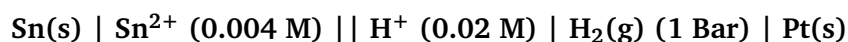
Step 2: Assign the IUPAC locant Take benzaldehyde as the parent and count the ring carbon bearing the aldehyde group as position 1. The hydroxyl group is on the adjacent carbon, position 2. Therefore use the substituent prefix 2-hydroxy before the parent name benzaldehyde.

Step 3: Conclusion The IUPAC name is 2-hydroxybenzaldehyde. Its common name is salicylaldehyde.

Quick Tip to Solve: Give the aldehyde naming priority: call the ortho hydroxyl group 2-hydroxy and retain benzaldehyde as the parent.

Section E (15 marks)

31(A)(a). Write the cell reaction and calculate the e.m.f. of the following cell at 298 K :



(Given : $E^\circ_{\text{Sn}^{2+}/\text{Sn}} = -0.14 \text{ V}$, $E^\circ_{\text{H}^+|\text{H}_2(\text{g}), \text{Pt}} = 0.00 \text{ V}$)

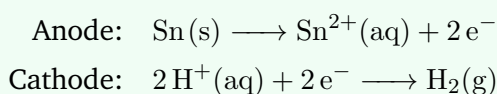
[3 marks]

Solution:

Concept:

- In cell notation the left electrode is the anode and the right electrode is the cathode. Oxidation supplies the electrons consumed by reduction.
- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n) \log Q$, where n is the number of electrons exchanged and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Write the electrode reactions Tin is oxidised at the left electrode and hydrogen ions are reduced at the platinum electrode. Platinum only provides a conducting surface.



Quick Tip to Solve: Square the hydrogen-ion concentration in Q : the balanced reaction consumes two hydrogen ions, while the hydrogen pressure factor is unity here.

Adding these reactions cancels two electrons, so $n = 2$.

Step 2: Evaluate the standard potential and reaction quotient The potential difference and quotient for this reaction are

$$E_{\text{cell}}^{\circ} = 0.00 - (-0.14) = 0.14 \text{ V.}$$
$$Q = \frac{[\text{Sn}^{2+}](p_{\text{H}_2}/p^{\circ})}{[\text{H}^+]^2} = \frac{0.004 \times 1}{(0.02)^2} = 10.$$

The concentration terms are understood relative to their standard concentration. The gas pressure is 1 bar, equal to the standard pressure, so its factor is unity. The coefficient 2 of hydrogen ions makes their concentration squared.

Step 3: Substitute in the Nernst equation Since $\log 10 = 1$,

$$E_{\text{cell}} = 0.14 - \frac{0.0591}{2} \log 10$$
$$= 0.14 - 0.02955 = 0.11045 \text{ V.}$$

The positive potential is consistent with oxidation of tin and reduction of hydrogen ions in the stated direction. Because $Q > 1$, the non-standard potential is lower than the standard value.

Step 4: Conclusion The cell reaction is $\text{Sn(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Sn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$, and its e.m.f. at 298 K is $E_{\text{cell}} \approx 0.110 \text{ V}$.

Quick Tip to Solve: Square the hydrogen-ion concentration in Q : the balanced reaction consumes two hydrogen ions, while the hydrogen pressure factor is unity here.

31(A)(b). Account for the following :

(i) On the basis of E° values, O_2 gas should be liberated at anode but it is Cl_2 gas which is liberated in the electrolysis of aqueous NaCl .

(ii) Conductivity of CH_3COOH decreases on dilution.

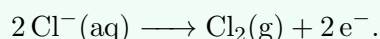
[2 marks]

Solution:

Concept:

- Electrolysis products depend on the electrode potentials and the extra potential needed to overcome kinetic barriers, called overpotential or overvoltage.
- Conductivity κ measures conductance for a specified geometry and depends on the number of mobile ions per unit volume. Molar conductivity is $\Lambda_m = 1000\kappa/c$, with c in mol L^{-1} .

Step 1: Explain chlorine liberation at the anode From standard potentials, oxidation of water to oxygen is thermodynamically preferred over oxidation of chloride ions. However, oxygen evolution has a substantial overpotential at the anode. This raises the practical potential needed for oxygen liberation, allowing chloride ions to discharge and form chlorine during electrolysis of aqueous sodium chloride:

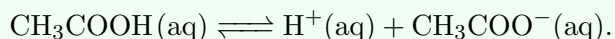


Thus the actual electrode process cannot be predicted from standard potentials alone; the kinetic

Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole; a weak electrolyte can show opposite trends for these quantities.

barrier for oxygen evolution must also be considered.

Step 2: Explain the effect of dilution on conductivity Acetic acid is a weak electrolyte:



Dilution increases its degree of ionisation, but the larger volume reduces the number of ions per unit volume. For this acid, the reduction in ionic concentration predominates, so its conductivity κ decreases. This should be distinguished from molar conductivity, which increases because a greater fraction of each mole becomes ionised on dilution.

Step 3: Conclusion (i) Chlorine is liberated because oxygen evolution requires a high overpotential. (ii) The conductivity of CH_3COOH falls on dilution because the number of ions per unit volume decreases, although its molar conductivity rises.

Quick Tip to Solve: For dilution questions, distinguish conductivity per unit volume from molar conductivity per mole; a weak electrolyte can show opposite trends for these quantities.

OR

31(B)(a). Write the anode and cathode reactions and the overall cell reaction occurring in a lead storage battery during its use. [2 marks]

Solution:

Concept:

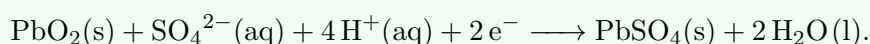
- During discharge, a lead storage battery acts as a galvanic cell: oxidation occurs at the lead anode and reduction at the lead dioxide cathode in sulphuric acid electrolyte.
- Both electrodes form PbSO_4 . Half-reactions must balance atoms and charge before they are added, and the electrons must cancel in the overall equation.

Step 1: Write the anode reaction during discharge Lead metal loses two electrons and its oxidation state changes from 0 to +2. The resulting lead(II) combines with sulphate ions to form lead sulphate on the anode:

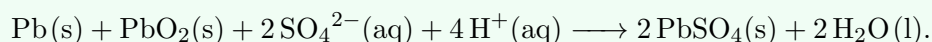


The electrons are released to the external circuit. The total charge on each side is -2 , so the half-reaction is charge-balanced.

Step 2: Write the cathode reaction and add the half-reactions Lead in lead dioxide changes from +4 to +2 by accepting two electrons. Hydrogen ions convert its oxygen atoms into water, while sulphate forms lead sulphate:



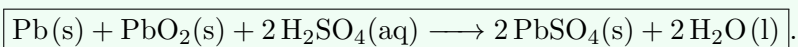
Adding the two half-reactions cancels the two electrons:



Quick Tip to Solve: For discharge, remember that both plates become lead sulphate: lead is oxidised, lead dioxide is reduced, and sulphuric acid is consumed.

Combining the sulphate and hydrogen ions as sulphuric acid gives the conventional overall cell reaction. Acid is consumed during discharge, so its concentration decreases.

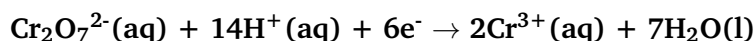
Step 3: Conclusion During use, the anode and cathode reactions are the oxidation and reduction reactions written above. The overall cell reaction is



Quick Tip to Solve: For discharge, remember that both plates become lead sulphate: lead is oxidised, lead dioxide is reduced, and sulphuric acid is consumed.

31(B)(b). Calculate the potential for half-cell containing 0.01 M $\text{K}_2\text{Cr}_2\text{O}_7\text{(aq)}$, 0.01 M $\text{Cr}^{3+}\text{(aq)}$ and 1.0×10^{-4} M $\text{H}^+\text{(aq)}$.

The half cell reaction is



and the standard electrode potential is given as $E^\circ = 1.33$ V.

[Given : $\log 10 = 1$]

[3 marks]

Solution:

Concept:

- The Nernst equation for a reduction half-cell at 298 K is $E = E^\circ - (0.0591/n) \log Q$, where E° is the standard reduction potential and n is the number of electrons accepted.
- In the reaction quotient, products enter the numerator and reactants the denominator, with powers equal to their balanced coefficients. Electrons are omitted and pure liquid water has unit activity.
- For $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$, $n = 6$ and $Q = [\text{Cr}^{3+}]^2 / ([\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14})$, using standard-state concentration ratios.

Step 1: Identify the concentrations and electron transfer Each formula unit of dissolved $\text{K}_2\text{Cr}_2\text{O}_7$ supplies one dichromate ion. Therefore $[\text{Cr}_2\text{O}_7^{2-}] = 0.01 \text{ mol L}^{-1}$. The other given concentrations are $[\text{Cr}^{3+}] = 0.01 \text{ mol L}^{-1}$ and $[\text{H}^+] = 10^{-4} \text{ mol L}^{-1}$. The printed half-reaction accepts six electrons, so use $n = 6$, not the coefficient 2 of chromium(III).

Step 2: Calculate the reaction quotient Substitute the concentrations with the stoichiometric powers:

$$\begin{aligned} Q &= \frac{(0.01)^2}{0.01 (10^{-4})^{14}} \\ &= \frac{10^{-4}}{10^{-2} \times 10^{-56}} \\ &= 10^{54}. \end{aligned}$$

Hence $\log Q = 54 \log 10 = 54$. The high power of the hydrogen-ion concentration makes the quotient very large in this weakly acidic solution.

Quick Tip to Solve: For dichromate reduction, write the hydrogen-ion term to the fourteenth power before taking logarithms; six electrons determine the Nernst denominator.

Step 3: Evaluate the half-cell potential Apply the Nernst equation using the standard potential 1.33 V:

$$E = 1.33 - \frac{0.0591}{6} \times 54$$
$$= 1.33 - 0.5319 = 0.7981 \text{ V.}$$

This is the reduction potential of the stated half-cell relative to the standard hydrogen electrode. Its decrease from E° is consistent with the very low concentration of hydrogen ions, a reactant in the reduction.

Step 4: Conclusion The half-cell reduction potential is $E = 0.7981 \text{ V} \approx 0.80 \text{ V}$ at 298 K.

Quick Tip to Solve: For dichromate reduction, write the hydrogen-ion term to the fourteenth power before taking logarithms; six electrons determine the Nernst denominator.

32(A). Answer the following :

- (a) Low spin tetrahedral complexes are not known.
- (b) Co^{2+} is easily oxidised to Co^{3+} in the presence of a strong ligand. [At. No. of Co = 27]
- (c) What type of isomerism is shown by the complex $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$?
- (d) Why a solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green while a solution of $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless. (At. No. of Ni = 28)
- (e) Write the IUPAC name of the following complex : $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$ [5 marks]

Solution:

Concept:

- Crystal-field splitting separates the five metal d orbitals into groups of different energies. Electrons pair only when the splitting energy Δ exceeds the pairing energy P .
- Strong-field ligands produce large splitting and can stabilise a low-spin configuration. The oxidation state and the atomic number determine the metal ion's d -electron count.
- Coordination isomerism occurs when both the cation and anion are complex ions and ligands can be interchanged between their metal centres.
- A complex appears coloured when it absorbs visible light. In naming a complex, name its ligands before the central metal and indicate the metal oxidation state in Roman numerals.

Step 1: (a) Compare tetrahedral splitting with pairing energy In a tetrahedral ligand field the splitting Δ_t is much smaller than the octahedral splitting for the same metal ion and ligands:

$$\Delta_t = \frac{4}{9} \Delta_o.$$

For ordinary tetrahedral complexes, $\Delta_t < P$. An electron therefore occupies a higher-energy orbital singly rather than pairing in a lower-energy orbital. The tetrahedral arrangement consequently gives the high-spin configuration; the splitting is insufficient to produce a low-spin tetrahedral complex.

Step 2: (b) Explain the stabilisation of cobalt(III) Cobalt has atomic number 27, so its atom has

Quick Tip to Solve: First find the metal oxidation state and its d -electron count; then compare splitting with pairing energy. For the final name, use the outside chloride to fix the complex charge before naming the neutral ammine and anionic carbonato ligands.

configuration $[\text{Ar}]3d^74s^2$. Removing the $4s$ electrons first gives Co^{2+} as $3d^7$, whereas Co^{3+} is $3d^6$. In an octahedral strong-ligand field, the cobalt(III) ion adopts the low-spin configuration $t_{2g}^6e_g^0$. All six electrons occupy the lower t_{2g} set, giving substantial crystal-field stabilisation and an especially stable complex. The corresponding low-spin cobalt(II) configuration is $t_{2g}^6e_g^1$, with one electron in the higher set. Strong ligands therefore preferentially stabilise cobalt(III), making oxidation of cobalt(II) to cobalt(III) easier.

Step 3: (c) Identify the isomerism and give the partner The salt $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$ contains the complex cation $[\text{Co}(\text{NH}_3)_6]^{3+}$ and the complex anion $[\text{Cr}(\text{CN})_6]^{3-}$. Interchanging the ammine and cyanido ligands between the two metal ions gives $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$. The composition stays the same, while the allocation of ligands to the cationic and anionic complexes changes. This is coordination isomerism.

Step 4: (d) Relate nickel's colour to the ligand field Nickel has atomic number 28. The ion Ni^{2+} has the $3d^8$ configuration. Water is a weak-field ligand, and $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is an octahedral complex with configuration $t_{2g}^6e_g^2$ and two unpaired electrons. Its ligand-field energy gaps permit absorption of visible light through $d-d$ transitions, and the transmitted light gives the solution its green colour. Cyanide is a strong-field ligand. It causes pairing and forms the square-planar dsp^2 complex $[\text{Ni}(\text{CN})_4]^{2-}$, which has no unpaired electrons and is diamagnetic. Its stronger splitting shifts the relevant absorption outside the visible region, so it appears colourless. The absence of visible absorption is the reason for the colour difference; electron pairing by itself is not a universal test for colourlessness.

Step 5: (e) Determine the oxidation state and name the salt In $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$, the chloride ion outside the coordination sphere has charge -1 ; hence the complex cation has charge $+1$. Each ammine ligand is neutral and the carbonate ligand has charge -2 . If cobalt's oxidation state is x , then

$$x + 5(0) - 2 = +1 \quad \Rightarrow \quad x = +3.$$

Name the ligands alphabetically, ignoring the multiplying prefix: ammine precedes carbonate. Five ammine ligands give pentaammine, and the positively charged complex uses the metal name cobalt. The counter-ion is named last.

Step 6: Conclusion (a) Tetrahedral splitting is smaller than pairing energy, so tetrahedral complexes are high spin. (b) Strong ligands stabilise low-spin d^6 cobalt(III) and facilitate oxidation of cobalt(II). (c) The salt shows coordination isomerism. (d) The aqua complex absorbs visible light and is green; the square-planar cyanido complex does not absorb visibly and is colourless. (e) The name is pentaamminecarbonatocobalt(III) chloride.

Quick Tip to Solve: First find the metal oxidation state and its d -electron count; then compare splitting with pairing energy. For the final name, use the outside chloride to fix the complex charge before naming the neutral ammine and anionic carbonate ligands.

32(B). (a) What is meant by 'Chelate effect'? Give an example. ($2 + 2 + 1 = 5$)

(b) Write the hybridization and magnetic behaviour of $[\text{Fe}(\text{CN})_6]^{4-}$. (Atomic number: Fe = 26)

(c) If $\text{PtCl}_2 \cdot 2\text{NH}_3$ does not react with AgNO_3 , what will be its formula?

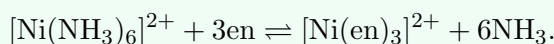
[5 marks]

Solution:

Concept:

- A chelating ligand uses two or more donor atoms to coordinate to the same metal ion, producing one or more rings. Such complexes generally have greater stability than analogous complexes of comparable monodentate ligands.
- For iron, the neutral configuration is $[\text{Ar}]3d^6 4s^2$. Oxidation to Fe^{2+} removes the two $4s$ electrons, giving $3d^6$. Strong-field cyanide produces pairing in an octahedral complex.
- Chloride outside the coordination sphere ionises in water and forms AgCl with silver nitrate. Chloride coordinated inside the sphere does not give this immediate precipitation test.

Step 1: (a) Define and illustrate the chelate effect The chelate effect is the enhanced stability of a complex formed by a multidentate ligand relative to a similar complex formed by monodentate ligands. The ligand attaches through several donor atoms to the same metal, forming chelate rings. For example, ethane-1,2-diamine, abbreviated as en, is a bidentate ligand: both nitrogen atoms donate lone pairs to one metal ion. The complex $[\text{Ni}(\text{en})_3]^{2+}$ contains three such ligands and three five-membered chelate rings. It is more stable than the analogous ammine complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$. The replacement may be represented as



Release of several free ligands contributes favourably to the entropy of this process and hence to chelate stability.

Step 2: (b) Determine the iron ion and its orbital occupation Let the oxidation state of iron be x . Each cyanide ion has charge -1 , so

$$x + 6(-1) = -4 \Rightarrow x = +2.$$

Thus, the metal ion is Fe^{2+} , with configuration $[\text{Ar}]3d^6$. The six cyanide ligands are strong-field ligands. They pair the six $3d$ electrons in three orbitals, leaving two inner $3d$ orbitals vacant. In crystal-field notation the low-spin octahedral occupation is $t_{2g}^6 e_g^0$.

Step 3: (b) Infer hybridisation and magnetic behaviour The two vacant $3d$ orbitals, one $4s$ orbital and three $4p$ orbitals give six $d^2 sp^3$ hybrid orbitals in valence-bond theory. Each accepts a lone pair from a cyanide ligand. Therefore the complex is an inner-orbital octahedral complex. All six d electrons are paired, so the number of unpaired electrons is $n = 0$. Its spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \mu_B = 0$, where μ_B is the Bohr magneton; consequently it is diamagnetic.

Step 4: (c) Place the chlorides inside the coordination sphere The printed composition is $\text{PtCl}_2 \cdot 2\text{NH}_3$. Failure to give AgCl with AgNO_3 shows that there are no freely ionisable chloride counterions. Both chlorides must therefore be coordinated to platinum, together with the two neutral ammonia ligands.

Quick Tip to Solve: In a silver nitrate test, count only chlorides outside square brackets as immediately precipitable; for ferrocyanide, first obtain $\text{Fe}(\text{II})$, then pair its six d electrons because cyanide is strong-field.

The coordination number is four, platinum has oxidation state +2, and the neutral coordination entity is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. This observation establishes the coordination formula but does not distinguish its cis and trans geometrical isomers.

Step 5: Conclusion (a) The chelate effect is the greater stability imparted by multidentate ligands; $[\text{Ni}(\text{en})_3]^{2+}$ is an example. (b) $[\text{Fe}(\text{CN})_6]^{4-}$ has d^2sp^3 hybridisation and is diamagnetic. (c) The formula is $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Quick Tip to Solve: In a silver nitrate test, count only chlorides outside square brackets as immediately precipitable; for ferrocyanide, first obtain $\text{Fe}(\text{II})$, then pair its six d electrons because cyanide is strong-field.

33(A). (a) Carry out the following conversions : (2+3=5)

(i) Ethanal to But-2-enal

(ii) Propanoic acid to ethane

(b) An alkene A with molecular formula C_5H_{10} on ozonolysis gives a mixture of two compounds B and C. Compound B gives positive Fehling test and also reacts with iodine and NaOH solution. Compound C does not give Fehling solution test but forms iodoform. Identify the compounds A, B and C.

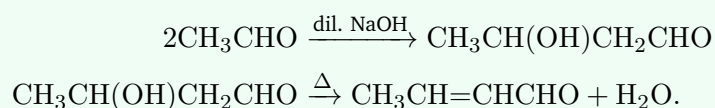
[5 marks]

Solution:

Concept:

- Ethanal contains an alpha hydrogen and undergoes aldol addition with dilute alkali. The beta-hydroxy aldehyde formed loses water on heating to give an alpha,beta-unsaturated aldehyde.
- Heating a sodium carboxylate with soda lime, a mixture of NaOH and CaO , gives an alkane with one carbon atom fewer than the parent carboxylic acid.
- Reductive ozonolysis cleaves the carbon-carbon double bond and converts each double-bond carbon into a carbonyl carbon. Fehling's test is positive for aliphatic aldehydes; the iodoform test is positive for ethanal and methyl ketones, CH_3COR .

Step 1: (a)(i) Convert ethanal into but-2-enal Treat ethanal with dilute sodium hydroxide. Two molecules combine to give 3-hydroxybutanal, the aldol product. On heating, this loses water and forms but-2-enal:

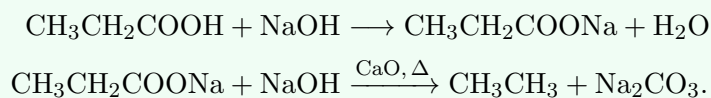


The intermediate is a beta-hydroxy aldehyde because its hydroxyl group lies on the beta carbon relative to $-\text{CHO}$. Dehydration introduces the double bond between carbon 2 and carbon 3 of the four-carbon aldehyde.

Step 2: (a)(ii) Convert propanoic acid into ethane First neutralise propanoic acid with sodium hydroxide to prepare sodium propanoate. Heat the dry salt with soda lime to remove its carboxyl

Quick Tip to Solve: In ozonolysis identification, allocate the five carbons between the two products first: a Fehling-positive iodoform-positive aldehyde uses two as ethanal, leaving three for propanone. Rejoin their carbonyl carbons to recover the double bond.

carbon as sodium carbonate:



Propanoic acid has three carbon atoms and ethane has two; soda-lime decarboxylation gives the required decrease of one carbon atom. Kolbe electrolysis of sodium propanoate would couple ethyl groups to give butane, so it does not achieve this conversion.

Step 3: (b) Identify the two carbonyl products B and C Compound B gives Fehling's test, so it is an aliphatic aldehyde. It also gives the iodoform test with iodine and sodium hydroxide. Ethanal is the aldehyde that satisfies both tests; therefore B is CH_3CHO .

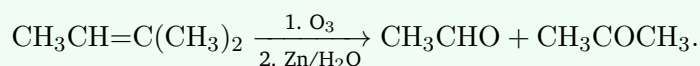


B contains two carbon atoms. Since A contains five carbon atoms, C must contain the remaining three. C gives a negative Fehling's test but a positive iodoform test, identifying it as the methyl ketone propanone, CH_3COCH_3 .



Both positive iodoform tests produce yellow CHI_3 ; propanone lacks an aldehyde group and hence does not reduce Fehling's solution.

Step 4: (b) Reconstruct alkene A and verify its ozonolysis Join the carbonyl carbons of ethanal and propanone with a double bond, removing their oxygen atoms. The ethanal carbon retains one hydrogen and one methyl group; the propanone carbon retains two methyl groups. Hence A is $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2$, or 2-methylbut-2-ene.



The proposed alkene contains five carbons and ten hydrogens, agreeing with C_5H_{10} . Cleavage produces exactly the two compounds with the specified test results.

Step 5: Conclusion (a)(i) Ethanal $\xrightarrow{\text{dil. NaOH}}$ 3-hydroxybutanal $\xrightarrow{\Delta}$ but-2-enal. (a)(ii) Propanoic acid $\xrightarrow{\text{NaOH}}$ sodium propanoate $\xrightarrow{\text{soda lime}, \Delta}$ ethane. (b) A is 2-methylbut-2-ene, B is ethanal, and C is propanone.

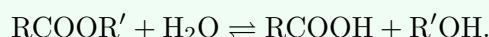
Quick Tip to Solve: In ozonolysis identification, allocate the five carbons between the two products first: a Fehling-positive iodoform-positive aldehyde uses two as ethanal, leaving three for propanone. Rejoin their carbonyl carbons to recover the double bond.

33(B). An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to get a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives But-1-ene. Identify (A), (B) and (C) and write chemical equations for the reactions involved.

[5 marks]

Solution:**Concept:**

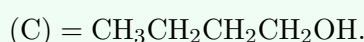
- Acid-catalysed hydrolysis of an ester gives a carboxylic acid and an alcohol:



The acid and alcohol together account for all carbon atoms in the ester.

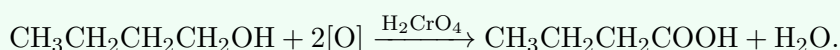
- A primary alcohol is oxidised by chromic acid to the carboxylic acid with the same carbon skeleton. A secondary alcohol instead gives a ketone, so the alcohol here must be primary.
- Dehydration removes water from an alcohol and produces an alkene. The position of the double bond in but-1-ene helps identify the position of the hydroxyl group in the starting alcohol.

Step 1: Identify alcohol (C) But-1-ene has the structure $CH_2=CHCH_2CH_3$. The corresponding primary alcohol, which loses water to give this terminal alkene, is butan-1-ol:



This assignment also satisfies the oxidation clue. Butan-2-ol would give a ketone on oxidation, whereas the question specifies a carboxylic acid. Thus the alcohol is unambiguously a primary four-carbon alcohol.

Step 2: Identify carboxylic acid (B) by oxidation Oxidation converts the terminal $-CH_2OH$ group of butan-1-ol into $-COOH$, without changing the number or arrangement of carbon atoms. Therefore (B) is butanoic acid. With chromic acid as the oxidising agent, the balanced equation is

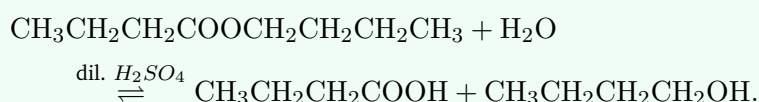


Here $[O]$ denotes oxygen supplied by the oxidising agent; two equivalents are required for complete oxidation of the primary alcohol to the acid.

Step 3: Identify ester (A) and write its hydrolysis The ester must contain the butanoate group from (B) and the butyl group from (C). Hence (A) is butyl butanoate (butan-1-yl butanoate), with structure



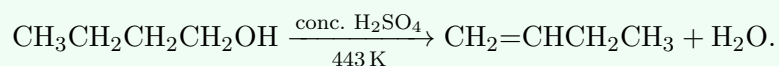
Its molecular formula is $C_8H_{16}O_2$, matching the printed formula. Acid-catalysed hydrolysis gives



The dilute sulphuric acid supplies the acid catalyst for this reversible hydrolysis.

Quick Tip to Solve: Work backwards from but-1-ene to a primary four-carbon alcohol, oxidise it to the four-carbon acid, then combine the acid and alcohol to obtain the eight-carbon ester.

Step 4: Write the dehydration equation Heating butan-1-ol with concentrated sulphuric acid eliminates water between the first two carbon atoms:



The product is but-1-ene, as specified. Hydrolysis, oxidation and dehydration therefore all support the same set of structures.

Step 5: Conclusion (A) is **butyl butanoate**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$; (B) is **butanoic acid**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$; and (C) is **butan-1-ol**, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$.

Quick Tip to Solve: Work backwards from but-1-ene to a primary four-carbon alcohol, oxidise it to the four-carbon acid, then combine the acid and alcohol to obtain the eight-carbon ester.