CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **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 :

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

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

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

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

$\varepsilon_0 = 8.854 \times 10^{-12}$ C^2 N^{-1} m^{-2}

$\frac{1}{4\pi\varepsilon_0} = 9 \times 10^9$ N m^2 C^{-2}

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

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

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

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

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

Section A (16 marks)

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

1. Standard electrode potential for Sn^{4+}/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 couple with the higher standard reduction potential undergoes reduction at the cathode; the other undergoes oxidation at the anode.
- Using reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Electrode potential is an intensive quantity and is not multiplied by stoichiometric coefficients.

Step 1: Identify the two electrodes Since $+0.15\,\text{V} > -0.74\,\text{V}$, tin(IV) is reduced at the cathode and chromium is oxidised at the anode:

$$\text{Sn}^{4+} + 2\text{e}^- \longrightarrow \text{Sn}^{2+},$$
$$\text{Cr} \longrightarrow \text{Cr}^{3+} + 3\text{e}^-.$$

The tabulated chromium value remains a reduction potential when inserted in the subtraction formula.

Step 2: Subtract the standard reduction potentials

$$E^\circ_{\text{cell}} = 0.15 - (-0.74) = +0.89\,\text{V}.$$

Electron balancing does not change either potential. Thus the values $+1.19\,\text{V}$, $+0.18\,\text{V}$ and $+1.83\,\text{V}$ in options (A), (C) and (D) do not equal the required difference and are rejected.

Step 3: Conclusion The standard cell potential is $\boxed{+0.89\,\text{V}}$. Hence, the correct option is (B).

Quick Tip to Solve: Choose the higher reduction potential as the cathode, then subtract the lower value with its sign; never multiply potentials to balance electrons.

2. 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.
- In forming a transition-metal cation, electrons are removed from the outer $4s$ orbital before the $3d$ orbitals.

Step 1: Find the electronic configuration Chromium has atomic number 24 and ground-state configuration $[\mathrm{Ar}]\,3d^5 4s^1$. To form Cr^{3+}, remove one $4s$ electron and two $3d$ electrons. The ion therefore has configuration $[\mathrm{Ar}]\,3d^3$. By Hund's rule, its three d electrons occupy separate orbitals, so $n = 3$.

Step 2: Calculate the spin-only moment Substituting the unpaired-electron count gives

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

The positive square root is approximately 3.87. The values 2.87, 3.47 and 3.57 do not equal $\sqrt{15}$; they cannot result from the three unpaired electrons in this ion.

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 $4s$ electron first from chromium, then count unpaired $3d$ electrons before using $\sqrt{n(n+2)}$.

3. 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 solute particles present, rather than their chemical identity.
- The van't Hoff factor satisfies $i = M_{\text{normal}}/M_{\text{observed}}$, where M denotes molar mass. Association gives $i < 1$.

Step 1: Identify the effect of association During association, two or more solute molecules combine to form a larger unit. For a fixed mass of solute, the number of independently moving particles is therefore smaller than expected for unassociated molecules. The observed colligative effect is consequently reduced.

Step 2: Relate particle count to apparent molar mass A colligative-property calculation that assumes no association interprets the reduced particle count as fewer moles in the given mass. Thus

$$M_{\text{observed}} = \frac{M_{\text{normal}}}{i} > M_{\text{normal}} \quad (i < 1).$$

A decrease instead corresponds to dissociation. An unchanged value corresponds to no net change in particle number; an initial increase followed by a decrease is not the consequence of association stated here.

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

Quick Tip to Solve: Association means fewer particles: a smaller colligative effect gives a larger calculated molar mass.

4. 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:

- An S_N2 reaction is a bimolecular nucleophilic substitution with rate k[alkyl halide][nucleophile].

Quick Tip to Solve: Pair S_N2 with backside attack and inversion; a free planar carbocation belongs to S_N1.

- Bond formation and bond breaking occur together in a single concerted step, with backside attack at the carbon bearing the leaving group.

Step 1: Identify the direction of nucleophilic attack The nucleophile approaches the carbon from the side opposite the carbon-halogen bond. As the new bond forms, the halide leaves through the same transition state. The three remaining groups around carbon turn over like an umbrella in the wind. At a stereogenic carbon this reverses the spatial configuration.

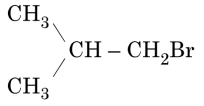
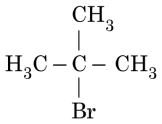
Step 2: Eliminate the alternative mechanisms Retention would preserve the original arrangement and is inconsistent with a single backside displacement. A racemic mixture is associated with attack on both faces of a planar intermediate, whereas an S_N2 reaction has a preferred backside approach. No free carbocation forms, so the carbocation option describes an S_N1 feature instead.

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

Quick Tip to Solve: Pair S_N2 with backside attack and inversion; a free planar carbocation belongs to S_N1.

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

The correct order is [1 mark]

(i)  (ii) $CH_3CH_2CH_2CH_2Br$ (iii) 

(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 usually lowers the boiling point.
- Branching makes molecules more compact, reducing surface contact and weakening intermolecular London dispersion attractions.

Step 1: Identify the three carbon skeletons Compound (i) is $(CH_3)_2CHCH_2Br$, a branched primary bromide (isobutyl bromide). Compound (ii) is $CH_3CH_2CH_2CH_2Br$, the straight-chain isomer (1-bromobutane). Compound (iii) is $(CH_3)_3CBr$, the compact tertiary isomer (tert-butyl bromide). All have molecular formula C_4H_9Br, so their molar masses are equal.

Step 2: Compare intermolecular contact The straight-chain molecule (ii) offers the greatest surface contact and requires the most energy to separate its molecules. The compact molecule (iii) offers the least contact; (i) lies between them. Thus any order placing (iii) highest, as in (A) and (B), reverses

Quick Tip to Solve: First verify that the bromides are isomers, then place the most compact structure lowest and the straight chain highest.

the branching effect. Option (D) incorrectly places the branched isomer (i) above the straight-chain isomer (ii).

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

Quick Tip to Solve: First verify that the bromides are isomers, then place the most compact structure lowest and the straight chain highest.

6. The correct IUPAC name of $[Pt(NH_3)_2Cl_2]^{2+}$ is [1 mark]

(A) Diamminedichloridoplatinum(II)

(B) Diamminedichloridoplatinum(IV)

(C) Diamminedichloridoplatinum(O)

(D) Diamminedichloridoplatinate(IV)

Correct Answer: (B) Diamminedichloridoplatinum(IV)

Solution:

Concept:

- The oxidation state of the central metal plus the charges on all ligands equals the net charge on the complex ion.
- Ligands are named alphabetically, ignoring multiplicative prefixes. A cationic complex retains the metal name; an anionic complex uses the ending "ate".

Step 1: Determine the oxidation state of platinum In $[Pt(NH_3)_2Cl_2]^{2+}$, each ammine ligand NH_3 is neutral and each chlorido ligand Cl^- carries charge -1. If platinum has oxidation state x, then

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

Thus the metal numeral must be IV. The numerals II and zero in options (A) and (C) do not reproduce the printed charge.

Step 2: Assemble the coordination name Two NH_3 ligands give "diammine" and two Cl^- ligands give "dichlorido". Ammine precedes chlorido alphabetically. Since the coordination entity is positively charged, use "platinum", not "platinate"; the latter in option (D) is reserved for an anionic platinum complex.

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

Quick Tip to Solve: Use the outer $2+$ charge when finding platinum's oxidation state; neutral NH_3 contributes no charge.

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

(A) C_3H_7COOH

(B) C_2H_5COOH

(C) CH_3COOH

(D) C_3H_7OH

Correct Answer: (A) C_3H_7COOH

Solution:

Concept:

- A Grignard reagent RMgBr reacts with CO_2 to form a magnesium carboxylate, which gives a carboxylic acid on acid hydrolysis.
- The carbon of CO_2 becomes the carboxyl carbon, so the acid contains one more carbon atom than the alkyl group R.

Step 1: Add the propyl group to carbon dioxide Here R is the three-carbon propyl group C_3H_7. Its carbon bonded to magnesium attacks the electrophilic carbon of CO_2, giving the magnesium salt of a carboxylic acid:

$$C_3H_7MgBr + CO_2 \longrightarrow C_3H_7COOMgBr.$$

The original three-carbon chain is retained and a fourth carbon is added as the carboxyl group.

Step 2: Hydrolyse the carboxylate salt Acid treatment protonates the carboxylate:

$$C_3H_7COOMgBr + HCl \longrightarrow C_3H_7COOH + MgBrCl.$$

Propanoic acid in (B) and ethanoic acid in (C) have too few carbons. The substance in (D) is an alcohol, whereas carbon dioxide followed by hydrolysis produces a carboxylic acid.

Step 3: Conclusion The acid formed is C_3H_7COOH (butanoic acid). Hence, the correct option is (A).

Quick Tip to Solve: With a Grignard reagent and CO_2, append COOH to the alkyl group and count one additional carbon.

8. Acidified $KMnO_4$ oxidises sulphite to [1 mark]

(A) $S_2O_3^{2-}$

(B) $S_2O_8^{2-}$

(C) $SO_2(g)$

(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+}.

Quick Tip to Solve: Track sulphur's oxidation state: a strong oxidant converts sulphite, S(+4), into sulphate, S(+6).

- Oxidation of sulphite raises the oxidation state of sulphur from $+4$ in SO_3^{2-} to $+6$ in SO_4^{2-}.

Step 1: Identify the oxidation product Sulphite loses two electrons on conversion to sulphate. Its oxidation half-reaction in acidic medium is

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,e^-.$$

Combining this with permanganate reduction gives

$$2\,MnO_4^- + 5\,SO_3^{2-} + 6\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,SO_4^{2-} + 3\,H_2O.$$

Step 2: Check the alternative products Thiosulphate, $S_2O_3^{2-}$, and peroxodisulphate, $S_2O_8^{2-}$, are not the products of this oxidation. Acid alone can liberate SO_2 from sulphite, but sulphur remains at $+4$ in SO_2; that is not its oxidation product with acidified permanganate.

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

Quick Tip to Solve: Track sulphur's oxidation state: a strong oxidant converts sulphite, S(+4), into sulphate, S(+6).

9. 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 increases when the conjugate base formed by loss of H^+ is more stable.
- Resonance stabilises phenoxide, whereas the electron-releasing inductive effect of an alkyl group destabilises the negative charge on alkoxide oxygen.

Step 1: Compare phenol with water and alcohol Phenol, C_6H_5OH, gives the phenoxide ion, $C_6H_5O^-$. Its negative charge is delocalised by resonance into the aromatic ring. The conjugate bases of water and alcohol, OH^- and RO^-, lack this resonance stabilisation. Phenol is therefore more acidic than either water or an ordinary alcohol.

Step 2: Compare water with alcohol In RO^-, the alkyl group R pushes electron density towards an already negatively charged oxygen by its $+I$ effect. This makes an alkoxide ion less stable than OH^-, so an ordinary alcohol is less acidic than water. Option (B) reverses this comparison; (C) incorrectly puts alcohol above phenol; (D) incorrectly puts water above phenol.

Step 3: Conclusion The correct order is $C_6H_5OH > H_2O > ROH$. Hence, the correct option is (A).

Quick Tip to Solve: Compare conjugate bases: resonance puts phenol first, and the alkyl group's +I effect puts ordinary alcohol last.

10. 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 the spontaneous passage of solvent through a semipermeable membrane from a dilute solution towards a more concentrated solution.
- Reverse osmosis requires external pressure greater than the osmotic pressure to force solvent in the opposite direction.

Step 1: Compare the solutions across the cell membrane The concentrated salt solution outside the mango cells has a higher solute concentration than the cell sap. The cell membrane allows water to pass. Water therefore moves from the mango cells into the surrounding salt solution by osmosis, specifically exosmosis.

Step 2: Relate water movement to shrivelling As the cells lose water, their turgidity decreases and the mango shrivels. Options (A) and (C) predict water gain, which would not explain this shrinkage. Option (B) gives the correct water loss but calls it reverse osmosis; no external pressure is applied here, so that mechanism does not apply.

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

Quick Tip to Solve: For fruit in concentrated brine, draw the water arrow outwards; reverse osmosis needs an applied pressure.

11. 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, $LiAlH_4$, reduces an amide group, $-CONH_2$, to $-CH_2NH_2$, preserving the carbon skeleton.
- Hofmann bromamide degradation using Br_2/NaOH produces a primary amine with one carbon

Quick Tip to Solve: Count carbons before choosing: an amide-to-amine conversion retaining all carbons calls for lithium aluminium hydride.

atom fewer than the amide.

Step 1: Count carbons in the required conversion Propanamide, $CH_3CH_2CONH_2$, and propanamine, $CH_3CH_2CH_2NH_2$, both contain three carbon atoms. The carbonyl group must therefore be reduced to a methylene group without removing its carbon. Reduction with $LiAlH_4$ in dry ether, followed by work-up, gives

$$CH_3CH_2CONH_2 + 4\,[H] \longrightarrow CH_3CH_2CH_2NH_2 + H_2O.$$

Step 2: Eliminate the other reagents Br_2 in aqueous NaOH gives ethanamine, $CH_3CH_2NH_2$, so it loses the required carbon. Excess H_2 alone, without specified catalytic conditions, is not the standard reagent for this amide reduction. Iodine with red phosphorus is also not the appropriate selective reagent for converting this amide into propanamine.

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

Quick Tip to Solve: Count carbons before choosing: an amide-to-amine conversion retaining all carbons calls for lithium aluminium hydride.

12. 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 carbon atoms and an aldehyde group.
- The usual cyclic forms of glucose are six-membered hemiacetal rings called pyranose forms; a furanose ring is five-membered.

Step 1: Identify the incorrect ring description In glucose, the hydroxyl group at C-5 reacts with the aldehyde group at C-1 to form a cyclic hemiacetal. The resulting ring contains five carbon atoms and one oxygen atom, giving the α- and β-glucopyranose forms. Thus the statement assigning glucose the furanose form does not describe its standard cyclic structure.

Step 2: Verify the remaining statements Statement (A) is true because open-chain glucose is an aldohexose. Statement (B) is true: prolonged heating with HI produces n-hexane, supporting an unbranched six-carbon skeleton. Statement (D) is also true: glucose does not give Schiff's test, despite its aldehydic open-chain representation; its predominantly cyclic hemiacetal structure accounts for the absence of a freely available aldehyde group in the usual test.

Step 3: Conclusion The statement "It exists in furanose form" is the incorrect statement in this question. Hence, the correct option is (C).

Quick Tip to Solve: Count ring members: glucose is normally represented as pyranose, a six-membered ring including its oxygen atom.

13. 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 tetrahedral carbon attached to four different groups is chiral; a single enantiomer is optically active.
- L-configuration specifies relative spatial configuration. It does not specify whether optical rotation is clockwise or anticlockwise.

Step 1: Evaluate the Assertion In the naturally occurring α-amino acids considered here, the α-carbon carries $-NH_2$, $-COOH$, $-H$ and a side chain R. These are four different groups except in glycine, where R is also H. The amino acids other than glycine therefore have a chiral α-carbon and are optically active; glycine is achiral. Assertion (A) is true.

Step 2: Evaluate the Reason Most naturally occurring amino acids belong to the L-series. This is a statement about their relative configuration, so Reason (R) is true. The letter L must not be interpreted as a minus sign for optical rotation.

Step 3: Test whether the Reason explains the Assertion Optical activity follows from chirality, specifically the four different groups attached to the α-carbon, rather than from belonging to the L-series. The corresponding D-enantiomer is also optically active. Thus the Reason does not supply the cause stated in the Assertion. Options (C) and (D) wrongly call one statement false, while (A) incorrectly asserts an explanatory link.

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

Quick Tip to Solve: For amino-acid optical activity, inspect the four groups on the alpha-carbon; use D/L only for relative configuration.

14. 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:

- Stronger intermolecular attractions require more energy to separate molecules, raising the boiling point.
- Intermolecular hydrogen bonding occurs between different molecules; intramolecular hydrogen bonding occurs within a single molecule.

Step 1: Evaluate the Assertion Ethanol, CH_3CH_2OH, contains an O–H group and forms hydrogen bonds between its molecules. Methoxymethane, CH_3OCH_3, has an oxygen atom but no hydrogen directly attached to oxygen, so its pure molecules cannot form such hydrogen bonds with one another. Ethanol consequently has stronger intermolecular attractions and a higher boiling point. Assertion (A) is true.

Step 2: Evaluate the Reason The hydrogen of the O–H group of one ethanol molecule interacts with the oxygen of another ethanol molecule. This is intermolecular hydrogen bonding, not intramolecular hydrogen bonding. Ethanol has no second suitable group within the same molecule to form the stated internal hydrogen bond. Reason (R) is false.

Step 3: Check the explanatory link and code The increase in boiling point is explained by intermolecular hydrogen bonding. The printed Reason incorrectly calls it intramolecular and therefore cannot explain the true Assertion. Options (A) and (B) incorrectly treat the Reason as true, while (D) incorrectly treats the Assertion as false.

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

Quick Tip to Solve: Read the prefix carefully: ethanol's higher boiling point comes from hydrogen bonds between molecules, so use inter-, not intra-.

15. 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, stronger intermolecular attractions require a higher temperature for boiling.
- Larger halogen atoms have more polarisable electron clouds and produce stronger London dispersion forces.

Step 1: Evaluate the assertion With the alkyl group fixed, size and polarisability increase from fluorine to iodine. Dispersion forces therefore increase in the order RF, RCl, RBr, RI, giving the stated decreasing boiling-point order. Assertion (A) is true.

Step 2: Evaluate the reason Alkyl chlorides, bromides and iodides have polar carbon-halogen bonds and intermolecular attractions stronger than those in hydrocarbons of comparable molecular mass. Their boiling points are consequently higher. Reason (R) is also true.

Step 3: Check the explanatory connection The reason compares haloalkanes with hydrocarbons; it does not compare different halogens within the same alkyl series. The assertion instead requires the size and polarisability trend. Thus (A) is ruled out because the reason does not explain the order, while (C) and (D) incorrectly make one statement false.

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

Quick Tip to Solve: Keep the alkyl group fixed and compare halogen polarisability; do not confuse a true comparison with an explanation of a trend.

16. Assertion (A): $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ 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 has only one kind of ligand bonded directly to its central metal ion.
- The square brackets enclose the coordination sphere; ions outside them are counter-ions, not coordinated ligands.

Step 1: Evaluate the assertion In both $[Cr(H_2O)_6]Cl_2$ and $[Fe(H_2O)_6]Cl_2$, the six ligands within the square brackets are water molecules. Each metal is thus surrounded by only one ligand type. Both complexes are homoleptic, so Assertion (A) is true.

Step 2: Evaluate the reason Every ligand attached to chromium is H_2O, and every ligand attached to iron is also H_2O. The chloride ions are outside the coordination sphere and balance charge. Reason (R) correctly describes the attached ligands and is true.

Step 3: Link the reason to the definition Having identical coordinated ligands is precisely the condition for a homoleptic complex. Hence the reason directly explains the assertion. Option (B) wrongly denies this connection; (C) and (D) each wrongly reject a true statement. The two different central metals do not affect the homoleptic classification of either complex.

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: Count ligand types inside the square brackets only; ignore chloride counter-ions outside when deciding whether a complex is homoleptic.

Section B (10 marks)

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

Solution:

Concept:

- A nucleophile attacks the electron-deficient carbon atom of a carbonyl group; greater positive character at that carbon favours addition.

Quick Tip to Solve: For aromatic versus aliphatic aldehydes, check carbonyl-ring conjugation before comparing alkyl inductive effects.

- Conjugation of an aromatic ring with a carbonyl group delocalises electrons and stabilises the original carbonyl compound.

Step 1: Compare the electronic effects In benzaldehyde, C_6H_5CHO, the carbonyl group is conjugated with the benzene ring. Resonance donation from the ring reduces the positive character of the carbonyl carbon and stabilises the reactant. The carbonyl carbon is therefore less susceptible to nucleophilic attack. Propanal, CH_3CH_2CHO, has no corresponding aromatic conjugation; although its ethyl group has an electron-releasing inductive effect, it does not provide this resonance stabilisation.

Step 2: Compare access to the carbonyl carbon The phenyl group in benzaldehyde is also bulkier than the ethyl group in propanal, creating greater steric hindrance for the approaching nucleophile. Both the reduced electrophilicity due to conjugation and the greater crowding disfavor addition to benzaldehyde. In particular, nucleophilic addition changes the carbonyl carbon to a tetrahedral centre and disrupts its conjugation with the ring.

Step 3: Conclusion Benzaldehyde is less reactive than propanal in nucleophilic addition reactions, chiefly because of resonance stabilisation and also because of greater steric hindrance.

Quick Tip to Solve: For aromatic versus aliphatic aldehydes, check carbonyl-ring conjugation before comparing alkyl inductive effects.

18. Complete and balance the following chemical equations :

(a) $8MnO_4^- + 3S_2O_3^{2-} + H_2O \rightarrow$

(b) $Cr_2O_7^{2-} + 3Sn^{2+} + 14H^+ \rightarrow$ [2 marks]

Solution:

Concept:

- A redox equation must conserve both atoms and total electrical charge; electrons lost and gained must be equal.
- Permanganate forms MnO_2 in neutral or alkaline medium, while acidified dichromate is reduced to Cr^{3+}.

Step 1: Balance the permanganate reaction Each manganese atom changes from oxidation state $+7$ to $+4$, accepting three electrons. Oxidation of one thiosulphate ion to two sulphate ions releases eight electrons overall. Thus eight permanganate ions and three thiosulphate ions exchange 24 electrons. Balancing oxygen and hydrogen with water and hydroxide gives

$$8\,MnO_4^- + 3\,S_2O_3^{2-} + H_2O \longrightarrow 8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-.$$

There are 8 Mn, 6 S, 42 O and 2 H atoms on each side. The total charge is -14 on each side.

Step 2: Balance the dichromate reaction Each chromium atom changes from $+6$ to $+3$, so one dichromate ion accepts six electrons. Each Sn^{2+} ion loses two electrons to form Sn^{4+}; therefore three tin ions supply the required six electrons. In acid medium, the seven oxygen atoms form seven water

Quick Tip to Solve: Use electron exchange to set the metal coefficients, then check the total ionic charge after balancing water and hydrogen or hydroxide ions.

molecules using the given fourteen hydrogen ions:

$$Cr_2O_7^{2-} + 3\,Sn^{2+} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 3\,Sn^{4+} + 7\,H_2O.$$

Both sides contain 2 Cr, 3 Sn, 7 O and 14 H atoms, and both have charge $+18$.

Step 3: Conclusion (a) The products are $8\,MnO_2 + 6\,SO_4^{2-} + 2\,OH^-$.
(b) The products are $2\,Cr^{3+} + 3\,Sn^{4+} + 7\,H_2O$; the balanced equations are shown above.

Quick Tip to Solve: Use electron exchange to set the metal coefficients, then check the total ionic charge after balancing water and hydrogen or hydroxide ions.

19(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 the boiling temperature.
- Stronger attractions between unlike molecules can cause negative deviation from Raoult's law, volume contraction and exothermic mixing.

Step 1: Explain faster cooking in a pressure cooker (a) Trapped steam increases the pressure inside a pressure cooker above atmospheric pressure. Water must reach a higher temperature before its vapour pressure equals this increased pressure, so its boiling point rises above its value in an open pan. The food therefore cooks at a higher temperature, which speeds up the cooking processes.

Step 2: Relate contraction to intermolecular attraction (b) The volume contraction indicates that X–Y attractions are stronger than the original X–X and Y–Y attractions. The molecules pack more closely and escape into the vapour less readily. The partial vapour pressures are consequently lower than the ideal Raoult's-law values, $p_X < x_X p_X^0$ and $p_Y < x_Y p_Y^0$, where x denotes liquid mole fraction and p^0 the pure-liquid vapour pressure at the same temperature. The solution thus shows negative deviation.

Step 3: Predict the temperature change Establishing the stronger X–Y attractions releases more energy than is needed to disrupt the original attractions. Mixing is exothermic, with $\Delta H_{\text{mix}} < 0$, so the temperature rises on mixing the liquids before the released heat is lost to the surroundings.

Step 4: Conclusion (a) Increased pressure raises water's boiling point and hence the cooking temperature. (b) The solution shows negative deviation from Raoult's law, and its temperature increases on mixing.

Quick Tip to Solve: Link volume contraction to stronger unlike attractions, then infer lower vapour pressure and heat release on mixing.

OR

19(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 liquid mixture that boils at a constant temperature and has the same composition in its liquid and vapour phases at that temperature.
- Negative deviation from Raoult's law means that the vapour pressure is lower than the ideal-solution value because unlike molecules attract one another more strongly than the like molecules do.

Step 1: Define the constant-boiling mixture At the azeotropic composition, vaporisation does not change the composition: the vapour and the remaining liquid contain the components in the same proportion. Therefore, an azeotrope distils without a change in composition and cannot be separated into its pure components by fractional distillation.

Step 2: Relate negative deviation to the boiling point A sufficiently large negative deviation produces a minimum in the total vapour pressure. More heating is then needed for this pressure to equal the external pressure, so the corresponding mixture is a maximum-boiling azeotrope. A standard example is nitric acid and water, containing approximately 68% nitric acid by mass at atmospheric pressure.

Step 3: Conclusion An azeotrope is a constant-boiling mixture with identical liquid and vapour compositions. Large negative deviation gives a **maximum-boiling azeotrope**, for example HNO_3–water.

Quick Tip to Solve: Link lower vapour pressure with a higher boiling point: negative deviation gives the maximum-boiling azeotrope.

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

(a) $CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2/Ni} B$

(b) $C_6H_5NH_2 \xrightarrow[0-5\,^\circ C]{NaNO_2/HCl} A \xrightarrow[H^+]{C_6H_5NH_2} B$ [2 marks]

Solution:

Concept:

- With $NaCN$, an alkyl halide undergoes nucleophilic substitution through the carbon end of cyanide, forming a nitrile with one additional carbon atom. Catalytic hydrogenation converts $-CN$ into $-CH_2NH_2$.
- Aniline reacts with nitrous acid, generated from $NaNO_2$ and HCl, at $0-5\,^\circ C$ to form a diazonium salt. This salt undergoes azo coupling with aniline mainly at the para position in mildly acidic medium.

Step 1: Identify the nitrile and its reduction product in (a) Cyanide replaces chlorine in chloroethane. Its carbon joins the original two-carbon chain, giving propanenitrile, A. Hydrogenation reduces the

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), retain the diazonium nitrogen pair as the azo linkage and place the aniline amino group para to it.

triple bond without removing that carbon, giving propan-1-amine, B:

$$CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN + NaCl$$

$$CH_3CH_2CN + 2\,H_2 \xrightarrow{Ni} CH_3CH_2CH_2NH_2$$

Step 2: Identify the diazonium salt and azo product in (b) Diazotisation replaces the amino group of aniline by the diazonium group, yielding benzenediazonium chloride, A:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O$$

A couples with a second molecule of aniline at its para position. B is p-aminoazobenzene (4-aminoazobenzene), with the amino group para to the azo linkage:

$$C_6H_5N_2{}^+Cl^- + C_6H_5NH_2 \longrightarrow C_6H_5{-}N{=}N{-}C_6H_4{-}NH_2 + HCl$$

Step 3: Conclusion (a) A = CH_3CH_2CN, propanenitrile; B = $CH_3CH_2CH_2NH_2$, propan-1-amine. (b) A = $C_6H_5N_2{}^+Cl^-$, benzenediazonium chloride; B = $C_6H_5{-}N{=}N{-}C_6H_4{-}NH_2$, p-aminoazobenzene.

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), retain the diazonium nitrogen pair as the azo linkage and place the aniline amino group para to it.

21. What are the hydrolysis products of :

(a) Sucrose

(b) Lactose [2 marks]

Solution:

Concept:

- Hydrolysis breaks a disaccharide's glycosidic linkage by the addition of water, releasing its constituent monosaccharides. Dilute acid or a suitable enzyme can catalyse this process.
- Sucrose contains glucose and fructose units, whereas lactose contains galactose and glucose units. One mole of either disaccharide yields one mole of each of its two constituent sugars.

Step 1: Hydrolyse sucrose in (a) Breaking the linkage between the glucose and fructose units in sucrose gives an equimolar mixture of D-glucose and D-fructose:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}.$$

The products share a molecular formula but differ in structure: glucose is an aldose and fructose is a ketose.

Step 2: Hydrolyse lactose in (b) Hydrolysis of the glycosidic linkage in lactose, the sugar found in

Quick Tip to Solve: Glucose is common to both: pair it with fructose for sucrose and with galactose for lactose.

milk, yields D-galactose and D-glucose:

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{D-galactose}}{C_6H_{12}O_6} + \underset{\text{D-glucose}}{C_6H_{12}O_6}.$$

Both products are aldohexoses. Writing their names is essential because the molecular formula alone does not distinguish these sugars.

Step 3: Conclusion (a) Sucrose gives **D-glucose and D-fructose**.

(b) Lactose gives **D-galactose and D-glucose**.

Quick Tip to Solve: Glucose is common to both: pair it with fructose for sucrose and with galactose for lactose.

Section C (21 marks)

22. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the number of moles of CO_2 in 500 ml of soda water when packed under 2.53×10^5 Pa at the same temperature. [3 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the partial pressure of the gas over the solution, K_H is Henry's law constant at the specified temperature, and x is the mole fraction of the dissolved gas.
- For a binary solution, $x = n_{CO_2}/(n_{CO_2} + n_{H_2O})$. For dilute soda water, take the density as approximately $1.00\,\text{g mL}^{-1}$ and the mass of water in $500\,\text{mL}$ as approximately $500\,\text{g}$.

Step 1: Calculate the dissolved carbon dioxide mole fraction At $298\,\text{K}$, both the gas pressure and Henry's law constant are given in pascals, so their ratio directly gives the dimensionless mole fraction. Taking the stated packing pressure as the carbon dioxide pressure,

$$x = \frac{p}{K_H} = \frac{2.53 \times 10^5}{1.67 \times 10^8} = 1.515 \times 10^{-3}.$$

Step 2: Convert the water volume into moles Using the dilute-solution density approximation and the molar mass of water, $18.0\,\text{g mol}^{-1}$,

$$n_{H_2O} = \frac{500\,\text{g}}{18.0\,\text{g mol}^{-1}} = 27.78\,\text{mol}.$$

This large solvent amount is consistent with treating the dissolved gas as a dilute solute.

Step 3: Solve the mole-fraction expression for gas moles Let n be the moles of dissolved carbon dioxide. Retaining the gas moles in the denominator,

$$x = \frac{n}{n + 27.78} \quad \Longrightarrow \quad n = \frac{27.78x}{1 - x}.$$

Quick Tip to Solve: First find the mole fraction using pressure divided by Henry's constant; multiply by solvent moles only after recognising that the solution is dilute.

Substituting the mole fraction gives

$$n = \frac{27.78(1.515 \times 10^{-3})}{1 - 1.515 \times 10^{-3}} = 0.04215\,\text{mol}.$$

The usual dilute approximation $n \ll 27.78$ gives $n \simeq 27.78x = 0.04208\,\text{mol}$, agreeing at the precision appropriate to the water-mass approximation.

Step 4: Conclusion The $500\,\text{mL}$ sample of soda water contains approximately $\boxed{4.2 \times 10^{-2}\,\text{mol}}$ of dissolved CO_2 at $298\,\text{K}$.

Quick Tip to Solve: First find the mole fraction using pressure divided by Henry's constant; multiply by solvent moles only after recognising that the solution is dilute.

23. Calculate $\Delta_r G^\circ$ and log K_C of the reaction.

$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$

Given $E^\circ_{Cr^{3+}/Cr}$ = -0.74 V, $E^\circ_{Cd^{2+}/Cd}$ = -0.40 V

[R = 8.314 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}] [3 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using both tabulated values as reduction potentials.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of moles of electrons transferred per mole of reaction as written and F is the Faraday constant.
- The equilibrium relation is $\Delta_r G^\circ = -RT \ln K_C$, so $\log K_C = nFE^\circ_{\text{cell}}/(2.303RT)$. For the numerical equilibrium constant, take the usual standard-temperature convention $T = 298\,\text{K}$.

Step 1: Identify oxidation, reduction and electron transfer Chromium is oxidised and cadmium ions are reduced in the given reaction. The balanced half-reactions are

$$2\,\text{Cr}\,(\text{s}) \longrightarrow 2\,\text{Cr}^{3+}(\text{aq}) + 6\,\text{e}^-$$
$$3\,\text{Cd}^{2+}(\text{aq}) + 6\,\text{e}^- \longrightarrow 3\,\text{Cd}\,(\text{s}).$$

Hence $n = 6$. Electrode potentials are intensive quantities: do not multiply them by the stoichiometric coefficients 2 and 3.

Step 2: Calculate the cell potential and Gibbs energy The cadmium electrode is the cathode and the chromium electrode is the anode. Therefore,

$$E^\circ_{\text{cell}} = (-0.40) - (-0.74) = 0.34\,\text{V}.$$

Substitution gives

$$\Delta_r G^\circ = -6 \times 96500 \times 0.34 = -196860\,\text{J}\,\text{mol}^{-1}.$$

The negative sign is consistent with the positive cell potential: the forward reaction is thermodynami-

Quick Tip to Solve: Balance electrons first: the coefficients require six electrons. Subtract reduction potentials without scaling them, and use kelvin when calculating the equilibrium constant.

cally favourable under standard conditions.

Step 3: Relate the cell potential to the equilibrium constant Equating the two expressions for standard Gibbs energy and converting natural logarithm to common logarithm gives

$$2.303RT \log K_C = nFE^\circ_{\text{cell}}.$$

At 298 K,

$$\log K_C = \frac{6 \times 96500 \times 0.34}{2.303 \times 8.314 \times 298} = 34.50.$$

The large positive logarithm indicates that equilibrium strongly favours products.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -196.86\,\text{kJ mol}^{-1}}$ for the reaction as written, and $\boxed{\log K_C \approx 34.5}$ at 298 K.

Quick Tip to Solve: Balance electrons first: the coefficients require six electrons. Subtract reduction potentials without scaling them, and use kelvin when calculating the equilibrium constant.

24. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.
[Given : log 4 = 0.602, log 2 = 0.301, R = 8.314 J K^{-1} mol^{-1}] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- With activation energy and frequency factor treated as constant over the temperature interval, $\log(k_2/k_1) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Comparing rates at unchanged concentrations makes the rate ratio equal to the rate-constant ratio.

Step 1: Assign the temperatures and rate ratio The initial temperature is $T_1 = 293\,\text{K}$ and the higher temperature is $T_2 = 313\,\text{K}$. Since the rate quadruples at the same concentrations,

$$\frac{k_2}{k_1} = 4, \qquad \log \frac{k_2}{k_1} = 0.602.$$

The temperature values are already on the absolute scale, so no Celsius conversion is required.

Step 2: Rearrange the two-temperature Arrhenius equation Subtracting the Arrhenius logarithmic equations at the two temperatures eliminates $\log A$. Since

$$\frac{1}{T_1} - \frac{1}{T_2} = \frac{T_2 - T_1}{T_1 T_2},$$

the activation energy can be written as

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

Quick Tip to Solve: Use the full rate ratio 4 over the full temperature rise of 20 K; place the smaller temperature first in the reciprocal-temperature difference to keep the sign positive.

Both the logarithm and the reciprocal-temperature difference are positive, as expected for a positive activation energy.

Step 3: Substitute the numerical data Using the supplied common logarithm and $R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$,

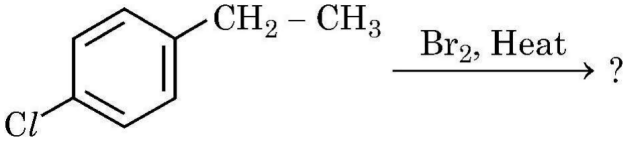
$$E_a = \frac{2.303 \times 8.314 \times 0.602 \times 293 \times 313}{313 - 293}$$
$$= 52854.6\,\text{J mol}^{-1}$$
$$\approx 52.85\,\text{kJ mol}^{-1}.$$

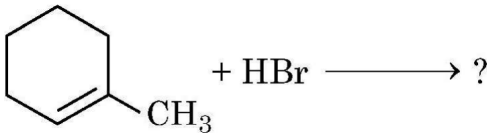
The factor $T_1T_2/(T_2 - T_1)$ has unit kelvin, which cancels the inverse-kelvin unit in the gas constant.

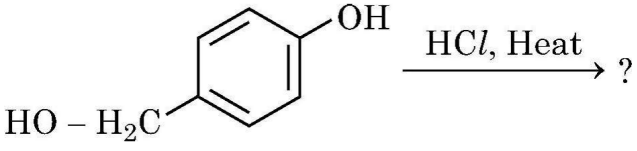
Step 4: Conclusion The energy of activation of the reaction is $\boxed{E_a \approx 52.9\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Use the full rate ratio 4 over the full temperature rise of 20 K; place the smaller temperature first in the reciprocal-temperature difference to keep the sign positive.

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

(a) 

(b) 

(c) 

Solution:

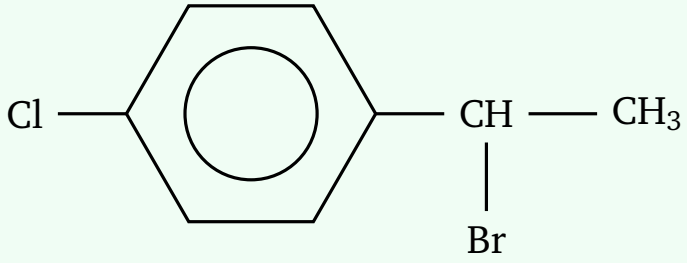
Concept:

- Bromine in the presence of heat produces free-radical side-chain substitution in alkylbenzenes. A benzylic hydrogen is preferentially replaced because the resulting benzylic radical is resonance-stabilised.
- Addition of HBr to an unsymmetrical alkene without peroxide follows Markovnikov's rule: hydrogen adds to the double-bond carbon bearing more hydrogens, producing the more stable carbocation before bromide attacks.
- Benzylic alcohols undergo substitution with HCl to form benzylic chlorides. The phenolic C–OH group is not replaced by chlorine under these conditions because its aryl carbon–oxygen bond has partial double-bond character.

Step 1: Brominate the benzylic position in reaction (a) The starting compound is para-

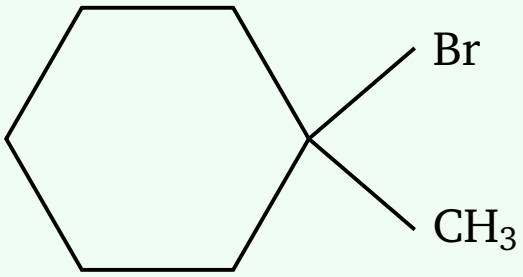
Quick Tip to Solve: Match each reagent to its reactive site: heated bromine attacks the benzylic C–H bond, HBr adds across the alkene, and HCl replaces the benzylic OH while retaining phenolic OH.

chloroethylbenzene. Heat initiates radical bromination, and abstraction of a hydrogen from the carbon immediately adjacent to the ring gives a resonance-stabilised secondary benzylic radical. Replacement of that hydrogen by bromine gives $\text{p-ClC}_6\text{H}_4\text{CH(Br)CH}_3$. The existing ring chlorine remains attached. Ring bromination would require electrophilic aromatic substitution conditions, whereas the given heat favours side-chain substitution. The product is 1-(1-bromoethyl)-4-chlorobenzene; the benzylic stereocentre is formed as a racemic mixture.



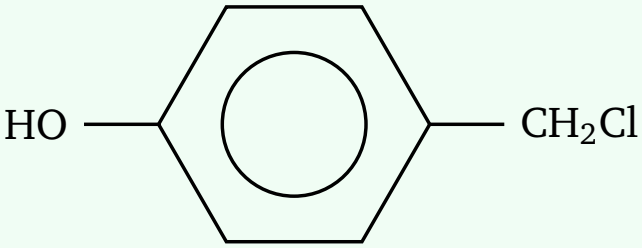
(a) Benzylic bromination product; ring chlorine is retained.

Step 2: Apply Markovnikov addition in reaction (b) The alkene is 1-methylcyclohex-1-ene. Hydrogen adds to the less substituted double-bond carbon, leaving a tertiary carbocation on the ring carbon already bearing the methyl group. Bromide then attacks that carbon. Thus bromine and methyl are attached to the same ring carbon, giving 1-bromo-1-methylcyclohexane. No peroxide is specified, so the anti-Markovnikov product is not selected. The double bond becomes a single bond in the saturated ring.



(b) 1-Bromo-1-methylcyclohexane.

Step 3: Replace the benzylic alcohol group in reaction (c) The starting compound has a phenolic hydroxyl group and a para benzylic $-\text{CH}_2\text{OH}$ group. Protonation of the benzylic hydroxyl group allows water to leave and chloride to replace it, producing $\text{p-HOC}_6\text{H}_4\text{CH}_2\text{Cl}$. The phenolic hydroxyl group remains unchanged because its bond to the aromatic carbon does not undergo the ordinary alcohol substitution with HCl. The product is 4-(chloromethyl)phenol.



(c) 4-(Chloromethyl)phenol; phenolic OH is retained.

Quick Tip to Solve: Match each reagent to its reactive site: heated bromine attacks the benzylic C–H bond, HBr adds across the alkene, and HCl replaces the benzylic OH while retaining phenolic OH.

Step 4: Conclusion The structures above are:

(a) p-$ClC_6H_4CH(Br)CH_3$;

(b) 1-bromo-1-methylcyclohexane;

(c) p-$HOC_6H_4CH_2Cl$.

Quick Tip to Solve: Match each reagent to its reactive site: heated bromine attacks the benzylic C–H bond, HBr adds across the alkene, and HCl replaces the benzylic OH while retaining phenolic OH.

OR

25(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.
- Coupling replaces the two carbon-halogen bonds by a carbon-carbon bond between the two aromatic rings.

Step 1: Select the coupling reagent Treat chlorobenzene, C_6H_5Cl, with sodium metal in dry ether. The anhydrous solvent is essential because water would react with sodium and consume it.

Step 2: Write the balanced Fittig reaction Two chlorobenzene molecules provide the two phenyl groups, while their chlorine atoms form sodium chloride:

$$2\,C_6H_5Cl + 2\,Na \xrightarrow{\text{dry ether}} C_6H_5{-}C_6H_5 + 2\,NaCl$$

The new bond joins the carbons that originally carried chlorine; the aromatic rings remain intact.

Step 3: Conclusion Chlorobenzene is converted to biphenyl, $C_6H_5-C_6H_5$, by the Fittig reaction using sodium in dry ether.

Quick Tip to Solve: For aryl halide to biaryl conversion, choose sodium in dry ether and couple two aryl groups.

25(B)(b). How do you convert :

Propene to 1-Iodopropane [1 mark]

Solution:

Concept:

- Addition of HBr to an unsymmetrical alkene in the presence of peroxide follows the anti-Markovnikov rule.
- The Finkelstein reaction replaces bromide by iodide using NaI in dry acetone; precipitation of NaBr drives the reaction.

Quick Tip to Solve: To obtain a terminal iodide from propene, first place bromine at the terminal carbon with the peroxide effect, then exchange it for iodine.

Step 1: Prepare the primary bromide Add HBr to propene in the presence of an organic peroxide, ROOR. Bromine attaches to the terminal carbon, giving 1-bromopropane:

$$CH_3CH{=}CH_2 + HBr \xrightarrow{ROOR} CH_3CH_2CH_2Br$$

The peroxide effect applies to HBr; direct addition of HI does not provide this anti-Markovnikov route.

Step 2: Exchange bromide for iodide Treat the primary bromide with sodium iodide in dry acetone:

$$CH_3CH_2CH_2Br + NaI \xrightarrow{\text{dry acetone}} CH_3CH_2CH_2I + NaBr\downarrow$$

The carbon skeleton and terminal position of the halogen are retained during this nucleophilic substitution.

Step 3: Conclusion Use HBr/peroxide followed by NaI in dry acetone to convert propene into 1-iodopropane.

Quick Tip to Solve: To obtain a terminal iodide from propene, first place bromine at the terminal carbon with the peroxide effect, then exchange it for iodine.

25(B)(c). How do you convert :

2-bromobutane to but-2-ene. [1 mark]

Solution:

Concept:

- Heating a haloalkane with alcoholic KOH causes beta-elimination, also called dehydrohalogenation.
- Saytzeff's rule predicts the more substituted alkene as the major product when more than one elimination product is possible.

Step 1: Choose elimination conditions Heat 2-bromobutane with alcoholic KOH. The base removes a hydrogen from an adjacent carbon while bromide leaves, producing a carbon-carbon double bond. Aqueous KOH would favour substitution instead.

Step 2: Form the more substituted alkene Remove hydrogen from carbon 3 and bromine from carbon 2:

$$CH_3CHBrCH_2CH_3 + KOH \xrightarrow[\text{heat}]{\text{alcohol}} CH_3CH{=}CHCH_3 + KBr + H_2O$$

But-2-ene is favoured over but-1-ene because its double bond has more alkyl substituents and is therefore more stable.

Step 3: Conclusion Heating 2-bromobutane with alcoholic KOH gives but-2-ene as the major elimination product.

Quick Tip to Solve: Use alcoholic base and heat for alkene formation; select the more substituted double bond as the major product.

26. The elements of 3d transition series are given as :

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

Answer the following :

(a) Copper has exceptionally positive $E^{\circ}_{M^{2+}/M}$ value, why ?

(b) Which element is a strong reducing agent in +2 oxidation state and why ?

(c) Zn^{2+} salts are colourless. Why ? [3 marks]

Solution:

Concept:

- A metal's standard reduction potential reflects the combined effects of atomisation, ionisation and hydration; it cannot be predicted from ionisation enthalpy alone.
- A reducing agent donates electrons and is itself oxidised. The relative stability of successive oxidation states determines this tendency.
- The usual colour of transition-metal ions arises from absorption of visible light in transitions between split d orbitals; a filled d^{10} shell cannot undergo such d-d transitions.

Step 1: Explain copper's positive reduction potential For part (a), formation of aqueous Cu^{2+} from copper metal involves atomisation and two successive ionisations, followed by hydration of the gaseous ion. Copper has high atomisation and ionisation enthalpies; its second ionisation also disrupts the stable $3d^{10}$ configuration of Cu^{+}. The energy needed to form Cu^{2+} is not sufficiently compensated by hydration enthalpy. Copper therefore has little tendency to oxidise to aqueous Cu^{2+}; the reverse reduction is favoured under standard conditions, giving a positive $E^{\circ}_{Cu^{2+}/Cu}$.

Step 2: Identify the reducing divalent ion For part (b), chromium in the +2 oxidation state, Cr^{2+}, is a strong reducing agent. Its configuration is $[Ar]\,3d^4$, and it readily loses an electron:

$$Cr^{2+} \longrightarrow Cr^{3+} + e^{-}$$

The resulting Cr^{3+} has a stable $3d^3$ configuration, with a half-filled lower t_{2g} set in its octahedral aqua complex. The ease of this oxidation explains the reducing action of Cr^{2+}.

Step 3: Explain the absence of colour in zinc salts For part (c), zinc loses its two $4s$ electrons to give Zn^{2+} with configuration $[Ar]\,3d^{10}$. All five d orbitals are filled, so d-d excitation is unavailable. Hence Zn^{2+} itself does not absorb visible light through d-d transitions and its salts with colourless anions are colourless.

Step 4: Conclusion (a) Copper's high atomisation and ionisation energy costs are not offset by hydration, producing a positive standard reduction potential. (b) Cr^{2+} is strongly reducing because it forms stable Cr^{3+}. (c) Zn^{2+} is colourless because its $3d^{10}$ shell cannot undergo d-d transitions.

Quick Tip to Solve: Keep the three explanations distinct: copper needs an energy balance, chromium needs oxidation-state stability, and zinc needs its d-electron count.

27(a). Arrange the following compounds in increasing order of their boiling point :
$(CH_3)_2NH$, $CH_3CH_2NH_2$, CH_3CH_2OH. [1 mark]

Solution:

Concept:

- For molecules of comparable molar mass, stronger intermolecular hydrogen bonding generally produces a higher boiling point.
- Primary amines have two N-H bonds available for hydrogen-bond donation, whereas secondary amines have one. O-H hydrogen bonding in alcohols is stronger than N-H hydrogen bonding in amines.

Step 1: Compare the two isomeric amines Dimethylamine, $(CH_3)_2NH$, and ethylamine, $CH_3CH_2NH_2$, have the same molar mass. Ethylamine is primary and forms more extensive intermolecular hydrogen bonding than secondary dimethylamine because it has two N-H bonds. Thus dimethylamine boils at a lower temperature than ethylamine.

Step 2: Compare the alcohol with the amines Ethanol, CH_3CH_2OH, has a similar molar mass, but oxygen is more electronegative than nitrogen. Its O-H group forms stronger intermolecular hydrogen bonds, so more energy is needed to separate its molecules into the vapour phase. Ethanol therefore has the highest boiling point of the three.

Step 3: Conclusion The increasing order of boiling point is

$$(CH_3)_2NH < CH_3CH_2NH_2 < CH_3CH_2OH.$$

Quick Tip to Solve: For these similar-sized molecules, first compare hydrogen bonding: secondary amine, then primary amine, then alcohol.

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 uses the phthalimide anion as a nucleophile to displace halide from an alkyl halide; hydrolysis then gives a primary amine.
- Basicity depends on the availability of the nitrogen lone pair for accepting a proton. Delocalisation of this lone pair lowers its availability.

Step 1: Explain the limitation of Gabriel synthesis (i) To prepare an aromatic primary amine, the phthalimide anion would have to replace the halogen directly attached to an aromatic ring. Ordinary aryl halides do not undergo the nucleophilic substitution required in Gabriel synthesis. Their carbon–halogen bond has partial double-bond character due to resonance and is attached to an

Quick Tip to Solve: For Gabriel synthesis check whether halogen is bonded to an alkyl or aryl carbon; for basicity check whether the nitrogen lone pair participates in resonance.

sp^2-hybridised carbon; the usual displacement by phthalimide ion is therefore difficult. The required N-arylphthalimide is not formed by this method.

Step 2: Compare the nitrogen lone pairs (ii) In an amide, the nitrogen lone pair is delocalised into the adjacent carbonyl group through resonance:

$$\mathrm{R{-}C(=O){-}NH_2} \longleftrightarrow \mathrm{R{-}C(-O^-){=}NH_2{}^+}.$$

It is therefore less available to accept H^+. In an amine there is no adjacent carbonyl group to withdraw the lone pair in this way, so the nitrogen lone pair is more available for protonation. This accounts for the lower basicity of amides.

Step 3: Conclusion Aromatic primary amines cannot be obtained by ordinary Gabriel synthesis because aryl halides resist the required nucleophilic substitution. Amides are less basic than amines because their nitrogen lone pair is delocalised towards the carbonyl group.

Quick Tip to Solve: For Gabriel synthesis check whether halogen is bonded to an alkyl or aryl carbon; for basicity check whether the nitrogen lone pair participates in resonance.

28. Define the following terms :

(a) Native protein

(b) Nucleotide

(c) Essential amino acid [3 marks]

Solution:

Concept:

- A protein's biological function depends on its specific folded structure. Denaturation disrupts the native conformation and usually destroys biological activity.
- Nucleic acids are polymers of nucleotides. Nutritional classification of amino acids depends on whether the human body can synthesise enough of them.

Step 1: Define native protein (a) A native protein is a protein in its natural, biologically active state, with its characteristic three-dimensional conformation intact. Its secondary and tertiary structure, and quaternary structure where present, give it the specific shape required for its normal function. For example, a native enzyme has the conformation needed for its catalytic activity.

Step 2: Define nucleotide (b) A nucleotide is a compound consisting of a nitrogenous base, a pentose sugar and a phosphate group. A base linked to a sugar forms a nucleoside; attachment of phosphate to the sugar gives a nucleotide. The pentose is ribose in RNA nucleotides and 2-deoxyribose in DNA nucleotides. Nucleotides are the building units of nucleic acids.

Step 3: Define essential amino acid (c) An essential amino acid is an amino acid which the human body cannot synthesise in sufficient quantity to meet its needs and which must therefore be supplied through the diet. Valine and leucine are examples. The word essential refers to the need for dietary supply; it does not imply that other amino acids are unnecessary for protein synthesis.

Step 4: Conclusion A native protein has its natural active conformation; a nucleotide contains a base,

Quick Tip to Solve: Remember the three distinguishing features: native means natural active form, nucleotide means nucleoside plus phosphate, and essential means required in the diet.

pentose sugar and phosphate; an essential amino acid must be obtained through the diet because the body cannot produce enough of it.

Quick Tip to Solve: Remember the three distinguishing features: native means natural active form, nucleotide means nucleoside plus phosphate, and essential means required in the diet.

Section D (8 marks)

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

29. 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 : [4 marks]

29(a)(i). What is a rate determining step ? [1 mark]

Solution:

Concept:

- A reaction mechanism describes the elementary steps through which reactants become products.
- In a multistep mechanism, the slowest step limits the overall rate of product formation.

Step 1: Compare the elementary steps A complex reaction proceeds through several elementary steps. These steps need not occur at the same rate: one may be much slower than the others under the reaction conditions.

Step 2: Identify the controlling step The faster steps cannot make the complete sequence proceed faster than its slowest step permits. This slow step acts as a bottleneck and determines the overall reaction rate.

Step 3: Conclusion The rate determining step is the slowest elementary step in a multistep reaction mechanism, which controls the overall rate of the reaction.

Quick Tip to Solve: In a reaction mechanism, look for the step labelled slow to identify the rate determining step.

29(a)(ii). Define complex reaction. [1 mark]

Solution:

Concept:

- An elementary reaction occurs in a single step, while a reaction mechanism may contain a sequence of elementary steps.
- Adding the elementary steps and cancelling intermediates gives the overall chemical equation.

Step 1: Distinguish the overall equation from the mechanism An overall equation records the net conversion of reactants into products. It does not by itself show whether this conversion occurs in one event or through several successive elementary reactions.

Step 2: Recognise a multistep process When two or more elementary steps are needed to describe the conversion, the reaction is complex. Intermediates can be formed in one step and consumed in another, so they cancel from the overall equation.

Step 3: Conclusion A complex reaction is a chemical reaction that proceeds through two or more elementary steps.

Quick Tip to Solve: Classify a reaction by the number of elementary steps in its mechanism, not by the length of its overall equation.

29(b). What is the effect of temperature on the rate constant of a reaction ? [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 absolute temperature.
- Raising the temperature increases the fraction of molecules with sufficient energy to overcome the activation energy barrier.

Step 1: Examine the temperature term For a reaction with positive activation energy, an increase in T makes the exponent $-E_a/(RT)$ less negative. Consequently, the exponential factor and hence the rate constant increase.

Step 2: Relate the equation to the usual observation For many reactions near room temperature, the rate constant becomes approximately two to three times its original value for a rise of $10\,\mathrm{K}$. This is an empirical guide; the exact increase depends on the activation energy and the temperatures involved.

Step 3: Conclusion The rate constant generally increases with increasing temperature, in accordance with the Arrhenius equation; it commonly becomes about two to three times larger for a $10\,\mathrm{K}$ rise.

Quick Tip to Solve: In the Arrhenius equation, increasing temperature makes the negative exponent smaller in magnitude, so the rate constant increases.

OR

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

Solution:

Concept:

- Molecularity is the number of reacting species participating in a single elementary reaction event.
- Reaction order is the sum of the powers of concentration terms in the experimentally determined rate law.

Step 1: Apply molecularity to a single event An elementary reaction occurs in one step, so the participating species can be counted. A complex reaction consists of several elementary steps, each with its own molecularity; its overall equation does not represent one simultaneous collision. Thus, a single molecularity cannot be assigned to the overall complex reaction.

Step 2: Apply order to the observed rate law The rate dependence on reactant concentrations can be measured for either an elementary or a complex reaction. If the measured law is $r = k[A]^m[B]^n$, the order is $m + n$. Its definition uses the observed rate law and does not require the entire reaction to occur in one step.

Step 3: Conclusion Molecularity applies only to an elementary reaction because it counts species in a single event. Order applies to both elementary and complex reactions because it is obtained from their experimental rate laws.

Quick Tip to Solve: Ask whether you are counting species in one elementary event (molecularity) or adding measured concentration powers (order).

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 mark]

Solution:

Concept:

- For a second-order conversion of X into Y, the rate of formation of Y is proportional to the square of the concentration of X.
- The rate law is $r = k[\mathrm{X}]^2$, where k is the rate constant and $[\mathrm{X}]$ is the reactant concentration. Compare rates at the same temperature so that k is unchanged.

Step 1: Express the original rate Let the initial concentration be c. The original rate is therefore $r_1 = kc^2$. The given order, rather than merely the concentration factor, determines the change in rate.

Step 2: Substitute the tripled concentration After increasing the concentration to $3c$,

$$r_2 = k(3c)^2 = 9kc^2, \qquad \frac{r_2}{r_1} = 9.$$

Both factors of concentration in the second-order rate law increase by three, giving the square of three.

Quick Tip to Solve: If a concentration changes by a factor f, raise f to the order with respect to that reactant to find the rate factor.

Step 3: Conclusion The rate of formation of Y becomes $\boxed{9 \text{ times}}$ its original value.

Quick Tip to Solve: If a concentration changes by a factor f, raise f to the order with respect to that reactant to find the rate factor.

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30. 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 : [4 marks]

What happens when phenol reacts with

30(a)(i). Br_2/CS_2 [1 mark]

Solution:

Concept:

- The hydroxyl group activates the benzene ring towards electrophilic substitution and directs incoming bromine to the ortho and para positions.
- In a non-polar solvent such as CS_2, bromination of phenol gives monobrominated products; the solvent distinguishes this reaction from bromination in water.

Step 1: Identify the substitution sites Donation of an oxygen lone pair increases electron density at the positions ortho and para to OH. Bromine therefore replaces a ring hydrogen at either of these positions, while the hydroxyl group remains attached to the ring.

Step 2: Identify the products in carbon disulphide Phenol reacts with bromine in CS_2 to give a mixture of 2-bromophenol and 4-bromophenol. The para product predominates because substitution there is less sterically hindered. For either isomer the substitution equation is

$$C_6H_5OH + Br_2 \xrightarrow{CS_2} BrC_6H_4OH + HBr.$$

The white precipitate of 2,4,6-tribromophenol is characteristic of bromine water, rather than these non-polar solvent conditions.

Step 3: Conclusion A mixture of ortho-bromophenol (2-bromophenol) and para-bromophenol (4-bromophenol) forms, with para-bromophenol as the major product.

Quick Tip to Solve: Check the solvent first: bromine in CS_2 gives ortho and para monobromination, whereas bromine water gives tribromination.

30(a)(ii). Conc. HNO_3 [1 mark]

Solution:

Concept:

- The OH group strongly activates the phenol ring and directs electrophilic substitution to the two ortho positions and the para position.
- Concentrated nitric acid nitrates phenol at all three activated positions, giving a trinitro derivative.

Step 1: Apply the directing effect of the hydroxyl group Number the carbon bearing OH as carbon 1. The activated ortho sites are carbons 2 and 6, and the para site is carbon 4. Under the strong nitrating conditions, a nitro group replaces a ring hydrogen at each of these sites.

Step 2: Write the nitration reaction Three molecules of nitric acid supply the three nitro groups; replacement of the three ring hydrogens gives three molecules of water:

$$C_6H_5OH + 3\,HNO_3 \xrightarrow{\text{conc.}} C_6H_2(NO_2)_3OH + 3\,H_2O.$$

The hydroxyl group remains attached to carbon 1. The product is the yellow compound commonly called picric acid; dilute nitric acid instead gives mononitrophenols.

Step 3: Conclusion Phenol reacts with concentrated HNO_3 to form 2,4,6-trinitrophenol, commonly called picric acid.

Quick Tip to Solve: For phenol, link concentrated nitric acid with nitration at all three positions directed by OH: 2, 4 and 6.

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

Solution:

Concept:

- Protonation requires a lone pair on oxygen to form a bond with H^+; availability of that lone pair determines basicity.
- In phenol, an oxygen lone pair overlaps with the benzene ring's π-electron system and participates in resonance.

Step 1: Consider the oxygen lone pair The oxygen atom in phenol is directly attached to the aromatic ring. Its lone-pair electron density is delocalised into that ring, as represented by resonance structures with increased electron density at the ortho and para positions.

Step 2: Relate delocalisation to proton acceptance Because the lone pair participates in resonance, it is less available for donation to a proton than a localised lone pair. Phenol is therefore a very weak base and does not accept H^+ readily. This concerns donation of the oxygen lone pair, rather than loss of the hydroxyl proton.

Step 3: Conclusion Phenol does not undergo protonation readily because resonance delocalisation makes the oxygen lone pair less available for bonding to H^+.

Quick Tip to Solve: For protonation, compare the availability of the oxygen lone pair: resonance delocalisation reduces its proton-accepting ability.

30(c). Which is a stronger acid – phenol or cresol ? Give reason. [1 mark]

Solution:

Concept:

- The acidity of a phenol depends on the ease of losing its hydroxyl proton and on the stability of the conjugate-base anion formed.
- An electron-donating substituent such as CH_3 generally reduces phenolic acidity by increasing electron density in the conjugate base.

Step 1: Compare the conjugate bases Phenol loses H^+ to give the phenoxide ion, while cresol, a methyl-substituted phenol, gives a cresoxide ion. Both ions have resonance delocalisation of the negative charge into the aromatic ring, so the additional methyl group determines their relative stability.

Step 2: Apply the methyl group's electronic effect The methyl group has an electron-releasing inductive effect, denoted $+I$. Its donation increases electron density and makes the negative charge of the cresoxide ion less favourable relative to that of phenoxide. Thus, loss of the hydroxyl proton is less favourable for cresol, and its acid-dissociation constant is smaller.

Step 3: Conclusion Phenol is the stronger acid. The electron-releasing CH_3 group in cresol destabilises its conjugate base relative to phenoxide and decreases acidity.

Quick Tip to Solve: Compare the anions after removing the hydroxyl proton: an electron-releasing methyl group reduces phenolic acidity.

OR

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

Solution:

Concept:

- The Reimer–Tiemann reaction introduces a formyl group, $-CHO$, chiefly ortho to the hydroxyl group of phenol.
- In naming the resulting aromatic aldehyde, the aldehyde group has priority over the hydroxyl group, which is named as a hydroxy substituent.

Step 1: Locate the aldehyde group in the product Treatment of phenol with chloroform and aqueous alkali, followed by acidification, gives the ortho-formylated product o-HOC_6H_4CHO. Its common name is salicylaldehyde. The hydroxyl and formyl groups occupy adjacent carbons of the benzene ring.

Step 2: Name the product as a benzaldehyde derivative Choose benzaldehyde as the parent because $-CHO$ is the principal functional group. The ring carbon attached to $-CHO$ is position 1; the adjacent carbon bearing OH is position 2. Combining the hydroxy prefix, its locant and the parent name gives the required systematic name.

Step 3: Conclusion The product is **2-hydroxybenzaldehyde** (salicylaldehyde).

Quick Tip to Solve: Begin with benzaldehyde as the parent, then number the adjacent hydroxyl substituent as 2; do not name it as a phenol derivative.

Section E (15 marks)

31(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:

- Aldehydes having an alpha hydrogen undergo aldol addition in dilute alkali. Heating the beta-hydroxy aldehyde eliminates water to give an alpha,beta-unsaturated aldehyde.
- Heating a sodium carboxylate with soda lime (NaOH and CaO) gives an alkane containing one carbon atom fewer than the original acid.
- Ozonolysis cleaves an alkene's double bond into two carbonyl groups. An aliphatic aldehyde reduces Fehling's solution, while the iodoform test identifies methyl ketones of the form CH_3COR, where R is an alkyl or aryl group; ethanal also gives this test.

Step 1: (a)(i) Form an aldol from ethanal Ethanal contains alpha hydrogens, so two molecules combine in the presence of dilute NaOH to form 3-hydroxybutanal (aldol). The four-carbon chain is formed in this step:

$$2\,CH_3CHO \xrightarrow{\text{dil}\cdot\ NaOH} CH_3CH(OH)CH_2CHO.$$

On heating, the aldol loses water from its beta-hydroxyl group and an adjacent alpha hydrogen. The resulting double bond lies between carbon atoms 2 and 3 when numbered from the aldehyde carbon:

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH{=}CHCHO + H_2O.$$

The product is but-2-enal, also called crotonaldehyde.

Step 2: (a)(ii) Decarboxylate sodium propanoate First neutralise propanoic acid with aqueous sodium hydroxide to prepare sodium propanoate:

$$CH_3CH_2COOH + NaOH \longrightarrow CH_3CH_2COONa + H_2O.$$

Heat the dry sodium salt with soda lime. The carboxyl carbon is removed as carbonate, leaving the two-carbon alkane ethane:

$$CH_3CH_2COONa + NaOH \xrightarrow{CaO,\ \Delta} CH_3CH_3 + Na_2CO_3.$$

The carbon count decreases from three in propanoic acid to two in ethane, as required.

Step 3: (b) Identify compound B using both tests A positive Fehling test indicates an aliphatic aldehyde among the ozonolysis products. To also give iodoform with iodine and aqueous NaOH, that

Quick Tip to Solve: In ozonolysis questions, identify each carbonyl product first and then reconnect the carbonyl carbons. A Fehling-positive, iodoform-positive aldehyde is ethanal; use the remaining carbon count to identify the ketone.

aldehyde must be ethanal, CH_3CHO. Thus B is ethanal. Its aldehyde group gives the brick-red Cu_2O precipitate with Fehling's solution, and its iodoform reaction is

$$CH_3CHO + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + HCOONa + 3\,NaI + 3\,H_2O.$$

Here CHI_3 is the characteristic yellow precipitate.

Step 4: Identify compound C and account for the carbons C does not reduce Fehling's solution, so it is the ketone product. Since it gives iodoform, it must be a methyl ketone. The original alkene has five carbons and B contains two; therefore C has three carbons. The required three-carbon methyl ketone is propanone, CH_3COCH_3:

$$CH_3COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + CH_3COONa + 3\,NaI + 3\,H_2O.$$

Propanone therefore satisfies both the negative Fehling test and the positive iodoform test.

Step 5: Reconstruct alkene A from the carbonyl products Remove the oxygen atoms from the carbonyl carbons of ethanal and propanone, then join those two carbons by a double bond. The ethanal-derived carbon retains one hydrogen and one methyl group; the propanone-derived carbon retains two methyl groups. This gives $CH_3CH{=}C(CH_3)_2$, or 2-methylbut-2-ene. Its ozonolysis followed by reductive work-up is

$$CH_3CH{=}C(CH_3)_2 \xrightarrow[2.\,Zn/H_2O]{1.\,O_3} CH_3CHO + CH_3COCH_3.$$

The reconstructed alkene has formula C_5H_{10}, matching the question, and gives exactly the two identified products.

Step 6: Conclusion (a)(i) Ethanal gives but-2-enal by aldol addition followed by dehydration. (a)(ii) Propanoic acid gives ethane through sodium propanoate and soda-lime decarboxylation. (b) A is 2-methylbut-2-ene, B is ethanal and C is propanone.

Quick Tip to Solve: In ozonolysis questions, identify each carbonyl product first and then reconnect the carbonyl carbons. A Fehling-positive, iodoform-positive aldehyde is ethanal; use the remaining carbon count to identify the ketone.

OR

31(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:

- An ester hydrolyses in dilute acid to give a carboxylic acid and an alcohol: $RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$. The acyl group supplies the acid and the alkoxy group supplies the alcohol.

Quick Tip to Solve: Use the alkene to count the alcohol's carbons, then use oxidation to locate its hydroxyl group. Rebuild the ester from the resulting acid and alcohol, and check the molecular formula by subtracting water.

- Oxidation of a primary alcohol with chromic acid gives the corresponding carboxylic acid without changing its carbon skeleton: $\mathrm{RCH_2OH} + 2\,[\mathrm{O}] \longrightarrow \mathrm{RCOOH} + \mathrm{H_2O}$.
- Acid-catalysed dehydration eliminates water from an alcohol to form an alkene; the alcohol and the alkene have the same number of carbon atoms.

Step 1: Identify the alcohol from its two reactions The dehydration product is but-1-ene, $\mathrm{CH_2{=}CHCH_2CH_3}$, so alcohol (C) has four carbon atoms in a straight chain. Since oxidation of (C) produces a carboxylic acid (B), (C) must be a primary alcohol. Butan-2-ol would instead oxidise to a ketone and therefore cannot satisfy the oxidation clue. Thus the alcohol is butan-1-ol:

$$\text{(C)}: \mathrm{CH_3CH_2CH_2CH_2OH}.$$

Step 2: Determine the oxidation product Chromic acid oxidises the terminal primary alcohol group of butan-1-ol to a carboxyl group. All four carbon atoms remain in the product, so (B) is butanoic acid. The oxidation equation, with $[O]$ denoting oxygen supplied by the oxidising agent, is

$$\mathrm{CH_3CH_2CH_2CH_2OH} + 2\,[\mathrm{O}] \xrightarrow{\mathrm{H_2CrO_4}} \mathrm{CH_3CH_2CH_2COOH} + \mathrm{H_2O}.$$

Step 3: Reconstruct the ester and check its formula Hydrolysis gives butanoic acid and butan-1-ol. Therefore (A) has the butanoyl portion of the acid joined through oxygen to the butyl group of the alcohol:

$$\text{(A)}: \mathrm{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3}.$$

This ester is butyl butanoate. Combining the acid, $\mathrm{C_4H_8O_2}$, and the alcohol, $\mathrm{C_4H_{10}O}$, with loss of $\mathrm{H_2O}$ gives $\mathrm{C_8H_{16}O_2}$, exactly the molecular formula of (A).

Step 4: Write the hydrolysis equation Dilute sulphuric acid catalyses cleavage of the ester in water. The products are the acid (B) and the alcohol (C):

$$\mathrm{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3} + \mathrm{H_2O} \overset{\text{dil. } \mathrm{H_2SO_4}}{\rightleftharpoons} \mathrm{CH_3CH_2CH_2COOH} + \mathrm{CH_3CH_2CH_2CH_2OH}.$$

Acid hydrolysis is reversible; excess water favours the hydrolysis products.

Step 5: Verify the dehydration product Heating butan-1-ol with concentrated sulphuric acid at about $443\,\mathrm{K}$ removes its hydroxyl group and a hydrogen from the adjacent carbon as water. A double bond forms between the first two carbon atoms:

$$\mathrm{CH_3CH_2CH_2CH_2OH} \xrightarrow[443\,\mathrm{K}]{\text{conc. } \mathrm{H_2SO_4}} \mathrm{CH_2{=}CHCH_2CH_3} + \mathrm{H_2O}.$$

The product is but-1-ene, as required by the final clue.

Step 6: Conclusion (A) is **butyl butanoate**, $\mathrm{CH_3CH_2CH_2COOCH_2CH_2CH_2CH_3}$; (B) is **butanoic acid**, $\mathrm{CH_3CH_2CH_2COOH}$; and (C) is **butan-1-ol**, $\mathrm{CH_3CH_2CH_2CH_2OH}$. Their hydrolysis, oxidation and dehydration reactions satisfy all the given observations.

Quick Tip to Solve: Use the alkene to count the alcohol's carbons, then use oxidation to locate its hydroxyl group. Rebuild the ester from the resulting acid and alcohol, and check the molecular formula by subtracting water.

32(A). In the following complex ions, explain the type of hybridisation, shape and magnetic property :

[5 marks]

32(A)(a). $[Fe(H_2O)_6]^{2+}$ [2.5 marks]

Solution:

Concept:

- The metal oxidation state and its electronic configuration determine the number of d electrons available for pairing.
- Water is a weak-field ligand. In an octahedral iron(II) complex, it does not cause pairing of the initially unpaired $3d$ electrons.
- A complex with unpaired electrons is paramagnetic. Its spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\text{BM}$, where n is the number of unpaired electrons.

Step 1: Find the oxidation state and configuration Each water ligand is neutral, so the oxidation state of iron in $[Fe(H_2O)_6]^{2+}$ is $+2$. Iron has atomic number 26 and configuration $[\text{Ar}]\,3d^6 4s^2$. Removing the two $4s$ electrons gives

$$Fe^{2+}: \quad [\text{Ar}]\,3d^6.$$

Step 2: Identify the hybrid orbitals and shape The six water ligands give coordination number six. Since water is a weak-field ligand, the $3d^6$ electrons retain their high-spin arrangement: one $3d$ orbital contains a pair and the other four contain one electron each. There are no two vacant inner $3d$ orbitals for d^2sp^3 hybridisation. Instead, one $4s$, three $4p$ and two outer $4d$ orbitals form six sp^3d^2 hybrid orbitals. These point towards the vertices of an octahedron and accept the six ligand lone pairs.

Step 3: Count the unpaired electrons The high-spin octahedral configuration is $t_{2g}^4 e_g^2$. It contains four unpaired electrons, so the complex is attracted by a magnetic field. Its spin-only moment is

$$\mu = \sqrt{4(4+2)} = \sqrt{24} \approx 4.90\,\text{BM}.$$

Step 4: Conclusion $[Fe(H_2O)_6]^{2+}$ is an outer-orbital complex with sp^3d^2 hybridisation and octahedral shape. It is paramagnetic, with four unpaired electrons.

Quick Tip to Solve: First remove iron's two $4s$ electrons; then keep the resulting d^6 ion high spin because water is a weak-field ligand.

32(A)(b). $[NiCl_4]^{2-}$

(At. Nos. : Fe = 26, Ni = 28) [2.5 marks]

Solution:

Concept:

- The metal oxidation state follows from the overall complex charge and the charges of its ligands. Each chlorido ligand has charge -1.
- Chloride is a weak-field ligand. With nickel(II), it forms a tetrahedral complex using sp^3 hybrid orbitals rather than an inner-orbital square-planar complex.

Quick Tip to Solve: For a four-coordinate nickel(II) complex, check ligand strength: weak-field chloride gives tetrahedral sp^3 bonding and two unpaired electrons.

- Unpaired electrons cause paramagnetism. The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons.

Step 1: Obtain the metal-ion configuration Let the oxidation state of nickel be x. The four chloride ligands each carry charge -1, while the overall ion carries charge -2:

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

Nickel has atomic number 28 and configuration $[\mathrm{Ar}]\,3d^8 4s^2$. Loss of the two $4s$ electrons gives Ni^{2+} with configuration $[\mathrm{Ar}]\,3d^8$.

Step 2: Determine the hybridisation and geometry The coordination number is four. The weak-field chloride ligands do not cause the additional pairing needed to leave a vacant inner $3d$ orbital. One vacant $4s$ and three vacant $4p$ orbitals mix to form four sp^3 hybrid orbitals. Each accepts one lone pair from a chloride ligand. These four equivalent orbitals point towards the vertices of a tetrahedron; hence the geometry is tetrahedral.

Step 3: Determine the magnetic behaviour In the $3d^8$ arrangement, three orbitals contain electron pairs and two contain single electrons. Thus two electrons remain unpaired. Equivalently, the tetrahedral splitting gives $e^4 t_2^4$, with two unpaired electrons in the upper set. The spin-only magnetic moment is

$$\mu = \sqrt{2(2+2)} = \sqrt{8} \approx 2.83\,\mathrm{BM}.$$

Step 4: Conclusion $[\mathrm{NiCl_4}]^{2-}$ has sp^3 hybridisation and tetrahedral shape. It is paramagnetic, with two unpaired electrons.

Quick Tip to Solve: For a four-coordinate nickel(II) complex, check ligand strength: weak-field chloride gives tetrahedral sp^3 bonding and two unpaired electrons.

OR

32(B)(a). Write IUPAC names of the following :

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$

(ii) $[PtCl_4]^{2-}$

(iii) $[Cr(NH_3)_4Cl(ONO)]^{+}$ [3 marks]

Solution:

Concept:

- Name ligands in alphabetical order before the metal, ignoring multiplicative prefixes when alphabetising. Neutral water is aqua, NH_3 is ammine, CN^- is cyanido and Cl^- is chlorido.
- The metal oxidation state is obtained by equating the sum of the metal and ligand charges to the complex charge. Write it as a Roman numeral; an anionic complex uses the metal name ending in -ate.
- The neutral bidentate ligand en is ethane-1,2-diamine, with two such ligands named using bis. Oxygen-bound ONO^- is nitrito-O, distinguishing it from the nitrogen-bound linkage isomer.

Quick Tip to Solve: Calculate each metal charge first; use -ate only for the negative platinum complex and retain the O donor label for the nitrito ligand.

Step 1: Name the cobalt complex In $[Co(H_2O)(CN)(en)_2]^{2+}$, water and both en ligands are neutral, while cyanido has charge -1. If cobalt has oxidation state x,

$$x - 1 = +2 \quad \Rightarrow \quad x = +3.$$

The alphabetical sequence is aqua, cyanido, ethane-1,2-diamine. The positive complex retains the metal name cobalt. Its name is **aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion**.

Step 2: Name the platinum complex Each chlorido ligand in $[PtCl_4]^{2-}$ has charge -1, so

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

Four chlorido ligands give tetrachlorido. Since the complex is anionic, platinum becomes platinate: **tetrachloridoplatinate(II) ion**.

Step 3: Name the chromium complex In $[Cr(NH_3)_4Cl(ONO)]^{+}$, the four ammine ligands are neutral, while chlorido and nitrito each contribute -1. Thus

$$x - 1 - 1 = +1 \quad \Rightarrow \quad x = +3.$$

List ammine, chlorido and nitrito-O alphabetically. The written ONO linkage shows oxygen as the donor atom. The name is **tetraamminechloridonitrito-O-chromium(III) ion**.

Step 4: Conclusion (i) Aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion; (ii) tetrachloridoplatinate(II) ion; (iii) tetraamminechloridonitrito-O-chromium(III) ion.

Quick Tip to Solve: Calculate each metal charge first; use -ate only for the negative platinum complex and retain the O donor label for the nitrito ligand.

32(B)(b). What is spectrochemical series ? Write the difference between a strong field ligand and a weak field ligand. [2 marks]

Solution:

Concept:

- Ligands split the metal d-orbitals into groups of different energies. The splitting energy, denoted by Δ, measures the ligand-field strength for a given metal ion and geometry.
- The competition between orbital splitting and electron-pairing energy P determines whether electrons pair in the lower set or occupy higher orbitals.

Step 1: Define the spectrochemical series The spectrochemical series is the arrangement of ligands in increasing order of their crystal-field splitting power. It is determined experimentally from spectra. A representative increasing sequence is

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < CN^- < CO.$$

Ligands towards the left produce smaller splitting than those towards the right when compared for the same metal ion and geometry.

Quick Tip to Solve: Compare Δ_o with P: splitting larger than pairing energy favours pairing, while smaller splitting favours high spin.

Step 2: Distinguish strong and weak field ligands A strong field ligand, such as CN^- or CO, produces a large splitting. For an octahedral complex, when $\Delta_o > P$, electrons preferentially pair in the lower-energy orbitals, giving a low-spin arrangement where a spin choice exists. A weak field ligand, such as F^- or Cl^-, produces a small splitting. When $\Delta_o < P$, electrons occupy the higher-energy orbitals before additional pairing, giving a high-spin arrangement. Hence strong and weak fields can give different numbers of unpaired electrons for the same suitable d-electron count.

Step 3: Conclusion The spectrochemical series orders ligands by increasing splitting power. Strong field ligands give larger splitting and favour pairing; weak field ligands give smaller splitting and favour unpaired occupancy where alternative spin arrangements are possible.

Quick Tip to Solve: Compare Δ_o with P: splitting larger than pairing energy favours pairing, while smaller splitting favours high spin.

33(A)(a). Write the cell reaction and calculate the e.m.f. of the following cell at 298 K :
Sn(s) | Sn^{2+} (0.004 M) || H^+ (0.02 M) | H_2(g) (1 Bar) | Pt(s)
(Given : $E^\circ_{Sn^{2+}/Sn}$ = -0.14 V, $E^\circ_{H^+|H_2(g),\,Pt}$ = 0.00 V) [3 marks]

Solution:

Concept:

- In the written galvanic cell, the left electrode is the anode (oxidation) and the right electrode is the cathode (reduction). Using reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- 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 transferred and Q is the dimensionless reaction quotient. Pure solids have unit activity.

Step 1: Balance the electrode reactions Tin is oxidised at the left electrode, while hydrogen ions are reduced at the platinum electrode:

$$\text{Anode: } \mathrm{Sn(s)} \longrightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-}$$
$$\text{Cathode: } 2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}.$$

Adding cancels two electrons, so $n = 2$. The overall cell reaction is

$$\mathrm{Sn(s)} + 2\,\mathrm{H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}.$$

Step 2: Calculate the standard cell potential and quotient Both given electrode potentials are reduction potentials. Therefore,

$$E^\circ_{\text{cell}} = 0.00 - (-0.14) = 0.14\,\mathrm{V}.$$

With aqueous activities approximated by concentrations relative to 1 M, and gas activity by pressure relative to 1 bar,

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.004 \times 1}{(0.02)^2} = 10.$$

Quick Tip to Solve: Balance the reaction before forming Q: two hydrogen ions give the square in the denominator and also set $n = 2$.

The hydrogen-ion concentration is squared because its coefficient in the balanced reaction is two; solid tin does not enter the quotient.

Step 3: Apply the Nernst correction Substituting $n = 2$, $Q = 10$ and $\log 10 = 1$,

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

Since $Q > 1$, the correction lowers the e.m.f. below its standard value, as the calculation shows.

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 the e.m.f. at 298 K is $E_{\text{cell}} \approx 0.110\,\text{V}$.

Quick Tip to Solve: Balance the reaction before forming Q: two hydrogen ions give the square in the denominator and also set $n = 2$.

33(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:

- Standard electrode potentials describe thermodynamic tendency. The actual product of electrolysis also depends on the additional potential, or overpotential, needed to make an electrode reaction proceed at an appreciable rate.
- Conductivity κ depends on the number of charge-carrying ions per unit volume and their mobility. Molar conductivity Λ_m, however, measures conduction per mole of electrolyte; these are different quantities.

Step 1: Explain chlorine evolution at the anode The standard potentials suggest oxidation of water to oxygen in preference to oxidation of chloride ions. However, oxygen evolution has a high overpotential: its electrode reaction is kinetically hindered and requires a substantially greater applied potential than the equilibrium value. Consequently, chloride oxidation occurs preferentially under the stated aqueous sodium chloride electrolysis conditions:

$$2\,\text{Cl}^-\text{(aq)} \longrightarrow \text{Cl}_2\text{(g)} + 2\,\text{e}^-.$$

Thus the thermodynamic prediction from standard potentials alone does not decide the observed anode product.

Step 2: Explain the decrease in conductivity on dilution Acetic acid is a weak electrolyte:

$$\text{CH}_3\text{COOH(aq)} \rightleftharpoons \text{H}^+\text{(aq)} + \text{CH}_3\text{COO}^-\text{(aq)}.$$

Dilution increases its degree of ionisation, but also increases the solution volume. The number of ions

Quick Tip to Solve: For electrolysis include overpotential; for dilution check whether the question asks for conductivity or molar conductivity before deciding the trend.

per unit volume decreases overall, so conductivity κ decreases. This must be distinguished from molar conductivity, which increases because a larger fraction of each mole ionises on dilution.

Step 3: Conclusion (i) The high overpotential for oxygen evolution permits preferential liberation of Cl_2 at the anode. (ii) The ionic concentration per unit volume falls on dilution of CH_3COOH, so its conductivity decreases despite increased ionisation.

Quick Tip to Solve: For electrolysis include overpotential; for dilution check whether the question asks for conductivity or molar conductivity before deciding the trend.

OR

33(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 use, a lead storage battery discharges as a galvanic cell: oxidation occurs at its lead anode and reduction occurs at its lead dioxide cathode.
- Sulfuric acid supplies H^+ and $SO_4{}^{2-}$ ions. Both electrode materials are converted into $PbSO_4$; electrons cancel when the half-reactions are added.

Step 1: Write the anode oxidation Lead at the negative electrode loses two electrons. The resulting lead(II) ions combine with sulfate ions to form insoluble lead sulfate:

$$Pb\,(s) + SO_4{}^{2-}(aq) \longrightarrow PbSO_4(s) + 2\,e^-.$$

Thus, the oxidation state of lead increases from 0 to $+2$.

Step 2: Write the cathode reduction Lead dioxide at the positive electrode accepts the two electrons released by the anode. In the acidic electrolyte, lead(IV) is reduced to lead(II):

$$PbO_2(s) + SO_4{}^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O\,(l).$$

The hydrogen ions and oxygen atoms combine to produce water.

Step 3: Combine the electrode reactions Add the two half-reactions and cancel the two electrons. The consumed $4H^+$ and $2SO_4{}^{2-}$ together correspond to $2H_2SO_4$. Sulfuric acid is consumed during discharge, so its concentration decreases as the battery is used.

Step 4: Conclusion The overall discharge reaction is

$$Pb\,(s) + PbO_2(s) + 2\,H_2SO_4(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O\,(l).$$

The lead electrode is the anode and the lead dioxide electrode is the cathode during use.

Quick Tip to Solve: For discharge, remember that both lead electrodes become $PbSO_4$. Put electrons on the right at the lead anode and on the left at the lead dioxide cathode.

33(B)(b). Calculate the potential for half-cell containing 0.01 M $K_2Cr_2O_7$(aq), 0.01 M Cr^{3+}(aq) and 1.0×10^{-4} M H^+(aq).

The half cell reaction is

$Cr_2O_7^{2-}$(aq) + 14H^+(aq) + 6e^- $\rightarrow$ 2Cr^{3+}(aq) + 7H_2O(l)

and the standard electrode potential is given as E° = 1.33 V.

[Given : log 10 = 1] [3 marks]

Solution:

Concept:

- The Nernst equation gives the reduction potential at 298 K: $E = E^\circ - (0.0591/n)\log Q$, where n is the number of electrons in the balanced half-reaction and Q is its reaction quotient.
- Concentrations enter Q raised to their stoichiometric coefficients. Electrons are excluded, and the activity of pure liquid water is unity; dilute ionic concentrations are used relative to the standard concentration.

Step 1: Identify the electron transfer and reaction quotient In the given reduction, one dichromate ion accepts six electrons to form two chromium(III) ions. Hence $n = 6$, and

$$Q = \frac{[Cr^{3+}]^2}{[Cr_2O_7{}^{2-}][H^+]^{14}}.$$

The power of fourteen for hydrogen ions is essential because the balanced half-reaction consumes fourteen hydrogen ions. The pure water product does not contribute a concentration factor.

Step 2: Substitute the ionic concentrations Each formula unit of $K_2Cr_2O_7$ supplies one dichromate ion. Thus, $[Cr_2O_7{}^{2-}] = 0.01$ M, while $[Cr^{3+}] = 0.01$ M and $[H^+] = 10^{-4}$ M. Therefore,

$$\begin{aligned} Q &= \frac{(10^{-2})^2}{(10^{-2})(10^{-4})^{14}} \\ &= \frac{10^{-4}}{10^{-58}} = 10^{54}, \\ \log Q &= 54 \log 10 = 54. \end{aligned}$$

The potassium ions are spectators and do not enter the electrode reaction or its quotient.

Step 3: Evaluate the reduction potential Using the given standard reduction potential $E^\circ = 1.33$ V in the Nernst equation,

$$\begin{aligned} E &= 1.33 - \frac{0.0591}{6}(54) \\ &= 1.33 - 0.5319 \\ &= 0.7981 \text{ V}. \end{aligned}$$

Since $Q > 1$, the correction is subtracted and the reduction potential is lower than its standard value. The very small hydrogen-ion concentration strongly reduces the tendency of dichromate to undergo this reduction.

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

Quick Tip to Solve: Write the hydrogen-ion factor as $(10^{-4})^{14} = 10^{-56}$ before simplifying Q; overlooking the power fourteen changes the potential substantially.