CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.

(iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section –A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is NOT allowed.

Section A (16 marks)

1. Consider the following reaction:

$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightarrow Zn^{2+}{}_{(aq)} + 2Ag_{(s)} + 2OH^-{}_{(aq)}$

Given: $E^\circ_{Ag^+/Ag} = 0.80\ V$, $E^\circ_{Zn^{2+}/Zn} = -0.76\ V$, **1 F = 96500 C mol^{-1}.**

$\Delta_r G^\circ$ for the above reaction is: [1 mark]

(A) -301.080 kJ mol^{-1}

(B) $+310.080$ kJ mol^{-1}

(C) -326.070 kJ mol^{-1}

(D) -375.060 kJ mol^{-1}

Correct Answer: (A) -301.080 kJ mol^{-1}

Solution:

Concept:

- The standard Gibbs energy change is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- Using the supplied standard reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

Step 1: Identify the electron transfer Zinc is oxidised according to $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\,\text{e}^-$. The two silver atoms are reduced from oxidation state $+1$ to zero, so the reaction as written transfers $n = 2$ electrons. Using the given potentials, the cathode value is $0.80\,\text{V}$ and the anode reduction value is $-0.76\,\text{V}$.

Step 2: Calculate the energy change

$$E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56\,\text{V}.$$

$$\Delta_r G^\circ = -2(96500)(1.56) = -301080\,\text{J mol}^{-1}.$$

Divide by 1000 to convert joules to kilojoules. A positive Gibbs energy, as in (B), has the wrong sign for this positive cell potential. The magnitudes in (C) and (D) do not follow from the supplied potentials and the two-electron transfer.

Step 3: Conclusion $\Delta_r G^\circ = -301.080\,\text{kJ mol}^{-1}$. Hence, the correct option is (A).

Quick Tip to Solve: Count electrons from zinc oxidation first, then subtract the negative zinc reduction potential before using $-nFE^\circ$.

2. Identify the correct statement: [1 mark]

(A) Molecularity of a reaction is an experimental quantity.

(B) For complex reactions molecularity has no meaning.

(C) Molecularity of a reaction can be zero or even a fraction.

(D) Molecularity more than three is very common in chemical reactions.

Correct Answer: (B) For complex reactions molecularity has no meaning.

Solution:

Concept:

- Molecularity counts the reacting species participating in one elementary reaction step; it is a positive whole number.
- For a complex reaction, elementary steps can each have molecularity, but a single molecularity is not assigned to the overall reaction.

Step 1: Apply the definition A complex reaction proceeds through a sequence of elementary steps. Its overall balanced equation does not represent one simultaneous molecular collision, so molecularity has no meaning for that overall reaction. This is the statement in (B).

Step 2: Check the other statements Option (A) confuses molecularity with reaction order, which is determined experimentally from the rate law. Option (C) is false because a count of participating reacting species cannot be zero or fractional. Option (D) is false because simultaneous collisions involving more than three reacting species are extremely unlikely; such high molecularity is not common.

Step 3: Conclusion For complex reactions molecularity has no meaning for the overall reaction. Hence, the correct option is (B).

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

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3. The order for the given reaction is:

A + 2B $\rightarrow$ Products

Rate = $k[A]^{1/2}[B]^{1}$ [1 mark]

(A) 1.5

(B) 1

(C) 0.5

(D) 2

Correct Answer: (A) 1.5

Solution:

Concept:

- The overall order of a reaction is the sum of the concentration exponents in its experimentally determined rate law.

Quick Tip to Solve: Underline only the powers attached to concentrations in the rate law and add them; ignore the balanced-equation coefficients.

- Stoichiometric coefficients in the overall reaction equation do not, in general, determine the order.

Step 1: Read the concentration powers The given rate law is Rate $= k[A]^{1/2}[B]^{1}$. Thus the partial order with respect to A is $1/2$, while the partial order with respect to B is 1. These values come from the rate expression rather than the coefficients in $\mathrm{A} + 2\,\mathrm{B} \longrightarrow \mathrm{Products}$.

Step 2: Add the partial orders

$$\text{Overall order} = \frac{1}{2} + 1 = \frac{3}{2} = 1.5.$$

Option (B) uses only the exponent of B, and option (C) uses only the exponent of A. Option (D) is not the sum of the given exponents and may result from incorrectly using the coefficient of B. Fractional orders are allowed because order is an experimental kinetic quantity.

Step 3: Conclusion The reaction is of order 1.5. Hence, the correct option is (A).

Quick Tip to Solve: Underline only the powers attached to concentrations in the rate law and add them; ignore the balanced-equation coefficients.

4. Electronic configuration of chromium is: [1 mark]

(A) [Ar] $3d^4\ 4s^1$

(B) [Ar] $3d^4\ 4s^2$

(C) [Ar] $3d^5\ 4s^1$

(D) [Ar] $3d^5\ 4s^2$

Correct Answer: (C) [Ar] $3d^5\ 4s^1$

Solution:

Concept:

- Chromium has atomic number 24, so its ground-state configuration must account for 24 electrons.
- A half-filled $3d^5$ subshell has enhanced stability; chromium adopts $[\mathrm{Ar}]\,3d^5\,4s^1$.

Step 1: Count electrons beyond argon The argon core contains 18 electrons. Chromium therefore has $24 - 18 = 6$ electrons outside this core. Both $3d^4 4s^2$ and $3d^5 4s^1$ have the correct count, so electron counting alone cannot distinguish (B) and (C).

Step 2: Use the stable ground-state arrangement The small energy separation between the $3d$ and $4s$ orbitals allows the configuration with a half-filled $3d$ subshell to be favoured. Enhanced exchange stabilisation is associated with $3d^5$, giving $[\mathrm{Ar}]\,3d^5\,4s^1$. Option (B) is the simple expected filling arrangement, but not the actual ground state. Option (A) totals 23 electrons and option (D) totals 25, so neither describes neutral chromium.

Step 3: Conclusion The electronic configuration is $[\mathrm{Ar}]\,3d^5\,4s^1$. Hence, the correct option is (C).

Quick Tip to Solve: For chromium, retain six electrons beyond argon but distribute them as five in $3d$ and one in $4s$.

5. The correct IUPAC name of the complex $[Pt(NH_3)_2Cl_2]$ is: [1 mark]

(A) diamminedichloridoplatinum (IV)

(B) diamminedichloridoplatinum (II)

(C) dichloridodiammineplatinum (IV)

(D) dichloridodiammineplatinum (II)

Correct Answer: (B) diamminedichloridoplatinum (II)

Solution:

Concept:

- In $[Pt(NH_3)_2Cl_2]$, ammine ligands are neutral and each chlorido ligand has charge -1.
- Ligand names are placed alphabetically, ignoring multiplicative prefixes; the metal oxidation state is stated in Roman numerals.

Step 1: Determine the platinum oxidation state Let the oxidation state of platinum be x. The complex is neutral, so

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

Consequently, the metal is named platinum(II). Options (A) and (C), which specify platinum(IV), contradict the charge balance.

Step 2: Arrange the ligand names Two NH_3 ligands give diammine, and two Cl^- ligands give dichlorido. Alphabetical order is determined by ammine and chlorido, not by the prefix di, so ammine precedes chlorido. The complete name is diamminedichloridoplatinum(II). Option (D) has the right oxidation state but reverses the ligand-name order.

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

Quick Tip to Solve: First calculate the metal charge, then alphabetise ammine before chlorido while ignoring the prefix di.

6. Which of the following is a heteroleptic complex? [1 mark]

(A) $[Co(NH_3)_6]^{3+}$

(B) $[Cr(NH_3)_6]^{3+}$

(C) $[Ni(H_2O)_6]^{2+}$

(D) $[Co(NH_3)_4Cl_2]^{+}$

Correct Answer: (D) $[Co(NH_3)_4Cl_2]^{+}$

Solution:

Concept:

- A heteroleptic complex contains more than one type of ligand bonded to the central metal ion.
- A homoleptic complex contains only one ligand type, even when several copies of that ligand are present.

Step 1: Inspect the ligand types In $[Co(NH_3)_6]^{3+}$ and $[Cr(NH_3)_6]^{3+}$, all six ligands are ammine. In

Quick Tip to Solve: Look inside the coordination brackets and count different ligand types, rather than total ligands or metal charges.

$[Ni(H_2O)_6]^{2+}$, all six are aqua ligands. Thus (A), (B) and (C) are homoleptic; changing the central metal or total charge does not create a second ligand type.

Step 2: Identify the mixed-ligand complex The complex $[Co(NH_3)_4Cl_2]^+$ has four ammine ligands and two chlorido ligands attached to cobalt. Because these are two chemically different ligand types in the same coordination sphere, the complex is heteroleptic. The number of ligands is not the deciding test; their chemical identities are.

Step 3: Conclusion $[Co(NH_3)_4Cl_2]^+$ is heteroleptic. Hence, the correct option is (D).

Quick Tip to Solve: Look inside the coordination brackets and count different ligand types, rather than total ligands or metal charges.

7. Which of the following molecules is chiral in nature? [1 mark]

(A) Propan-2-ol

(B) Butan-2-ol

(C) 1-Bromobutane

(D) 2-Bromopropane

Correct Answer: (B) Butan-2-ol

Solution:

Concept:

- A tetrahedral carbon bonded to four different substituents is an asymmetric carbon and can make these simple molecules chiral.
- A carbon bonded to two identical substituents is not an asymmetric centre.

Step 1: Examine butan-2-ol Butan-2-ol has the condensed structure $CH_3CH(OH)CH_2CH_3$. Its second carbon is bonded to H, OH, CH_3 and CH_2CH_3. All four substituents differ, so it has an asymmetric carbon and exists as a pair of non-superimposable mirror-image forms.

Step 2: Check the remaining molecules In propan-2-ol, the carbon bearing OH has two identical methyl groups. In 2-bromopropane, the carbon bearing bromine also has two identical methyl groups. In 1-bromobutane, the carbon bonded to bromine is CH_2, with two identical hydrogen atoms, and no other carbon has four different substituents. These three molecules are achiral.

Step 3: Conclusion Butan-2-ol is chiral in nature. Hence, the correct option is (B).

Quick Tip to Solve: At the substituted carbon, compare the two carbon chains: methyl and ethyl differ in butan-2-ol, but two methyl groups do not.

8. Identify the correct increasing order of boiling points of the given compounds: [1 mark]

(A) Propan-1-ol $<$ butan-1-ol $<$ butan-2-ol $<$ pentan-1-ol

(B) Pentan-1-ol $<$ butan-1-ol $<$ butan-2-ol $<$ propan-1-ol

(C) Propan-1-ol $<$ butan-2-ol $<$ butan-1-ol $<$ pentan-1-ol

(D) Butan-1-ol $<$ butan-2-ol $<$ propan-1-ol $<$ pentan-1-ol

Correct Answer: (C) Propan-1-ol $<$ butan-2-ol $<$ butan-1-ol $<$ pentan-1-ol

Solution:

Concept:

- All four alcohols have one hydroxyl group, so intermolecular hydrogen bonding operates in each.
- Within a homologous series, greater molecular size strengthens London dispersion forces; a less compact carbon framework generally has a larger effective contact area.

Step 1: Compare the carbon-chain lengths Propan-1-ol has three carbon atoms and pentan-1-ol has five. With one hydroxyl group in each molecule, increasing the carbon-chain length increases dispersion forces and generally raises the boiling point. Hence propan-1-ol has the lowest and pentan-1-ol the highest boiling point among these compounds.

Step 2: Compare the two four-carbon alcohols Butan-1-ol and butan-2-ol have the same molecular formula. Butan-1-ol has its hydroxyl group at the end of the chain and stronger effective intermolecular association than butan-2-ol, whose hydroxyl group is on an internal carbon. Thus butan-2-ol boils below butan-1-ol. Option (A) reverses this pair; (B) places the largest alcohol first; and (D) incorrectly places both butanols below propan-1-ol.

Step 3: Conclusion The increasing order is propan-1-ol $<$ butan-2-ol $<$ butan-1-ol $<$ pentan-1-ol. Hence, the correct option is (C).

Quick Tip to Solve: Place the three-carbon alcohol first and the five-carbon alcohol last; then put butan-2-ol before butan-1-ol.

9. Identify the compound produced by the reduction of Ethanenitrile with Lithium aluminium hydride: [1 mark]

(A) Ethylamine

(B) Ethanal

(C) Propylamine

(D) Methylamine

Correct Answer: (A) Ethylamine

Solution:

Concept:

- Lithium aluminium hydride, $LiAlH_4$, reduces a nitrile group to a primary amine.
- The conversion is $R{-}C \equiv N \rightarrow R{-}CH_2NH_2$; the nitrile carbon remains in the product.

Step 1: Write the structure of ethanenitrile Ethanenitrile is $CH_3C \equiv N$. Its two-carbon skeleton

Quick Tip to Solve: Count the nitrile carbon as part of the chain: a two-carbon nitrile gives a two-carbon primary amine.

includes the carbon of the nitrile group. Reduction adds hydrogen to the carbon-nitrogen group without adding or removing a carbon atom.

Step 2: Identify the reduction product On reduction with lithium aluminium hydride followed by hydrolysis, the reaction is

$$CH_3C \equiv N + 4[H] \longrightarrow CH_3CH_2NH_2.$$

The product is the two-carbon primary amine. Ethanal is an aldehyde, whereas this reagent gives the amine from a nitrile. Propylamine would require three carbons, and methylamine would have only one carbon; neither preserves the ethanenitrile skeleton.

Step 3: Conclusion Ethanenitrile gives ethylamine, $CH_3CH_2NH_2$. Hence, the correct option is (A).

Quick Tip to Solve: Count the nitrile carbon as part of the chain: a two-carbon nitrile gives a two-carbon primary amine.

10. The base which is present in DNA but not in RNA is: [1 mark]

(A) Guanine

(B) Cytosine

(C) Thymine

(D) Adenine

Correct Answer: (C) Thymine

Solution:

Concept:

- DNA contains the nitrogenous bases adenine, guanine, cytosine and thymine.
- RNA contains adenine, guanine, cytosine and uracil; uracil replaces thymine in the standard base set.

Step 1: Compare the base sets The purine bases adenine and guanine occur in both DNA and RNA. Cytosine, a pyrimidine base, also occurs in both. Consequently options (A), (B) and (D) cannot identify the base that distinguishes DNA from RNA.

Step 2: Identify the distinguishing pyrimidine The remaining DNA base is thymine. In RNA the corresponding base is uracil, which pairs with adenine. Therefore the difference asked here concerns the nitrogenous base set, rather than the sugar difference between deoxyribose in DNA and ribose in RNA.

Step 3: Conclusion Thymine is present in DNA but not in the standard base set of RNA. Hence, the correct option is (C).

Quick Tip to Solve: Use the base sets A, G, C, T for DNA and A, G, C, U for RNA; only T is unique to DNA in this comparison.

11. Proteins are polymers of α-amino acids which are joined to each other by: [1 mark]

(A) Covalent Bond

(B) Peptide Bond

(C) Glycosidic Bond

(D) Coordinate Bond

Correct Answer: (B) Peptide Bond

Solution:

Concept:

- A peptide linkage is the amide group $-CO-NH-$ joining successive amino-acid residues.
- It forms by condensation of the carboxyl group of one amino acid with the amino group of another, with elimination of water.

Step 1: Identify the groups that join Each α-amino acid contains an amino group and a carboxyl group attached to the same α-carbon. During protein formation, the carboxyl group of one amino acid reacts with the amino group of the next, eliminating a molecule of water and forming the linkage $-CO-NH-$.

Step 2: Choose the specific name of the linkage This linkage is specifically called a peptide bond. It is covalent in nature, so option (A) gives only a broad class of bond; option (B) names the characteristic linkage between amino-acid residues. Glycosidic bonds join sugar units in carbohydrates, while coordinate bonds are not the backbone linkages joining amino acids in proteins.

Step 3: Conclusion Proteins contain peptide bonds, $-CO-NH-$, between successive amino-acid residues. Hence, the correct option is (B).

Quick Tip to Solve: When amino acids join through carboxyl and amino groups, select the specific name peptide bond, not the general category covalent bond.

12. Which of the following reactions is not explained by the open chain structure of glucose? [1 mark]

(A) Glucose on prolonged heating with HI forms *n*-hexane.

(B) Glucose reacts with hydroxylamine to form an oxime.

(C) Glucose gets oxidized to gluconic acid on reaction with bromine water.

(D) Glucose exists in two different crystalline forms, alpha (α) and beta (β).

Correct Answer: (D) Glucose exists in two different crystalline forms, alpha (α) and beta (β).

Solution:

Concept:

- The open-chain formula of glucose is $CHO-(CHOH)_4-CH_2OH$; it has an aldehyde group and an unbranched six-carbon chain.
- The α and β forms are cyclic hemiacetal anomers differing in the configuration at the anomeric carbon.

Step 1: Test reactions explained by the open chain Prolonged heating with HI gives n-hexane, sup-

Quick Tip to Solve: Aldehyde reactions fit the open chain; the alpha/beta pair points to a cyclic hemiacetal and its anomeric carbon.

porting the straight six-carbon skeleton in option (A). The aldehyde group reacts with hydroxylamine to give an oxime, explaining option (B). Mild oxidation with bromine water converts this aldehyde group into a carboxyl group and gives gluconic acid, explaining option (C).

Step 2: Identify the observation requiring the cyclic structure The open chain contains no hemiacetal anomeric centre and does not explain the two distinct crystalline forms. Intramolecular reaction of the aldehyde group with a hydroxyl group forms a cyclic hemiacetal. Two configurations of the hydroxyl group at carbon 1 then account for α- and β-glucose. Thus option (D) requires the cyclic structure.

Step 3: Conclusion The existence of two crystalline forms, α- and β-glucose, is not explained by the open-chain structure. Hence, the correct option is (D).

Quick Tip to Solve: Aldehyde reactions fit the open chain; the alpha/beta pair points to a cyclic hemiacetal and its anomeric carbon.

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13. Assertion (A): The molecularity of the given reaction is 2.

$2HI \rightarrow H_2 + I_2$

Reason (R): Two molecules of the reactants are involved in simultaneous collision between them.

[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:

- Molecularity is the number of reacting species participating together in an elementary reaction step.
- A step involving two reactant molecules is bimolecular and has molecularity 2; product molecules are not counted.

Step 1: Judge the assertion For the stated reaction $2HI \longrightarrow H_2 + I_2$, the reacting event represented involves two HI molecules. The molecularity for this event is therefore 2, so the assertion is true. The two products do not enter the count of reacting molecules.

Step 2: Judge the reason The reason states that two molecules of the reactants participate in a simultaneous collision. This is the defining description of a bimolecular elementary event, so the reason is true.

Step 3: Check the explanatory connection Molecularity is obtained by counting the reactant molecules participating in that event. Since the reason gives precisely this count as two, it directly explains

Quick Tip to Solve: For molecularity, count the reactant molecules involved in the stated elementary event, not the product molecules or the total coefficients.

the asserted molecularity. Option (B) wrongly denies the explanatory link, and options (C) and (D) incorrectly declare one of the true statements false.

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

Quick Tip to Solve: For molecularity, count the reactant molecules involved in the stated elementary event, not the product molecules or the total coefficients.

14. Assertion (A): Zinc, cadmium and mercury are not considered as transition elements.

Reason (R): These elements have completely filled orbitals in their ground state as well as in their common oxidation states. [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 transition element has an incompletely filled d-subshell in its atom or in one of its common oxidation states.
- Zn, Cd and Hg retain a filled d^{10} subshell in their ground-state atoms and their common ions.

Step 1: Judge the assertion Zinc, cadmium and mercury belong to the d-block but do not meet the standard transition-element criterion. Their atoms have filled d-subshells, and their common ions do not introduce an incompletely filled d-subshell. Thus the assertion is true.

Step 2: Judge the reason The completely filled orbitals referred to here are the relevant d-orbitals. The ground-state configurations are $\mathrm{Zn} : [\mathrm{Ar}]3\mathrm{d}^{10}4\mathrm{s}^2$, $\mathrm{Cd} : [\mathrm{Kr}]4\mathrm{d}^{10}5\mathrm{s}^2$ and $\mathrm{Hg} : [\mathrm{Xe}]4\mathrm{f}^{14}5\mathrm{d}^{10}6\mathrm{s}^2$. Their common $+2$ ions lose the outer s-electrons and retain d^{10}. Hence the reason is true in this transition-element context.

Step 3: Check the explanatory connection The filled d-subshells explain why these elements fail the incomplete-d-subshell criterion. Therefore the reason directly explains the assertion. Option (B) incorrectly denies this link, while options (C) and (D) incorrectly classify one statement as false.

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

Quick Tip to Solve: For a transition element, check both the atom and common ions for an incomplete d subshell; a persistent d10 configuration excludes Zn, Cd and Hg.

15. Assertion (A): Aromatic primary amines can be prepared by Gabriel Phthalimide synthesis.
Reason (R): Aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

[1 mark]

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

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

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

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

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

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylating the phthalimide anion and then hydrolysing the product.
- Aryl halides resist the nucleophilic substitution needed for this synthesis because their carbon-halogen bond has partial double-bond character.

Step 1: Judge the assertion Assertion (A) is false. In Gabriel synthesis, the phthalimide anion reacts with an alkyl halide to form an alkyl-substituted phthalimide; hydrolysis then releases a primary aliphatic amine. An aromatic primary amine such as aniline cannot be prepared by using an aryl halide in this method.

Step 2: Judge the reason Reason (R) is true. In an aryl halide, resonance gives the carbon-halogen bond partial double-bond character, and the carbon bonded to halogen is sp^2-hybridised. Aryl halides therefore do not undergo the required nucleophilic substitution with the phthalimide anion under Gabriel synthesis conditions.

Step 3: Match the truth values to the options Since A is false and R is true, R identifies the limitation that makes A incorrect; it cannot explain A as a true statement. Options (A) and (B) wrongly classify A as true, while option (C) also wrongly classifies R as false.

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

Quick Tip to Solve: For Gabriel synthesis, check whether the halide is alkyl or aryl: alkyl halides give primary aliphatic amines, whereas aryl halides do not give aromatic amines by this route.

16. Assertion (A): Glucose gets oxidized to six carbon gluconic acid on reaction with bromine water.
Reason (R): The carbonyl group is absent in the open chain structure of glucose. [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:

- Open-chain glucose is an aldohexose: it contains six carbon atoms and a terminal aldehyde group, $-\mathrm{CHO}$.
- Bromine water is a mild oxidising agent that converts an aldehyde group into a carboxylic acid group without changing the carbon chain.

Step 1: Judge the assertion Assertion (A) is true. Bromine water oxidises the aldehyde group of glucose to a carboxylic acid group, giving gluconic acid. The six-carbon skeleton is retained:

$$\mathrm{CHO{-}(CHOH)_4{-}CH_2OH + Br_2 + H_2O \longrightarrow HOOC{-}(CHOH)_4{-}CH_2OH + 2\,HBr.}$$

The terminal primary alcohol group remains unchanged by this mild oxidation.

Step 2: Judge the reason Reason (R) is false. The open-chain structure of glucose has an aldehyde group at carbon 1. This group contains a carbonyl bond, $\mathrm{C{=}O}$; hence the claim that its open-chain structure lacks a carbonyl group is incorrect.

Step 3: Check the explanatory relationship Oxidation to gluconic acid occurs precisely because glucose has an aldehyde carbonyl group. The false reason cannot explain the true assertion. Options (A) and (B) incorrectly call the reason true, and option (D) incorrectly calls the assertion false.

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

Quick Tip to Solve: With bromine water, change the terminal $-\mathrm{CHO}$ group of glucose to $-\mathrm{COOH}$, keeping all six carbons and the terminal $-\mathrm{CH_2OH}$ group intact.

Section B (10 marks)

17(A). The concentration of the reactant is reduced from 0.6 mol L^{-1} to 0.2 mol L^{-1} in 5 minutes in a first order reaction. Calculate the rate constant of the reaction. (log 3 = 0.48) [2 marks]

Solution:

Concept:

- A first-order reaction obeys rate $= k[A]$, where k is the rate constant and $[A]$ is the reactant concentration.
- Its integrated rate equation is $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the initial and remaining concentrations at time t; the logarithm is to base 10.

Step 1: Identify the concentration ratio The initial concentration is $[A]_0 = 0.6\,\text{mol L}^{-1}$, the concentration remaining after $t = 5\,\text{min}$ is $[A]_t = 0.2\,\text{mol L}^{-1}$. The integrated equation uses concentration remaining, so

$$\frac{[A]_0}{[A]_t} = \frac{0.6}{0.2} = 3.$$

Both concentrations have the same units, making the ratio dimensionless.

Step 2: Substitute into the integrated rate equation Using the supplied $\log 3 = 0.48$,

$$\begin{aligned} k &= \frac{2.303}{5}\log 3 \\ &= \frac{2.303 \times 0.48}{5} \\ &= 0.221088\,\text{min}^{-1}. \end{aligned}$$

Since time was substituted in minutes, the rate constant is expressed in inverse minutes. If expressed in seconds, divide this value by 60 to obtain $3.68 \times 10^{-3}\,\text{s}^{-1}$.

Step 3: Conclusion The rate constant is $\boxed{k \approx 0.221\,\text{min}^{-1}}$, equivalent to $3.68 \times 10^{-3}\,\text{s}^{-1}$, using the supplied logarithm.

Quick Tip to Solve: In a first-order calculation, use initial concentration divided by concentration remaining, and keep the time unit consistent with the unit of k.

OR

17(B). Rate constant *k* for the first order reaction is 2.54 $\times$ 10^{-3} s^{-1}. Calculate the time required for three-fourth of the reactant to decompose. (log 4 = 0.60) [2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \dfrac{2.303}{k}\log\dfrac{[A]_0}{[A]_t}$, where k is the rate constant, $[A]_0$ the initial concentration and $[A]_t$ the concentration remaining at time t.

Quick Tip to Solve: Three-fourths decomposed means one-fourth remains; insert the ratio 4 in the first-order equation, or recognise that this corresponds to two half-lives.

- If a fraction f decomposes, the fraction remaining is $1-f$; the integrated equation uses the reactant remaining rather than the amount decomposed.

Step 1: Find the fraction of reactant remaining Three-fourths of the reactant decomposes, so one-fourth remains:

$$\frac{[A]_t}{[A]_0} = 1 - \frac{3}{4} = \frac{1}{4}, \qquad \frac{[A]_0}{[A]_t} = 4.$$

No particular initial concentration is needed because it cancels in this ratio. Taking the fraction decomposed as the remaining fraction would give the wrong time.

Step 2: Calculate the time using the given rate constant Substitute $k = 2.54 \times 10^{-3}\,\text{s}^{-1}$ and the supplied $\log 4 = 0.60$:

$$\begin{aligned} t &= \frac{2.303}{2.54 \times 10^{-3}} \log 4 \\ &= \frac{2.303 \times 0.60}{2.54 \times 10^{-3}} \\ &= \frac{1.3818}{0.00254} = 544.02\,\text{s}. \end{aligned}$$

The inverse-second unit of k makes the calculated time seconds. Dividing by 60 gives about 9.07 min.

Step 3: Conclusion The time required for three-fourths of the reactant to decompose is $\boxed{5.44 \times 10^2\,\text{s}}$, or about 9.07 min.

Quick Tip to Solve: Three-fourths decomposed means one-fourth remains; insert the ratio 4 in the first-order equation, or recognise that this corresponds to two half-lives.

18. (a) Define activation energy.

(b) Write the unit of rate constant for (i) zero order reaction, (ii) second order reaction. [2 marks]

Solution:

Concept:

- Activation energy, E_a, is the minimum additional energy reactants must acquire to reach the activated complex and undergo reaction.
- For a rate law rate $= k[A]^n$, n is the reaction order and k is the rate constant. Since rate has units mol $\text{L}^{-1}\text{s}^{-1}$, the units of k depend on n.

Step 1: Define activation energy for part (a) Activation energy is the minimum energy barrier that the reactants must overcome to form the activated complex, after which products can form. In an energy profile,

$$E_a = E_{\text{activated complex}} - E_{\text{reactants}}.$$

For molar energies, it is commonly expressed in kJ mol^{-1}. It is the barrier for reaction, rather than the overall energy difference between products and reactants.

Step 2: Derive the units requested in part (b) For a zero-order reaction, rate $= k[A]^0 = k$; therefore

Quick Tip to Solve: Divide the rate unit by concentration raised to the reaction order: zero order retains concentration per time, while second order gives inverse concentration per time.

the rate constant has the same units as reaction rate:

$$\boxed{[k]_0 = \text{mol L}^{-1}\text{s}^{-1}}.$$

For a second-order reaction, divide the rate unit by the square of the concentration unit:

$$\begin{aligned}[k]_2 &= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2} \\ &= \boxed{\text{L mol}^{-1}\text{s}^{-1}}.\end{aligned}$$

The same result holds when the second-order rate law contains the product of two reactant concentrations.

Step 3: Conclusion (a) Activation energy is the minimum additional energy needed by reactants to reach the activated complex. (b) The units of k are (i) mol $\text{L}^{-1}\text{s}^{-1}$ for zero order and (ii) L $\text{mol}^{-1}\text{s}^{-1}$ for second order.

Quick Tip to Solve: Divide the rate unit by concentration raised to the reaction order: zero order retains concentration per time, while second order gives inverse concentration per time.

19. (a) First ionization enthalpy of Cr is lower than that of Zn. Why?

(b) Mention any one property of the transition elements which makes them good catalysts. [2 marks]

Solution:

Concept:

- First ionization enthalpy is the energy required to remove one electron from each isolated gaseous atom to form a gaseous singly charged cation.
- Electron removal depends on electronic configuration and nuclear attraction. Transition elements can show variable oxidation states, allowing them to participate in intermediate reaction steps.

Step 1: (a) Compare the electronic configurations Chromium has configuration $[\text{Ar}]\,3d^5 4s^1$, whereas zinc has $[\text{Ar}]\,3d^{10}4s^2$. Removal of chromium's single $4s$ electron produces Cr^+ with the stable half-filled $3d^5$ configuration. In zinc, an electron must be removed from its filled $4s^2$ subshell; zinc also has a higher nuclear charge. Its outer electron is more strongly held. Thus, the first ionization enthalpy of chromium is lower than that of zinc.

Step 2: (b) Identify a property responsible for catalysis Transition elements exhibit variable oxidation states. They can accept and donate electrons during successive stages of a reaction, forming intermediates that provide a pathway with lower activation energy. The catalyst returns to its original state at the end of the catalytic cycle. This ability is one property that makes transition elements good catalysts.

Step 3: Conclusion (a) Chromium loses its $4s^1$ electron to give a stable half-filled $3d^5$ configuration, whereas zinc holds its electrons more strongly. (b) Variable oxidation states promote catalytic activity.

Quick Tip to Solve: Write the neutral and singly ionized configurations before comparing first ionization enthalpies; identify the electron removed from the outer 4s subshell.

20. (a) Define coordination number.

(b) Indicate the type of isomerism exhibited by the following complex: $[Co(en)_3]Cl_3$ [2 marks]

Solution:

Concept:

- Coordination number counts the ligand donor atoms directly bonded to the central metal atom or ion. A ligand can contribute more than one donor atom.
- Optical isomerism occurs when a complex and its mirror image cannot be superimposed. These mirror-image forms are called enantiomers.

Step 1: (a) Define coordination number The coordination number of a central metal atom or ion is the number of ligand donor atoms directly bonded to it by coordinate bonds. It is not necessarily the number of ligands: a bidentate ligand attaches through two donor atoms and therefore contributes two to the coordination number.

Step 2: (b) Identify the isomerism of the cobalt complex In $[Co(en)_3]Cl_3$, en denotes ethane-1,2-diamine, a bidentate ligand with two nitrogen donor atoms. Three such ligands supply six donor atoms, giving the complex ion an octahedral arrangement. The three chelate rings can have two opposite spatial arrangements, denoted Δ and Λ. These are non-superimposable mirror images, so the complex exhibits optical isomerism. The chloride ions are counterions outside the coordination sphere and do not contribute to the coordination number.

Step 3: Conclusion (a) Coordination number is the number of ligand donor atoms directly bonded to the central metal. (b) $[Co(en)_3]Cl_3$ exhibits optical isomerism.

Quick Tip to Solve: Count donor atoms rather than ligands: three bidentate en ligands give an octahedral coordination number of six and an optical-isomer pair.

21. (a) Draw the structure of the given compound: 4-Bromo-3-methylpent-2-ene.

(b) What happens when chloroethane is treated with aqueous potassium hydroxide? [2 marks]

Solution:

Concept:

- In an alkene name, the parent chain contains the double bond and is numbered to give that double bond the stated locant. Substituents occupy the numbered carbon atoms.
- Aqueous potassium hydroxide supplies OH^-, which acts as a nucleophile and replaces the halogen of a haloalkane to form an alcohol.

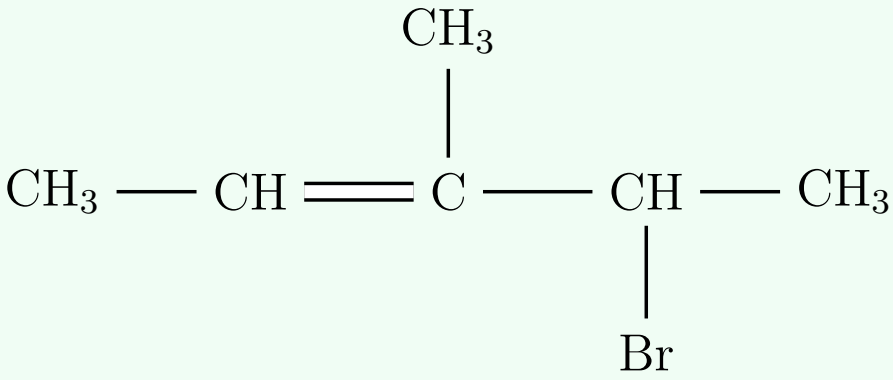
Step 1: (a) Construct 4-bromo-3-methylpent-2-ene The parent chain contains five carbon atoms, with a double bond between carbon atoms 2 and 3. Attach a methyl group to carbon 3 and bromine to carbon 4. The condensed structure is

$$CH_3 - CH = C(CH_3) - CH(Br) - CH_3.$$

Carbon 3 already has a double bond to carbon 2 and single bonds to carbon 4 and its methyl

Quick Tip to Solve: First place the double bond at C2, then add methyl at C3 and Br at C4; for KOH reactions, check whether the medium is aqueous or alcoholic.

substituent, so it carries no hydrogen. Carbon 4 carries one hydrogen and one bromine atom. The displayed connectivity is shown below; the name does not specify an E/Z configuration.



Connectivity of 4-bromo-3-methylpent-2-ene

Step 2: (b) React chloroethane with aqueous potassium hydroxide Chloroethane undergoes nucleophilic substitution (hydrolysis). The hydroxide ion replaces chlorine, producing ethanol; potassium chloride is also formed:

$$CH_3CH_2Cl + KOH(aq) \longrightarrow CH_3CH_2OH + KCl.$$

Aqueous KOH favours substitution. Alcoholic KOH would instead favour elimination to ethene, so the solvent specified in the question determines the product.

Step 3: Conclusion (a) The structure is $CH_3 - CH = C(CH_3) - CH(Br) - CH_3$. (b) Chloroethane gives ethanol with aqueous potassium hydroxide.

Quick Tip to Solve: First place the double bond at C2, then add methyl at C3 and Br at C4; for KOH reactions, check whether the medium is aqueous or alcoholic.

Section C (21 marks)

22. When 1.5 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point of benzene got raised from 353.23 K to 353.93 K. Calculate the molar mass of the solute. (Given K_b for benzene = 2.52 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- A non-volatile solute lowers the vapour pressure of a solvent, so a higher temperature is needed for the solution to boil at the same external pressure.
- Elevation in boiling point is $\Delta T_b = K_b m$, where K_b is the molal elevation constant and m is the molality, in moles of solute per kilogram of solvent.
- For a solute of mass w_2 and molar mass M_2, dissolved in solvent mass w_1 expressed in grams, $m = 1000 w_2/(M_2 w_1)$.

Quick Tip to Solve: Subtract the pure-solvent boiling point first, and convert the 90 g solvent mass to 0.090 kg before calculating molality.

Step 1: Calculate the boiling-point elevation The boiling point of the pure solvent is $353.23\,\text{K}$, while the solution boils at $353.93\,\text{K}$. Hence,

$$\Delta T_b = 353.93 - 353.23 = 0.70\,\text{K}.$$

We use this difference, rather than the absolute boiling temperature, in the colligative-property equation. The mass of solvent is $90\,\text{g} = 0.090\,\text{kg}$.

Step 2: Find molality and moles of solute Using $K_b = 2.52\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_b}{K_b} = \frac{0.70}{2.52} = 0.27778\,\text{mol kg}^{-1}.$$

Therefore, the number of moles present in $0.090\,\text{kg}$ of benzene is

$$n_2 = m \times 0.090 = 0.27778 \times 0.090 = 0.0250\,\text{mol}.$$

This uses the solvent mass, not the total solution mass, because molality is defined per kilogram of solvent.

Step 3: Determine and check the molar mass The solute mass is $w_2 = 1.5\,\text{g}$. Dividing mass by moles gives

$$M_2 = \frac{w_2}{n_2} = \frac{1.5}{0.0250} = 60\,\text{g mol}^{-1}.$$

Equivalently, $M_2 = 1000 K_b w_2/(\Delta T_b w_1)$. As a check, a solute of this molar mass gives $1.5/60 = 0.025\,\text{mol}$, and $2.52(0.025/0.090) = 0.70\,\text{K}$, exactly reproducing the observed elevation. No association or dissociation is specified, so the usual non-electrolyte relation applies.

Step 4: Conclusion The molar mass of the non-volatile solute is $\boxed{60\,\text{g mol}^{-1}}$.

Quick Tip to Solve: Subtract the pure-solvent boiling point first, and convert the 90 g solvent mass to 0.090 kg before calculating molality.

23. Calculate emf of the following cell at 298 K:

Sn | Sn^{2+} (0.001 M) || H^+ (0.01 M) | $H_{2(g)}$ (1 bar) | $Pt_{(s)}$

Given: $E^\circ_{Sn^{2+}/Sn} = -0.14\,V$, $E^\circ_{H^+/H_2} = 0.00\,V$, **[log 10 = 1]** [3 marks]

Solution:

Concept:

- The cell emf is the reduction potential of the right electrode minus that of the left electrode: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.
- At $298\,\text{K}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity; gas pressure is referred to 1 bar.

Step 1: Write the half-reactions and standard emf Tin at the left electrode undergoes oxidation, while

Quick Tip to Solve: First balance the cell reaction: it fixes both $n = 2$ and the square on $[H^+]$ in the reaction quotient.

hydrogen ions at the right electrode undergo reduction:

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

Thus the cell reaction is $\mathrm{Sn(s)} + \mathrm{2H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}$, with $n = 2$. Using the given standard reduction potentials,

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

Step 2: Substitute the concentrations in the Nernst equation Since hydrogen has pressure 1 bar, its pressure factor is unity. The hydrogen-ion concentration is squared because its coefficient in the reaction is two:

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

Therefore, using $\log 10 = 1$,

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

The quotient exceeds unity, so the actual emf is lower than the standard emf, consistent with the sign of this concentration correction.

Step 3: Conclusion The emf of the given cell at 298 K is $\boxed{E_{\text{cell}} \approx 0.110\,\text{V}}$.

Quick Tip to Solve: First balance the cell reaction: it fixes both $n = 2$ and the square on $[\mathrm{H^+}]$ in the reaction quotient.

24. (a) Complete and balance the following equations:

(i) $\mathbf{2KMnO_4 \xrightarrow{513\ K} ?}$

(ii) $\mathbf{Na_2Cr_2O_7 + 2KCl \rightarrow ?}$

(b) Why is it difficult to separate lanthanoid elements in pure state? [3 marks]

Solution:

Concept:

- On heating, potassium permanganate decomposes into potassium manganate, manganese dioxide and oxygen. A balanced equation conserves the number of atoms of each element.
- Potassium dichromate is less soluble than sodium dichromate, so adding potassium chloride to sodium dichromate gives potassium dichromate on crystallisation.
- Lanthanoids predominantly form $+3$ ions. Their closely similar ionic radii and chemical properties make their separation difficult.

Step 1: (a)(i) Complete the thermal decomposition At the given temperature, potassium permanganate decomposes as follows:

$$2\mathrm{KMnO_4} \xrightarrow{513\,\mathrm{K}} \mathrm{K_2MnO_4} + \mathrm{MnO_2} + \mathrm{O_2}.$$

Quick Tip to Solve: Keep the dichromate ion intact in (ii), and balance the cations using two chloride ions; for lanthanoids, connect similar radii with similar chemistry.

The products are potassium manganate, manganese dioxide and oxygen gas. Checking the balance: each side contains two potassium atoms, two manganese atoms and eight oxygen atoms. Manganese is reduced from $+7$ in permanganate to $+6$ in manganate and $+4$ in manganese dioxide, while some oxide oxygen is oxidised to elemental oxygen.

Step 2: (a)(ii) Complete the dichromate reaction Exchange of sodium and potassium ions gives

$$\mathrm{Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl.}$$

Potassium dichromate crystallises because it is less soluble than sodium dichromate. The coefficient two before each chloride salt balances both the two potassium ions and the two sodium ions. Chromium remains in oxidation state $+6$, so this is not a redox conversion of dichromate.

Step 3: (b) Explain the difficulty of lanthanoid separation The lanthanoids mainly show the same $+3$ oxidation state. Lanthanoid contraction makes the sizes of successive $\mathrm{Ln^{3+}}$ ions differ only slightly, so their compounds have very similar chemical properties. Thus ordinary chemical reactions do not selectively separate one lanthanoid from the others easily, making their isolation in the pure state difficult.

Step 4: Conclusion (a) The products are $\mathrm{K_2MnO_4 + MnO_2 + O_2}$ in (i), and $\mathrm{K_2Cr_2O_7 + 2NaCl}$ in (ii), with the balanced equations above. (b) Similar $+3$ ionic sizes and chemical properties make pure lanthanoid separation difficult.

Quick Tip to Solve: Keep the dichromate ion intact in (ii), and balance the cations using two chloride ions; for lanthanoids, connect similar radii with similar chemistry.

25. (a) $[Co(NH_3)_6]^{3+}$ is diamagnetic whereas $[CoF_6]^{3-}$ is paramagnetic. Justify the statement. [Atomic number of Co = 27]

(b) Write the electronic configuration for d^4 ion if $\Delta_o > P$ on the basis of crystal field theory. [3 marks]

Solution:

Concept:

- In an octahedral crystal field, the five d orbitals split into lower-energy t_{2g} and higher-energy e_g sets, separated by Δ_o. Pairing energy P is the energy needed to pair two electrons in one orbital.
- When $\Delta_o > P$, electrons pair in t_{2g} before occupying e_g, giving a low-spin complex. When $\Delta_o < P$, occupation of e_g is favoured before further pairing, giving a high-spin complex.
- A species with no unpaired electrons is diamagnetic; one with unpaired electrons is paramagnetic.

Step 1: (a) Determine the metal-ion configuration Cobalt has atomic number 27, hence its neutral configuration is $[\mathrm{Ar}]\,3d^7 4s^2$. In $[\mathrm{Co(NH_3)_6}]^{3+}$, ammonia is neutral, so cobalt has oxidation state $+3$. In $[\mathrm{CoF_6}]^{3-}$, six fluoride ligands contribute -6; therefore $x - 6 = -3$, again giving cobalt oxidation state $+3$. Removal of the two $4s$ electrons and one $3d$ electron gives $\mathrm{Co^{3+}}$: $[\mathrm{Ar}]\,3d^6$ in both complexes.

Step 2: (a) Compare the ligand-field strength and unpaired electrons For $\mathrm{Co^{3+}}$, ammonia produces a

Quick Tip to Solve: Find cobalt's oxidation state before counting d electrons; both complexes contain d^6 cobalt, so their magnetism differs because of ligand-field strength.

sufficiently strong field that $\Delta_o > P$. Its six d electrons pair within the three t_{2g} orbitals:

$$[Co(NH_3)_6]^{3+}: \quad t_{2g}^6 e_g^0.$$

All electrons are paired, explaining diamagnetism. Fluoride is a weak-field ligand with $\Delta_o < P$. Its high-spin distribution is

$$[CoF_6]^{3-}: \quad t_{2g}^4 e_g^2.$$

Within t_{2g}, one orbital contains a pair and the other two contain one electron each; both e_g orbitals contain one electron each. There are four unpaired electrons, explaining paramagnetism.

Step 3: (b) Fill the orbitals for the strong-field d-four ion For a d^4 ion with $\Delta_o > P$, the first three electrons singly occupy the three t_{2g} orbitals. The fourth electron pairs in one of these lower-energy orbitals because pairing costs less energy than excitation to e_g. Its configuration is therefore $t_{2g}^4 e_g^0$, with two unpaired electrons.

Step 4: Conclusion (a) $[Co(NH_3)_6]^{3+}$ is low-spin $t_{2g}^6 e_g^0$, with no unpaired electrons; $[CoF_6]^{3-}$ is high-spin $t_{2g}^4 e_g^2$, with four unpaired electrons. (b) For d^4 and $\Delta_o > P$, the configuration is $\boxed{t_{2g}^4 e_g^0}$.

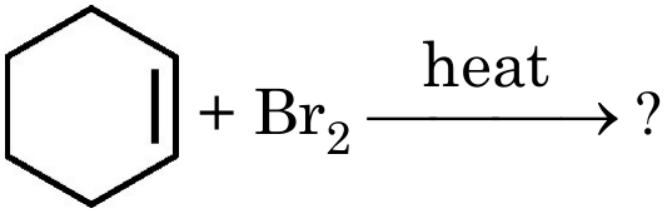
Quick Tip to Solve: Find cobalt's oxidation state before counting d electrons; both complexes contain d^6 cobalt, so their magnetism differs because of ligand-field strength.

26. (a) Write the major product in the following reactions:

(b) Define Racemic mixture.

(c) *p*-dichlorobenzene has a higher melting point as compared to its *ortho* and *meta* isomers. Why?

[3 marks]



Solution:

Concept:

- Heating bromine promotes free-radical substitution at an allylic carbon, the carbon next to a carbon-carbon double bond; the allylic radical is resonance-stabilised.
- Enantiomers rotate plane-polarised light by equal magnitudes in opposite directions. Their equimolar mixture has zero net optical rotation.
- Melting depends on the stability and packing of the crystal lattice. Greater molecular symmetry often allows closer packing in a solid.

Step 1: Identify the product of the heated bromination (a) The ring shown is cyclohexene. With Br_2

Quick Tip to Solve: In the heated bromination, keep the ring double bond and put Br on an adjacent carbon; for melting-point comparisons, examine crystal packing and molecular symmetry.

under heat, an allylic hydrogen is substituted by bromine, while the double bond remains in the ring. The product is **3-bromocyclohex-1-ene**, with bromine attached to the carbon adjacent to the double bond.

$$C_6H_{10} + Br_2 \xrightarrow{\text{heat}} C_6H_9Br + HBr$$

Number the double-bond carbons 1 and 2 and choose the direction giving bromine the lowest locant, 3. The allylic positions are equivalent by symmetry in cyclohexene. Formation of a resonance-stabilised allylic radical favours this substitution under the specified heated conditions.

Step 2: Define a racemic mixture (b) A racemic mixture is an equimolar, or 1:1, mixture of the two enantiomers of an optically active compound. One enantiomer is dextrorotatory and the other is laevorotatory. Their equal and opposite rotations cancel, so the mixture is optically inactive by external compensation. This cancellation concerns the mixture; its individual enantiomers remain optically active.

Step 3: Explain the higher melting point of the para isomer (c) In *p*-dichlorobenzene the two identical chlorine substituents occupy opposite positions on the benzene ring. Its more symmetrical molecular shape allows the molecules to pack more efficiently in the crystal lattice than the *ortho* and *meta* isomers. Consequently the solid lattice is more stable and more thermal energy is needed to disrupt it during melting, giving the para isomer a higher melting point.

Step 4: Conclusion (a) The major product is 3-bromocyclohex-1-ene. (b) A racemic mixture contains equal amounts of two enantiomers and has zero net optical rotation. (c) Efficient crystal packing due to symmetry raises the melting point of *p*-dichlorobenzene.

Quick Tip to Solve: In the heated bromination, keep the ring double bond and put Br on an adjacent carbon; for melting-point comparisons, examine crystal packing and molecular symmetry.

27. Write the reaction involved in:

(a) Rosenmund's reduction

(b) Cannizzaro's reaction

(c) Hell-Volhard-Zelinsky reaction [3 marks]

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen and poisoned palladium supported on barium sulphate.
- Cannizzaro reaction is the disproportionation of an aldehyde without an α-hydrogen in concentrated alkali: one molecule is oxidised and another is reduced.
- Hell-Volhard-Zelinsky (HVZ) reaction replaces an α-hydrogen of a carboxylic acid by chlorine or bromine using halogen and red phosphorus.

Step 1: Write Rosenmund reduction (a) Pass hydrogen over an acyl chloride in the presence of poisoned $Pd/BaSO_4$. The catalyst's reduced activity prevents further reduction of the aldehyde to the

Quick Tip to Solve: Associate Rosenmund with $Pd/BaSO_4$, Cannizzaro with no α-hydrogen and concentrated alkali, and HVZ with an α-hydrogen plus red phosphorus.

primary alcohol. For example, ethanoyl chloride gives ethanal:

$$CH_3COCl + H_2 \xrightarrow{Pd/BaSO_4} CH_3CHO + HCl$$

Thus the acid-chloride group $-COCl$ becomes the aldehyde group $-CHO$, with hydrogen chloride formed as the other product.

Step 2: Write Cannizzaro reaction (b) Benzaldehyde has no α-hydrogen and undergoes Cannizzaro reaction with concentrated aqueous sodium hydroxide:

$$2\,C_6H_5CHO + NaOH \xrightarrow{\text{concentrated}} C_6H_5CH_2OH + C_6H_5COONa$$

One benzaldehyde molecule is reduced to benzyl alcohol, while the other is oxidised to sodium benzoate. The carboxylic product is written as its salt because the reaction medium is strongly alkaline; acidification subsequently gives benzoic acid.

Step 3: Write Hell-Volhard-Zelinsky reaction (c) A carboxylic acid possessing an α-hydrogen undergoes halogenation at that carbon with bromine and red phosphorus. After hydrolysis, the corresponding α-bromo acid is obtained. For example:

$$CH_3COOH + Br_2 \xrightarrow{\text{red P}} CH_2BrCOOH + HBr$$

Here ethanoic acid becomes 2-bromoethanoic acid. The carbon next to the carboxyl group is the α-carbon, so bromine replaces a hydrogen on that carbon rather than the acidic hydrogen of $-COOH$.

Step 4: Conclusion Rosenmund reduction gives an aldehyde from an acyl chloride; Cannizzaro reaction gives an alcohol and a carboxylate salt from a non-enolisable aldehyde; HVZ reaction gives an α-halocarboxylic acid from an acid containing an α-hydrogen.

Quick Tip to Solve: Associate Rosenmund with $Pd/BaSO_4$, Cannizzaro with no α-hydrogen and concentrated alkali, and HVZ with an α-hydrogen plus red phosphorus.

28(A). (a) Define the following term: Reducing sugar.
(b) Differentiate between the following:
(i) Fibrous proteins and globular proteins
(ii) Nucleotide and nucleoside [3 marks]

Solution:

Concept:

- A reducing sugar has a free anomeric group that can open to a reactive carbonyl form and reduce mild oxidising reagents such as Tollens' or Fehling's reagent.
- Protein shape and water solubility depend on the arrangement of polypeptide chains: fibrous proteins form elongated structures, while globular proteins form compact structures.
- A nucleoside contains a nitrogenous base and a pentose sugar; adding a phosphate group produces a nucleotide, the repeating unit of nucleic acids.

Quick Tip to Solve: Compare protein shape and water solubility together; for nucleic-acid units, write base + sugar for nucleoside and add phosphate for nucleotide.

Step 1: Define a reducing sugar (a) A reducing sugar is a carbohydrate that reduces Tollens' reagent or Fehling's solution because it can furnish a free aldehydic or ketonic carbonyl group in solution. Glucose is an example; fructose also gives these tests through rearrangement in the alkaline medium. A free anomeric group permits ring opening. Sucrose is non-reducing because both anomeric centres are involved in its glycosidic bond and cannot open to free carbonyl forms.

Step 2: Compare fibrous and globular proteins (b)(i) **Fibrous proteins** have polypeptide chains arranged in long, fibre-like structures. They are generally insoluble in water and chiefly perform structural or protective functions. Examples include keratin in hair and wool, and collagen in connective tissue. **Globular proteins** have polypeptide chains folded into compact, approximately spherical shapes. They are generally soluble in water and perform functions such as catalysis and transport. Albumin and many enzymes are examples. Thus shape, typical solubility and function distinguish the two classes.

Step 3: Compare a nucleoside and a nucleotide (b)(ii) A **nucleoside** consists of a nitrogenous base joined to a pentose sugar by a glycosidic bond; it contains no phosphate group. For example, adenine joined to ribose forms adenosine. A **nucleotide** consists of a nitrogenous base, a pentose sugar and a phosphate group esterified to the sugar. Adenosine monophosphate is an example. The sugar is ribose in RNA and 2-deoxyribose in DNA. Hence a nucleotide is the phosphate ester of a nucleoside.

Step 4: Conclusion A reducing sugar reduces Tollens' or Fehling's reagent. Fibrous proteins are elongated and generally water-insoluble; globular proteins are compact and generally water-soluble. A nucleoside is base plus sugar, whereas a nucleotide is base plus sugar plus phosphate.

Quick Tip to Solve: Compare protein shape and water solubility together; for nucleic-acid units, write base + sugar for nucleoside and add phosphate for nucleotide.

OR

28(B). Write the reaction of glucose with the following:

(a) H_2N-OH

(b) $(CH_3CO)_2O$

(c) conc. HNO_3 [3 marks]

Solution:

Concept:

- Open-chain glucose contains one aldehyde group and five hydroxyl groups; different reagents identify these functional groups.
- Hydroxylamine converts an aldehyde into an oxime, acetic anhydride acetylates hydroxyl groups, and concentrated nitric acid oxidises both terminal groups to carboxyl groups.

Step 1: (a) React the aldehyde group with hydroxylamine The aldehyde group of the open-chain form reacts with NH_2OH, eliminating water and forming glucose oxime:

$$CHO-(CHOH)_4-CH_2OH + NH_2OH \longrightarrow HON{=}CH-(CHOH)_4-CH_2OH + H_2O.$$

Quick Tip to Solve: Match the reagent to the group: hydroxylamine tests the carbonyl, acetic anhydride counts hydroxyl groups, and concentrated nitric acid oxidises both ends.

The terminal oxime group is $-CH{=}N{-}OH$. The hydroxyl groups remain unchanged. Oxime formation supplies evidence for a carbonyl group in glucose.

Step 2: (b) Acetylate the five hydroxyl groups Glucose reacts with acetic anhydride to form glucose pentaacetate. Each hydroxyl hydrogen is replaced by an acetyl group, CH_3CO^-:

$$C_6H_7O(OH)_5 + 5\,(CH_3CO)_2O \longrightarrow C_6H_7O(OCOCH_3)_5 + 5\,CH_3COOH.$$

This functional-group equation accounts for all five hydroxyl groups without requiring the cyclic structure to be drawn. Formation of a pentaacetate establishes the presence of five hydroxyl groups in glucose.

Step 3: (c) Oxidise both terminal groups with concentrated nitric acid Concentrated HNO_3 is a strong oxidising agent. It oxidises the aldehyde group and the terminal primary alcohol group, giving saccharic acid (glucaric acid):

$$CHO{-}(CHOH)_4{-}CH_2OH + 3\,[O] \xrightarrow{\text{conc}\cdot HNO_3} HOOC{-}(CHOH)_4{-}COOH + H_2O.$$

The four secondary hydroxyl groups are retained in this standard reaction. Unlike a mild aldehyde oxidant, nitric acid converts both ends into carboxyl groups.

Step 4: Conclusion (a) Glucose oxime is formed; (b) glucose pentaacetate is formed; (c) saccharic acid, $HOOC{-}(CHOH)_4{-}COOH$, is formed.

Quick Tip to Solve: Match the reagent to the group: hydroxylamine tests the carbonyl, acetic anhydride counts hydroxyl groups, and concentrated nitric acid oxidises both ends.

Section D (8 marks)

The following questions are case – based questions. Each question has an internal choice and carries 4 (2+1+1) marks each. Read the passage carefully and answer the questions that follow :

29(a). Read the passage carefully and answer the questions that follow:

Osmosis is a process by which the molecules of a solvent pass from a solution of low solute concentration to a solution of high solute concentration through a semi-permeable membrane. Osmotic pressure is a colligative property. When the applied pressure on a solution exceeds its osmotic pressure, reverse osmosis occurs. When two solutions are separated by a semipermeable membrane and they have same osmotic pressure they are said to be isotonic. Of the two solutions separated by a semipermeable membrane, if one is at a lower osmotic pressure, it is said to be hypotonic relative to the second solution. If it has a higher osmotic pressure than the second solution, it is said to be hypertonic relative to the second solution. The osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution called normal saline solution and it is safe to inject intravenously. Osmotic pressure is vital in daily life and nature. It helps in explaining why IV fluids match blood's osmotic pressure; it is also the principle behind food preservation using salt or sugar.

(a) Calculate the amount of $CaCl_2$ (i = 2.59) dissolved in 2.46 litre of water such that its osmotic pressure is 0.70 atm at 27°C. [Given: R = 0.082 L atm K^{-1} mol^{-1}, molar mass of $CaCl_2$ = 111 g mol^{-1}] [2 marks]

Solution:

Concept:

- For a dilute electrolyte solution, osmotic pressure is $\pi = iCRT = i(n/V)RT$, where i is the van't Hoff factor, n the amount of solute in moles, V the solution volume, R the gas constant and T the absolute temperature.
- If the solute mass is w and its molar mass is M, then $n = w/M$, so $w = \pi VM/(iRT)$. Use the given factor for the actual electrolyte behaviour.

Step 1: Convert the temperature and collect the data The temperature in the gas-law expression must be in kelvin:

$$T = 27 + 273 = 300\,\text{K}.$$

Here $\pi = 0.70\,\text{atm}$, $i = 2.59$, $M = 111\,\text{g mol}^{-1}$ and $R = 0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1}$. For this dilute solution, take the volume as $V = 2.46\,\text{L}$, the stated volume of water.

Step 2: Substitute into the electrolyte osmotic-pressure equation Substitution gives

$$\begin{aligned} w &= \frac{\pi VM}{iRT} \\ &= \frac{0.70 \times 2.46 \times 111}{2.59 \times 0.082 \times 300}\,\text{g} \\ &= \frac{191.142}{63.714}\,\text{g}. \end{aligned}$$

The factor 2.59 accounts for the increased number of solute particles produced by $CaCl_2$. Using either

Quick Tip to Solve: For electrolyte osmotic pressure, keep the supplied van't Hoff factor in the denominator of the mass expression and convert Celsius to kelvin first.

$i = 1$ or the ideal value $i = 3$ would ignore the experimentally specified factor.

Step 3: Conclusion The required mass of $CaCl_2$ is $\boxed{3.0\,g}$.

Quick Tip to Solve: For electrolyte osmotic pressure, keep the supplied van't Hoff factor in the denominator of the mass expression and convert Celsius to kelvin first.

29(b). When raisins are kept in water, they get swollen. Name the phenomenon involved in this process. [1 mark]

Solution:

Concept:

- Osmosis is the movement of solvent through a semipermeable membrane from the dilute side to the more concentrated solution.
- When water enters a cell by osmosis, the inward movement is called endosmosis.

Step 1: Compare the water outside with the solution inside A raisin contains dissolved sugars and other solutes, so its internal solution is more concentrated than the surrounding water. The outer cell membranes act as semipermeable membranes, allowing water to pass.

Step 2: Identify the direction of water movement Water moves from the dilute external medium into the concentrated solution within the raisin. This increases the water content and volume of its cells, explaining why the raisin swells. The movement is inward, so the specific term is endosmosis.

Step 3: Conclusion The phenomenon is $\boxed{\text{endosmosis}}$, that is, inward osmosis of water.

Quick Tip to Solve: Use the prefix endo for water entering and swelling a raisin; exo describes water leaving it in a concentrated external solution.

OR

29(b). Why is osmotic pressure more advantageous than other colligative properties? [1 mark]

Solution:

Concept:

- Osmotic pressure obeys $\pi = CRT$ for a dilute nonelectrolyte solution, where C is molar concentration, R the gas constant and T the absolute temperature.
- A useful method for determining molar mass should give a measurable effect in very dilute solutions without damaging the solute.

Step 1: Compare the measurable changes in dilute solutions Osmotic pressure has an appreciable magnitude even for very dilute solutions, whereas their elevation in boiling point and depression in freezing point may be too small to measure accurately. This makes osmotic-pressure measurements especially useful for solutes of high molar mass.

Step 2: Consider the measurement temperature Osmotic pressure can be measured at room tempera-

Quick Tip to Solve: Remember the two practical advantages together: a measurable pressure in dilute solution and measurement at room temperature.

ture. Unlike a measurement involving boiling or freezing, it does not require a substantial temperature change, making it suitable for temperature-sensitive substances such as proteins and polymers.

Step 3: Conclusion Osmotic pressure is advantageous because it is measurable in very dilute solutions and can be determined at room temperature, particularly for high-molar-mass, temperature-sensitive solutes.

Quick Tip to Solve: Remember the two practical advantages together: a measurable pressure in dilute solution and measurement at room temperature.

29(c). Which phenomenon is responsible for desalination of sea water? [1 mark]

Solution:

Concept:

- In ordinary osmosis, solvent moves through a semipermeable membrane from the dilute solution towards the concentrated solution.
- Reverse osmosis reverses this flow when an external pressure greater than the osmotic pressure is applied on the concentrated solution side.

Step 1: Apply sufficient pressure to seawater Seawater contains dissolved salts and therefore has an osmotic pressure. Apply a pressure greater than this osmotic pressure to the seawater side of a suitable semipermeable membrane.

Step 2: Separate water from the dissolved salts The applied pressure forces water through the membrane towards the freshwater side, opposite to its natural osmotic direction. The membrane retains most dissolved salt ions, so the water collected on the other side has a much lower salt concentration.

Step 3: Conclusion Desalination of seawater is carried out by $\boxed{\text{reverse osmosis}}$.

Quick Tip to Solve: In seawater desalination, remember that the pressure is applied to the salty side and must exceed its osmotic pressure.

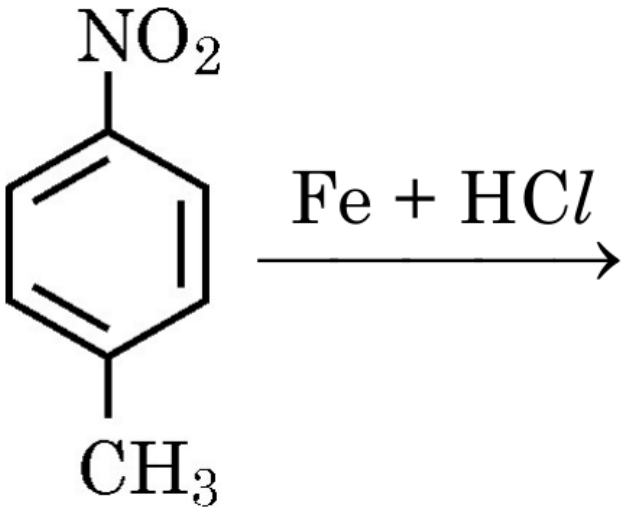
30(a). **Read the passage carefully and answer the questions that follow:**

Like NH_3, nitrogen atom of amine is trivalent and carries an unshared pair of electrons. Nitrogen orbitals in amines are therefore sp^3 hybridised and the geometry of amines is pyramidal. Lower aliphatic amines are soluble in water due to the formation of hydrogen bond with water molecules. The solubility decreases as the molar mass of amines increases due to increase in size of hydrophobic part. Higher amines are insoluble in water. However amines are less soluble in water than alcohols because of low electronegativity of nitrogen as compared to oxygen. Boiling points of isomeric amines follow the order $1^\circ > 2^\circ > 3^\circ$. It is due to the fact that amines are held together due to hydrogen bonding. Extent of hydrogen bonding is more in primary amines than in secondary amines as two hydrogen atoms are available for hydrogen bond formation. Tertiary amines do not show hydrogen bonding because of the absence of hydrogen atom attached to nitrogen. Amines can be prepared from nitro compounds, nitriles, amides, etc.

(a) Complete the following equations:

(i) $CH_3CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$ **?**

(ii) [2 marks]



Solution:

Concept:

- Lithium aluminium hydride reduces an amide to a primary amine: the carbonyl carbon becomes a methylene carbon, without shortening the carbon chain.
- Iron and hydrochloric acid reduce an aromatic nitro group, $-NO_2$, to an amino group, $-NH_2$; the methyl substituent remains unchanged.

Step 1: Reduce the amide in part (i) Acetamide, CH_3CONH_2, contains two carbon atoms. Reduction with $LiAlH_4$, followed by hydrolysis with water, replaces the carbonyl oxygen by two hydrogen atoms while retaining the carbon attached to nitrogen. Thus the amine also contains two carbon atoms; this reaction must not be confused with the Hofmann bromamide reaction, which removes one carbon.

Quick Tip to Solve: For amide reduction retain both carbons; for the printed aromatic nitro compound replace only NO_2 by NH_2, retaining the para methyl group.

The completed equation is

$$CH_3CONH_2 \xrightarrow[2.\,H_2O]{1.\,LiAlH_4} CH_3CH_2NH_2.$$

The product is ethanamine (ethylamine).

Step 2: Reduce the nitro group in part (ii) The printed ring is para-nitrotoluene: the NO_2 and CH_3 groups are opposite each other. With Fe/HCl, only the nitro group is reduced to an amino group. A balanced representation using reducing hydrogen is

$$p\text{-}CH_3C_6H_4NO_2 + 6\,[H] \xrightarrow{Fe/HCl} p\text{-}CH_3C_6H_4NH_2 + 2\,H_2O.$$

The product is 4-methylaniline, also called para-toluidine. The para relationship between the two substituents is retained. In the acidic reaction mixture the amine can be protonated; the organic amine product requested is written in its usual free-base form.

Step 3: Conclusion (i) $CH_3CH_2NH_2$, ethanamine; (ii) $p\text{-}CH_3C_6H_4NH_2$, 4-methylaniline (para-toluidine).

Quick Tip to Solve: For amide reduction retain both carbons; for the printed aromatic nitro compound replace only NO_2 by NH_2, retaining the para methyl group.

30(b). Why do primary amines have higher boiling points than tertiary amines? [1 mark]

Solution:

Concept:

- Boiling requires molecules to overcome intermolecular attractions; stronger attractions generally produce a higher boiling point.
- Intermolecular hydrogen bonding between amine molecules requires an N–H bond as donor and a nitrogen lone pair as acceptor.

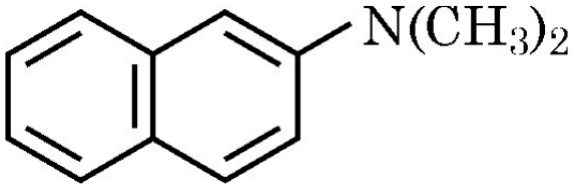
Step 1: Identify hydrogen bonding in primary amines Primary amines have the form RNH_2. Their N–H bonds allow one molecule to donate a hydrogen bond to the lone pair of another. This intermolecular association increases the energy needed to separate the molecules into the vapour.

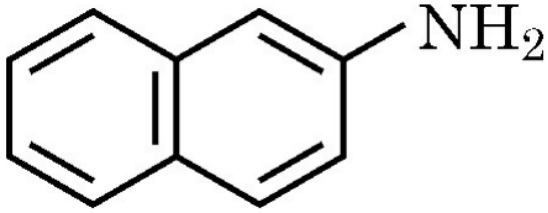
Step 2: Compare tertiary amines Tertiary amines, R_3N, contain no hydrogen bonded directly to nitrogen, so they cannot hydrogen-bond to one another. Therefore, for comparable or isomeric amines, their intermolecular attractions are weaker than those of primary amines. Their lone pair can still accept hydrogen bonds from water; the present comparison concerns the pure amines.

Step 3: Conclusion Primary amines have higher boiling points than comparable tertiary amines because primary amines form intermolecular hydrogen bonds, whereas tertiary amines lack N–H bonds and cannot self-associate in this way.

Quick Tip to Solve: Check for an N–H bond when comparing boiling points of pure amines; a lone pair by itself does not supply a hydrogen-bond donor.

30(c). **Classify the following amines as primary, secondary or tertiary:** [1 mark]

(i) 

(ii) 

Solution:

Concept:

- Classify an amine by the number of carbon groups directly attached to its nitrogen atom, not by the number of rings in the molecule.
- Primary, secondary and tertiary amines have the forms RNH_2, R_2NH and R_3N, respectively; R may be an alkyl or aryl group.

Step 1: Count groups attached to nitrogen in (i) The first structure has nitrogen bonded to the naphthyl group and to two methyl groups, as shown by $N(CH_3)_2$. Thus three carbon groups are directly attached to nitrogen, and no N–H bond remains. The two fused rings together constitute the one aryl substituent attached to nitrogen.

Step 2: Count groups attached to nitrogen in (ii) The second structure contains NH_2 attached to the naphthalene ring. Nitrogen is bonded to one aryl carbon group and to two hydrogen atoms. Consequently its classification follows the RNH_2 form, irrespective of the size or fused-ring nature of the aryl group.

Step 3: Conclusion (i) Tertiary amine; (ii) primary amine.

Quick Tip to Solve: Focus on nitrogen: $N(CH_3)_2$ plus an aryl bond gives three carbon attachments, whereas an aryl NH_2 group gives only one.

OR

30(c). **Out of Butan-1-amine and Butan-1-ol, which is more soluble in water?** [1 mark]

Solution:

Concept:

- Water solubility depends on hydrogen bonding between the polar functional group and water, opposed by the hydrophobic hydrocarbon chain.

Quick Tip to Solve: For equal carbon chains, compare the heteroatom in the polar group: oxygen in $-OH$ provides stronger hydrogen bonding with water than nitrogen in $-NH_2$.

- Oxygen is more electronegative than nitrogen, so an alcohol group interacts more strongly through hydrogen bonding with water than a comparable amino group.

Step 1: Compare the hydrocarbon portions Butan-1-amine, $CH_3CH_2CH_2CH_2NH_2$, and butan-1-ol, $CH_3CH_2CH_2CH_2OH$, have the same four-carbon chain. Their hydrophobic portions are therefore comparable, and the difference specified in the question is assessed through the terminal functional groups.

Step 2: Compare interactions with water Both functional groups can form hydrogen bonds with water. However, oxygen has greater electronegativity than nitrogen, making the alcohol group more effective in hydrogen bonding. Following the comparison stated in the passage, the alcohol therefore has greater water solubility than the corresponding amine.

Step 3: Conclusion Butan-1-ol is more soluble in water than butan-1-amine because it forms stronger hydrogen bonds with water.

Quick Tip to Solve: For equal carbon chains, compare the heteroatom in the polar group: oxygen in $-OH$ provides stronger hydrogen bonding with water than nitrogen in $-NH_2$.

Section E (15 marks)

31(A). (a) How will you convert the following:

(i) Propanone to Propene

(ii) Benzoic acid to Benzaldehyde

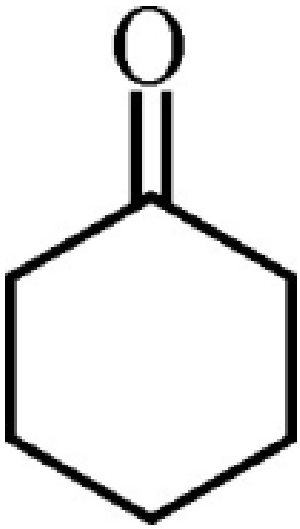
(iii) Benzene to *m*-Nitroacetophenone

(b) (i) Arrange the following compounds in increasing order of their reactivity towards HCN:

$(CH_3)_2C{=}O,\ \ ((CH_3)_3C)_2C{=}O,\ \ CH_3CHO$

(ii) Identify the compounds, which would undergo Aldol condensation: HCHO, C_6H_5CHO, CH_3CHO,

[5 marks]



Solution:

Concept:

- A ketone is reduced to a secondary alcohol; acid-catalysed dehydration of that alcohol gives an alkene.
- In Rosenmund reduction, an acyl chloride is hydrogenated using poisoned palladium on barium sulphate to obtain an aldehyde.
- The acetyl group $-COCH_3$ is deactivating and meta-directing in electrophilic aromatic substitution.
- Cyanide attacks the electrophilic carbonyl carbon. Electron-releasing alkyl groups and steric crowding decrease the rate of nucleophilic addition.
- Aldol condensation requires at least one alpha hydrogen, that is, a hydrogen on the carbon adjacent to the carbonyl group.

Step 1: (a)(i) Convert propanone into propene First reduce propanone with sodium borohydride to

Quick Tip to Solve: Install the acetyl group before nitrating benzene; for aldol, inspect the carbons immediately beside the carbonyl for hydrogen atoms.

propan-2-ol. Then heat the alcohol with concentrated sulphuric acid to remove water:

$$CH_3COCH_3 \xrightarrow{NaBH_4} CH_3CH(OH)CH_3,$$
$$CH_3CH(OH)CH_3 \xrightarrow[443\,K]{\text{conc. } H_2SO_4} CH_3CH{=}CH_2 + H_2O.$$

Reduction retains all three carbon atoms and creates the alcohol group needed for dehydration. Direct reduction to propane would not give the required alkene.

Step 2: (a)(ii) Convert benzoic acid into benzaldehyde Treat benzoic acid with thionyl chloride to form benzoyl chloride. Carry out Rosenmund reduction of this acyl chloride:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl,$$

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4 \text{ (poisoned)}} C_6H_5CHO + HCl.$$

The poisoned catalyst controls the reduction so that it stops at the aldehyde. Strong reduction of the acid itself would instead produce benzyl alcohol.

Step 3: (a)(iii) Convert benzene into meta-nitroacetophenone Perform Friedel-Crafts acylation first, using acetyl chloride and anhydrous aluminium chloride. Nitrate the acetophenone obtained:

$$C_6H_6 + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3} C_6H_5COCH_3 + HCl,$$

$$C_6H_5COCH_3 + HNO_3 \xrightarrow{\text{conc. } H_2SO_4} m\text{-}NO_2C_6H_4COCH_3 + H_2O.$$

The acetyl group directs the entering nitro group mainly to the meta position. The order matters: nitration first gives nitrobenzene, whose strongly deactivated ring does not undergo the required Friedel-Crafts acylation.

Step 4: (b)(i) Compare addition of HCN Cyanide attacks the carbonyl carbon, followed by protonation of the oxygen to form a cyanohydrin. The ketone with two tert-butyl groups has the greatest steric obstruction, as well as strong electron-releasing alkyl groups. It is therefore least reactive. Propanone has two smaller methyl groups; ethanal has only one methyl group and one hydrogen at its carbonyl carbon and is most reactive. Thus the increasing order is

$$((CH_3)_3C)_2C{=}O < (CH_3)_2C{=}O < CH_3CHO.$$

Both reduced electrophilicity and increased crowding favour the same order here.

Step 5: (b)(ii) Check for alpha hydrogens Ethanal, CH_3CHO, has alpha hydrogens on its methyl carbon. The cyclic ketone shown is cyclohexanone; each ring carbon immediately adjacent to its carbonyl carbon is a CH_2 group and supplies alpha hydrogens. Both can form an enolate in dilute base and undergo aldol condensation. Formaldehyde, $HCHO$, has no alpha carbon, and benzaldehyde, C_6H_5CHO, has no alpha hydrogen. They therefore do not undergo self-aldol condensation. For example, ethanal first forms an aldol and on heating loses water:

$$2CH_3CHO \xrightarrow{\text{dil. } NaOH} CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH{=}CHCHO + H_2O.$$

Quick Tip to Solve: Install the acetyl group before nitrating benzene; for aldol, inspect the carbons immediately beside the carbonyl for hydrogen atoms.

Step 6: Conclusion The conversions use reduction followed by dehydration, acyl-chloride formation followed by Rosenmund reduction, and acylation followed by nitration, respectively. HCN reactivity increases as $((CH_3)_3C)_2CO < (CH_3)_2CO < CH_3CHO$. Ethanal and cyclohexanone undergo aldol condensation.

Quick Tip to Solve: Install the acetyl group before nitrating benzene; for aldol, inspect the carbons immediately beside the carbonyl for hydrogen atoms.

OR

31(B). (a) Give chemical tests to distinguish between the following pairs of compounds:

(i) Acetophenone and Benzophenone

(ii) Propanal and Propanone

(iii) Pentan-2-one and Pentan-3-one

(b) (i) Which of the following acids is stronger and why? CH_2FCOOH, CH_3COOH

(ii) Arrange the following compounds in the increasing order of their boiling points: CH_3OCH_3, $CH_3CH_2CH_3$, CH_3CH_2OH, CH_3CHO [5 marks]

Solution:

Concept:

- A methyl ketone, $RCOCH_3$, gives yellow iodoform, CHI_3, on warming with iodine and aqueous sodium hydroxide.
- Tollens' reagent oxidises aldehydes to carboxylate ions while silver ions are reduced to metallic silver; ordinary ketones do not give this test.
- An electron-withdrawing substituent stabilises a carboxylate conjugate base through its negative inductive effect and increases the acid strength.
- Boiling point increases with intermolecular attraction: hydrogen bonding is stronger than ordinary dipole-dipole attraction for the small molecules given.

Step 1: (a)(i) Distinguish acetophenone and benzophenone Warm separate samples with iodine solution and aqueous sodium hydroxide. Acetophenone, $C_6H_5COCH_3$, contains the methyl-ketone group and gives a yellow precipitate of iodoform. Benzophenone, $C_6H_5COC_6H_5$, contains no $-COCH_3$ group and gives no yellow precipitate under these conditions. The positive reaction is

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 \downarrow + 3NaI + 3H_2O.$$

The observable yellow solid, rather than merely the presence of a carbonyl group, distinguishes this pair.

Step 2: (a)(ii) Distinguish propanal and propanone Warm each sample gently with freshly prepared Tollens' reagent. Propanal, CH_3CH_2CHO, produces a silver mirror on the test-tube wall because its aldehyde group is oxidised. Propanone, CH_3COCH_3, gives no silver mirror. The ionic equation for

Quick Tip to Solve: Locate a methyl group directly bonded to the carbonyl for iodoform; compare conjugate-base stability for acids and self hydrogen bonding for boiling points.

propanal is

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag\downarrow + 4NH_3 + 2H_2O.$$

Thus deposition of metallic silver identifies propanal. The reaction does not rely on a difference in colour between the original liquids.

Step 3: (a)(iii) Distinguish pentan-2-one and pentan-3-one Use the iodoform test: warm each sample with iodine and aqueous sodium hydroxide. Pentan-2-one, $CH_3COCH_2CH_2CH_3$, has the $-COCH_3$ group and gives yellow CHI_3. Pentan-3-one, $CH_3CH_2COCH_2CH_3$, has an ethyl group on each side of the carbonyl and gives no iodoform precipitate. For pentan-2-one,

$$CH_3COCH_2CH_2CH_3 + 3I_2 + 4NaOH \longrightarrow CH_3CH_2CH_2COONa + CHI_3\downarrow + 3NaI + 3H_2O.$$

Both compounds are ketones, so Tollens' reagent would give a negative result for both and would not distinguish them.

Step 4: (b)(i) Compare the acid strengths Fluoroacetic acid, CH_2FCOOH, is stronger than acetic acid, CH_3COOH. Fluorine withdraws electron density through sigma bonds by its strong negative inductive effect. This stabilises the negative charge in the conjugate base CH_2FCOO^-, making release of a proton more favourable. By contrast, the methyl group in acetic acid has an electron-releasing positive inductive effect and destabilises the carboxylate ion relative to the fluorinated one. Hence

$$CH_2FCOOH > CH_3COOH \quad \text{in acid strength.}$$

The relevant comparison is the stability of the conjugate bases after ionisation.

Step 5: (b)(ii) Arrange the boiling points Propane is nonpolar and has only London dispersion forces, so its boiling point is lowest. Dimethyl ether is polar and has dipole-dipole attractions but cannot hydrogen-bond to itself. Ethanal has a strongly polar carbonyl group, giving stronger intermolecular dipole attraction and a higher boiling point than dimethyl ether. Ethanol has an $O-H$ group and forms extensive intermolecular hydrogen bonds, so its boiling point is highest. For these small molecules of similar molar mass, the increasing order is

$$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH.$$

An oxygen atom alone does not enable self hydrogen bonding: a suitable hydrogen donor such as $O-H$ is also needed.

Step 6: Conclusion Use iodoform for acetophenone/benzophenone and pentan-2-one/pentan-3-one, and Tollens' reagent for propanal/propanone. CH_2FCOOH is stronger through fluorine's negative inductive effect. Boiling points increase as propane, dimethyl ether, ethanal, ethanol.

Quick Tip to Solve: Locate a methyl group directly bonded to the carbonyl for iodoform; compare conjugate-base stability for acids and self hydrogen bonding for boiling points.

32(A). (a) The conductivity of 0.1 mol L^{-1} solution of NaCl is 1.06×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.

$\lambda^{\circ}_{Na^+} = 50.1\ S\ cm^2\ mol^{-1}$, $\lambda^{\circ}_{Cl^-} = 76.5\ S\ cm^2\ mol^{-1}$

(b) (i) Following cell reaction occurs in a galvanic cell:

$2Ag^+_{(aq)} + Zn_{(s)} \rightarrow 2Ag_{(s)} + Zn^{2+}_{(aq)}$; $E^{\circ}_{cell} = +1.56\ V$

Predict the direction of flow of current.

(ii) Differentiate between a primary battery and a secondary battery. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa \times 1000/c$, where κ is conductivity in S cm^{-1} and c is concentration in mol L^{-1}. The factor 1000 converts litres to cubic centimetres.
- Kohlrausch's law gives $\Lambda^{\circ}_m = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-}$. The conductivity-ratio estimate of degree of dissociation is $\alpha = \Lambda_m/\Lambda^{\circ}_m$.
- Oxidation occurs at the anode and reduction at the cathode. Electrons flow from anode to cathode through the external circuit; conventional current flows in the opposite direction. Rechargeability depends on whether the cell reaction can be reversed by an external supply.

Step 1: (a) Calculate molar conductivity Substitute $\kappa = 1.06 \times 10^{-2}$ S cm^{-1} and $c = 0.1$ mol L^{-1}:

$$\Lambda_m = \frac{1.06 \times 10^{-2} \times 1000}{0.1} = 106\ \text{S cm}^2\ \text{mol}^{-1}.$$

Conductivity describes the conducting ability of the solution per unit geometry, whereas molar conductivity refers to the conducting contribution of one mole of electrolyte at the specified concentration.

Step 2: (a) Use the limiting ionic conductivities NaCl yields one sodium ion and one chloride ion per formula unit. Hence,

$$\Lambda^{\circ}_m = 50.1 + 76.5 = 126.6\ \text{S cm}^2\ \text{mol}^{-1}, \qquad \alpha = \frac{106}{126.6} = 0.8373.$$

The requested conductivity-ratio value corresponds to 83.73%. For a strong electrolyte such as NaCl, this ratio is an apparent estimate: interionic interactions lower conductivity at finite concentration, so it should not be interpreted as proof that the remaining fraction is undissociated.

Step 3: (b)(i) Identify electrodes and current direction The balanced half-reactions are

$$\text{Anode:} \quad \text{Zn(s)} \longrightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{e}^-,$$
$$\text{Cathode:} \quad 2\text{Ag}^+\text{(aq)} + 2\text{e}^- \longrightarrow 2\text{Ag(s)}.$$

Zinc supplies electrons and is the negative anode; silver receives electrons and is the positive cathode. Thus electrons travel from zinc to silver in the external wire. Conventional current travels from the silver electrode to the zinc electrode through the external circuit. The positive standard cell potential is consistent with the spontaneous reaction as written.

Step 4: (b)(ii) Compare battery types A primary battery has a cell reaction that cannot be reversed usefully by charging. Once its reactants are exhausted, it cannot be recharged for repeated use; a dry

Quick Tip to Solve: Use the sum of the two limiting ionic conductivities for NaCl, and reverse the electron-flow direction when the question asks for conventional current.

cell is an example. A secondary battery has a reversible cell reaction: an external electrical supply reverses the discharge reaction and regenerates the active materials. It can therefore be recharged and used repeatedly; the lead storage battery is an example.

Step 5: Conclusion (a) $\Lambda_m = 106\,\text{S cm}^2\,\text{mol}^{-1}$ and the conductivity-ratio estimate is $\alpha = 0.8373$, or 83.73%. (b)(i) External conventional current flows from Ag to Zn. (ii) Primary batteries are not rechargeable; secondary batteries are rechargeable because their cell reactions are reversible.

Quick Tip to Solve: Use the sum of the two limiting ionic conductivities for NaCl, and reverse the electron-flow direction when the question asks for conventional current.

OR

32(B). (a) Resistance of a conductivity cell filled with 0.1 M KCl solution is 100 Ω. If the resistance of the same cell when filled with 0.01 mol L^{-1} KCl solution is 300 Ω, calculate the conductivity and molar conductivity of 0.01 mol L^{-1} KCl solution. The conductivity of 0.1 M KCl solution is 1.29 × 10^{-2} S cm^{-1}.

(b) (i) Write any two advantages of H_2-O_2 fuel cell.

(ii) Why does the cell potential of mercury cell remain constant throughout the life? [5 marks]

Solution:

Concept:

- Conductance is $G = 1/R$, where R is resistance. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant in cm^{-1}; the same conductivity cell retains the same cell constant.
- Molar conductivity is $\Lambda_m = \kappa \times 1000/c$, with conductivity in S cm^{-1} and concentration c in mol L^{-1}.
- A fuel cell directly converts the chemical energy of continuously supplied reactants to electrical energy. A mercury cell has a constant reaction quotient because its net reaction does not change the electrolyte concentration.

Step 1: (a) Determine the cell constant from the standard solution For the 0.1 M KCl solution, the given resistance is $100\,\Omega$ and conductivity is 1.29×10^{-2} S cm^{-1}. Since $\kappa = (1/R)(l/A)$,

$$\frac{l}{A} = \kappa R = (1.29 \times 10^{-2})(100) = 1.29\,\text{cm}^{-1}.$$

This calibration fixes the geometrical factor for both measurements. It is the resistance, rather than the cell constant, that changes when the solution is replaced.

Step 2: (a) Find conductivity and molar conductivity of dilute KCl For the 0.01 mol L^{-1} solution, $R = 300\,\Omega$, so

$$\kappa = \frac{1.29}{300} = 4.30 \times 10^{-3}\,\text{S cm}^{-1}.$$

Using the concentration of this solution, rather than that of the calibration solution,

$$\Lambda_m = \frac{4.30 \times 10^{-3} \times 1000}{0.01} = 430\,\text{S cm}^2\,\text{mol}^{-1}.$$

Quick Tip to Solve: Calibrate the cell with κR, then divide that constant by the new resistance; for the mercury cell, cancel OH^- in the two half-reactions.

The units follow because dividing conductivity by concentration in moles per cubic centimetre gives conductivity multiplied by volume per mole. The resistance ratio also checks the calculation: the second resistance is three times the first, so its conductivity is one-third of the first.

Step 3: (b)(i) State two advantages of the hydrogen-oxygen fuel cell First, the cell converts chemical energy directly into electrical energy with high efficiency, avoiding the losses involved in first producing heat and then mechanical work. Second, its overall reaction produces water:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l).$$

Thus the cell's reaction product does not pollute the environment with smoke or harmful gaseous combustion products. These are two distinct advantages: efficient energy conversion and a clean reaction product.

Step 4: (b)(ii) Explain the constant mercury-cell potential In the alkaline mercury cell the electrode reactions are

$$\text{Anode:} \quad Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-,$$
$$\text{Cathode:} \quad HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-.$$

Addition cancels the hydroxide ions and water, giving

$$Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l).$$

No dissolved ion appears in the overall reaction, and the electrolyte concentration does not change during discharge. The activities of the solid and liquid phases remain effectively constant. Consequently, the reaction quotient and the Nernst-equation term remain constant, giving a nearly constant cell potential of about $1.35\,V$ throughout its useful life.

Step 5: Conclusion (a) For 0.01 mol L^{-1} KCl, $\kappa = 4.30 \times 10^{-3}$ S cm^{-1} and $\Lambda_m = 430$ S cm^2 mol^{-1}. (b)(i) The fuel cell has high conversion efficiency and produces water as its clean reaction product. (ii) The mercury-cell potential stays constant because its net reaction leaves the electrolyte concentration unchanged.

Quick Tip to Solve: Calibrate the cell with κR, then divide that constant by the new resistance; for the mercury cell, cancel OH^- in the two half-reactions.

33(A). An organic compound 'A', with molecular formula C_2H_6O reacts with active metals such as sodium to give compound 'B' and hydrogen gas. 'A' on treatment with iodine and sodium hydroxide gives 'C' and in presence of H_2SO_4 at 413 K gives 'D' ($C_4H_{10}O$). 'D' on reaction with excess of HI gives 'E'. Identify 'A', 'B', 'C', 'D' and 'E' and write all the reactions involved. [5 marks]

Solution:

Concept:

- An alcohol reacts with sodium by replacement of its hydroxyl hydrogen, liberating hydrogen gas. An ether has no hydroxyl hydrogen and does not show this reaction.
- Ethanol gives the iodoform test because it is first oxidised to ethanal, which contains the CH_3CO

Quick Tip to Solve: Use sodium first to distinguish the alcohol from the ether isomer, then use 413 K to select ether formation and excess HI to convert both ethyl groups to iodoethane.

group. The yellow precipitate is iodoform, CHI_3.

- Intermolecular dehydration of ethanol with concentrated sulphuric acid at $413\,K$ forms ethoxyethane. Excess hydrogen iodide cleaves an ether and converts the alcohol formed into an alkyl iodide.

Step 1: Identify A and its sodium derivative B The molecular formula C_2H_6O allows ethanol and methoxymethane. Reaction with sodium and evolution of hydrogen establish that A has an $-OH$ group, so A is ethanol, CH_3CH_2OH. B is sodium ethoxide, CH_3CH_2ONa. The balanced reaction is

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2 \uparrow .$$

Step 2: Identify C from the iodoform reaction Iodine in aqueous sodium hydroxide oxidises ethanol to ethanal, followed by exhaustive iodination and cleavage. C is iodoform (triiodomethane), CHI_3, obtained as a yellow precipitate. Sodium formate is the other organic product. The overall balanced reaction is

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 \downarrow + HCOONa + 5NaI + 5H_2O.$$

Step 3: Identify D from dehydration at 413 K At the stated temperature, two ethanol molecules undergo acid-catalysed intermolecular dehydration. D is ethoxyethane (diethyl ether), $CH_3CH_2OCH_2CH_3$, whose molecular formula is $C_4H_{10}O$, agreeing with the question:

$$2CH_3CH_2OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O.$$

The specified temperature is essential: the higher-temperature dehydration condition favouring ethene is not used here.

Step 4: Identify E from cleavage with excess HI Protonation of the ether oxygen enables iodide to cleave a carbon-oxygen bond, initially giving iodoethane and ethanol:

$$C_2H_5OC_2H_5 + HI \longrightarrow C_2H_5I + C_2H_5OH.$$

Since HI is present in excess, ethanol also reacts:

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O.$$

Thus E is iodoethane (ethyl iodide), C_2H_5I. The overall reaction is

$$C_2H_5OC_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O.$$

Step 5: Conclusion $A = CH_3CH_2OH$ (ethanol), $B = CH_3CH_2ONa$ (sodium ethoxide), $C = CHI_3$ (iodoform), $D = C_2H_5OC_2H_5$ (ethoxyethane), and $E = C_2H_5I$ (iodoethane).

Quick Tip to Solve: Use sodium first to distinguish the alcohol from the ether isomer, then use 413 K to select ether formation and excess HI to convert both ethyl groups to iodoethane.

OR

33(B). (a) Write the reagents which are used in the given conversions:

(i) Phenol to 2, 4, 6-tribromophenol

(ii) Propene to propan-1-ol

(iii) Butan-2-one to butan-2-ol

(b) Explain the mechanism of acid catalyzed hydration of alkene to form corresponding alcohol.

[5 marks]

Solution:

Concept:

- The hydroxyl group strongly activates phenol's benzene ring towards electrophilic substitution and directs substitution to the ortho and para positions.
- Hydroboration followed by oxidation hydrates an alkene with anti-Markovnikov orientation. A ketone is reduced to a secondary alcohol by a hydride reducing agent.
- Acid-catalysed hydration proceeds through protonation of the alkene, attack of water on the carbocation and deprotonation. The acid catalyst is regenerated in the final step.

Step 1: (a)(i) Phenol to 2,4,6-tribromophenol Use bromine water, $Br_2(aq)$, at room temperature. The activated ring is brominated at both ortho positions and the para position, producing a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3Br_2(aq) \longrightarrow C_6H_2Br_3OH + 3HBr.$$

An aqueous medium is appropriate for the required tribromination.

Step 2: (a)(ii) Propene to propan-1-ol Use (1) diborane, B_2H_6, followed by (2) alkaline hydrogen peroxide, $H_2O_2/NaOH$. Hydroboration places boron on the less substituted terminal carbon; oxidation replaces the carbon-boron bond by a carbon-oxygen bond. Thus the hydroxyl group is introduced at carbon 1:

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2/NaOH]{1.\ B_2H_6} CH_3CH_2CH_2OH.$$

Direct acid-catalysed hydration would instead give mainly propan-2-ol and is unsuitable for this conversion.

Step 3: (a)(iii) Butan-2-one to butan-2-ol Use sodium borohydride, $NaBH_4$, followed by aqueous work-up. It reduces the ketone carbonyl group to a secondary alcohol without changing the carbon skeleton:

$$CH_3COCH_2CH_3 \xrightarrow[\text{aqueous work-up}]{NaBH_4} CH_3CH(OH)CH_2CH_3.$$

Lithium aluminium hydride in dry ether, followed by hydrolysis, is an alternative suitable reagent.

Step 4: (b) Protonation of the alkene In aqueous dilute acid, the alkene's electron-rich π bond accepts a proton from hydronium, forming the more stable carbocation. For example, propene forms

Quick Tip to Solve: For propan-1-ol from propene, choose hydroboration-oxidation: ordinary acid hydration puts OH on carbon 2. In the mechanism, track the charge from carbon to oxygen and finally regenerate hydronium.

a secondary carbocation rather than a primary one:

$$CH_3CH{=}CH_2 + H_3O^+ \longrightarrow CH_3CH^+CH_3 + H_2O.$$

A carbon-hydrogen bond forms at the terminal carbon while the positive charge remains on the central carbon. This accounts for Markovnikov orientation in this example.

Step 5: (b) Nucleophilic attack by water A lone pair on the oxygen of a water molecule attacks the electron-deficient carbocation, forming a carbon-oxygen bond and a protonated alcohol (oxonium ion):

$$CH_3CH^+CH_3 + H_2O \longrightarrow CH_3CH(OH_2^+)CH_3.$$

Water is the nucleophile; the positive charge now lies on the oxygen, which has three bonds.

Step 6: (b) Deprotonation and regeneration of the catalyst Another water molecule removes a proton from the oxonium ion, giving the neutral alcohol and regenerating hydronium:

$$CH_3CH(OH_2^+)CH_3 + H_2O \longrightarrow CH_3CH(OH)CH_3 + H_3O^+.$$

The net process adds water across the double bond. In the example, the product is propan-2-ol; hydronium participates in the mechanism but is not consumed overall.

Step 7: Conclusion The reagents are (i) bromine water, (ii) diborane followed by alkaline hydrogen peroxide, and (iii) sodium borohydride followed by aqueous work-up. Acid-catalysed hydration occurs by alkene protonation, water attack and deprotonation to give the alcohol while regenerating the acid catalyst.

Quick Tip to Solve: For propan-1-ol from propene, choose hydroboration-oxidation: ordinary acid hydration puts OH on carbon 2. In the mechanism, track the charge from carbon to oxygen and finally regenerate hydronium.