CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-2-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is NOT allowed.

Section A (16 marks)

1. 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 a single elementary reaction step; it is a positive integer.
- Order is obtained experimentally from the rate law and can be zero or fractional; it must not be confused with molecularity.

Step 1: Apply the definition to complex reactions A complex reaction consists of several elementary steps. Each step has its own molecularity, but the overall complex reaction has no single molecularity assigned to it. Thus statement (B) follows from the definition.

Step 2: Check the remaining statements Statement (A) describes order rather than molecularity. Statement (C) is false because a count of participating species cannot be zero or fractional. Statement (D) is false because simultaneous encounters of more than three reacting species are extremely improbable; such molecularities are not common.

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

Quick Tip to Solve: First ask whether the reaction is elementary; only then count participating species to assign molecularity.

2. 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:

- For an electrochemical reaction, $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is electrons transferred and F is the Faraday constant.
- Using standard reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Potentials are not multiplied by stoichiometric coefficients.

Step 1: Use the supplied potential values Zinc changes from oxidation state zero to $+2$, releasing two electrons, so $n = 2$. Silver is reduced. The numerical cell potential obtained from the supplied values is

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

Step 2: Calculate the numerical Gibbs energy Using $F = 96500\,\text{C mol}^{-1}$,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(1.56)\\ &= -301080\,\text{J mol}^{-1}\\ &= -301.080\,\text{kJ mol}^{-1}.\end{aligned}$$

The positive value in (B) has the wrong sign for this calculation. Options (C) and (D) do not follow from the given potential difference and two-electron transfer.

Step 3: Interpret the printed electrode data carefully The supplied Ag^+/Ag potential strictly describes reduction of aqueous silver ions, whereas the printed reaction consumes Ag_2O and produces OH^-. A rigorous standard Gibbs energy for that literal reaction additionally requires the $Ag_2O/Ag, OH^-$ electrode potential or equivalent thermodynamic data. The printed choices clearly use the supplied silver-ion potential in the above calculation.

Step 4: Conclusion Using the supplied potentials, the numerical answer is $\boxed{-301.080\,\text{kJ mol}^{-1}}$, corresponding to option (A).

Quick Tip to Solve: Count two electrons from zinc, subtract the negative zinc potential, and divide joules by 1000 to obtain kilojoules.

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

(A) $[\mathrm{Ar}]\,3d^4\,4s^1$

(B) $[\mathrm{Ar}]\,3d^4\,4s^2$

(C) $[\mathrm{Ar}]\,3d^5\,4s^1$

(D) $[\mathrm{Ar}]\,3d^5\,4s^2$

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

Solution:

Concept:

- Chromium has atomic number 24, so its neutral atom contains 24 electrons; the $[\mathrm{Ar}]$ core contains 18.
- The half-filled $3d^5$ arrangement is stabilised by exchange energy and its symmetrical distribution; the actual ground state is an exception to simple filling order.

Step 1: Distribute the six valence electrons After the argon core, six electrons remain. A simple filling prediction would be $3d^4 4s^2$, but the close energies of the $3d$ and $4s$ subshells allow one $4s$ electron to occupy the $3d$ subshell, yielding $3d^5 4s^1$.

Step 2: Check electron count and ground-state stability Option (A), $[\mathrm{Ar}]3d^4 4s^1$, contains only 23 electrons. Option (D), $[\mathrm{Ar}]3d^5 4s^2$, contains 25. Option (B) has the correct count but is not the chromium ground state because it misses the stabilised half-filled $3d$ arrangement.

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

Quick Tip to Solve: Check both the total of 24 electrons and the half-filled d subshell; electron count alone does not eliminate option (B).

4. 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:

- For Rate $= k[A]^m[B]^n$, the overall reaction order is $m + n$, the sum of concentration exponents.
- Stoichiometric coefficients in the balanced equation do not generally determine the rate-law exponents.

Step 1: Read the partial orders from the rate law The given law is Rate $= k[A]^{1/2}[B]^1$. Thus the order

Quick Tip to Solve: Underline the powers on concentrations in the rate law and add them; ignore coefficients in the reaction equation.

with respect to A is $1/2$, and that with respect to B is 1. Fractional orders are allowed because orders describe experimentally observed rate dependence.

Step 2: Add the exponents and compare the choices The overall order is

$$m + n = \frac{1}{2} + 1 = \frac{3}{2} = 1.5.$$

Option (B) gives only the order with respect to B; option (C) gives only that with respect to A. The coefficient 2 of B in the reaction equation does not make the overall order 2, so (D) is incorrect.

Step 3: Conclusion The overall reaction order is $\boxed{1.5}$. Hence, the correct option is (A).

Quick Tip to Solve: Underline the powers on concentrations in the rate law and add them; ignore coefficients in the reaction equation.

5. 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 kind of ligand bonded to the central metal atom or ion.
- A homoleptic complex contains only one kind of ligand, even when several identical ligand molecules are attached.

Step 1: Count ligand types in the first three complexes In (A), $[Co(NH_3)_6]^{3+}$, and (B), $[Cr(NH_3)_6]^{3+}$, all six ligands are ammonia. In (C), $[Ni(H_2O)_6]^{2+}$, all six ligands are water. Each therefore contains only one ligand type and is homoleptic.

Step 2: Identify the complex with different ligands In (D), $[Co(NH_3)_4Cl_2]^{+}$, cobalt is coordinated to four ammonia ligands and two chlorido ligands. The two chemically different ligand types make it heteroleptic. Neither the identity of the central metal nor the overall ionic charge determines this classification.

Step 3: Conclusion The heteroleptic complex is $\boxed{[Co(NH_3)_4Cl_2]^{+}}$. Hence, the correct option is (D).

Quick Tip to Solve: Count distinct ligand formulas inside the square brackets, not the total number of ligands or the complex charge.

6. 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 coordination nomenclature, ligands are listed alphabetically; multiplicative prefixes such as di- do not affect their alphabetical order.
- NH_3 is neutral and named ammine; Cl^- has charge -1 and is named chlorido. The metal oxidation state follows in Roman numerals.

Step 1: Determine the platinum oxidation state The complex $[Pt(NH_3)_2Cl_2]$ is neutral. If platinum has oxidation state x, charge balance gives

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

Thus options (A) and (C), which specify platinum(IV), are eliminated.

Step 2: Arrange the ligand names alphabetically Ammine precedes chlorido alphabetically. With two of each ligand, the ligand portion is diammine followed by dichlorido. A neutral complex retains the metal name platinum. Option (D) has the right oxidation state but places chlorido before ammine, so its ligand order is incorrect.

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

Quick Tip to Solve: Use ligand charges to find Pt(II), then alphabetise ammine before chlorido while ignoring each di- prefix.

7. 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:

- Alcohol molecules form intermolecular hydrogen bonds; increasing the carbon chain generally strengthens dispersion attractions and raises boiling point.
- For these isomeric butanols, butan-2-ol has a lower boiling point than butan-1-ol because molecular shape and the secondary hydroxyl environment reduce effective intermolecular association.

Quick Tip to Solve: Place the C3 and C5 alcohols at the ends, then put secondary butan-2-ol before primary butan-1-ol.

Step 1: Place the shorter and longer primary alcohols Propan-1-ol has three carbon atoms and pentan-1-ol has five. Among these closely related monohydric alcohols, the greater size and contact area of the longer chain strengthen dispersion forces. Propan-1-ol is the lowest-boiling compound listed, and pentan-1-ol is the highest.

Step 2: Order the two four-carbon alcohols Butan-2-ol boils below butan-1-ol. Both possess hydrogen bonding, but placing the hydroxyl group on a secondary carbon changes molecular association; their boiling points are approximately $100\,^{\circ}\text{C}$ and $118\,^{\circ}\text{C}$, respectively. Thus (A) reverses this pair, (B) puts the largest alcohol first, and (D) incorrectly puts both butanols before 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 C3 and C5 alcohols at the ends, then put secondary butan-2-ol before primary butan-1-ol.

8. 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 is a chiral centre when it is bonded to four different groups.
- Two identical groups on the same carbon prevent that carbon from being a chiral centre.

Step 1: Examine carbon 2 Butan-2-ol has the structure $CH_3CH(OH)CH_2CH_3$. Carbon 2 is attached to H, OH, CH_3 and CH_2CH_3. All four groups are different, so this carbon is asymmetric and the molecule has non-superimposable mirror images.

Step 2: Eliminate the remaining structures Propan-2-ol and 2-bromopropane each have two identical methyl groups on their central carbon. In 1-bromobutane, the carbon bonded to bromine has two hydrogen atoms, and no other carbon has four different substituents. None of these three molecules has a chiral centre.

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

Quick Tip to Solve: At carbon 2, compare methyl with ethyl: these different groups make butan-2-ol chiral.

9. 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 takes the place of thymine.

Step 1: Compare the base sets The standard base set of DNA is A, G, C and T, whereas that of RNA is A, G, C and U. Here T denotes thymine and U denotes uracil. The question asks for the member of the DNA set that is absent from the RNA set.

Step 2: Check all four options Guanine, cytosine and adenine occur in both DNA and RNA, so options (A), (B) and (D) do not satisfy the distinction. Thymine is the only listed base specific to DNA in this comparison. Uracil would give the opposite distinction, since it belongs to RNA.

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

Quick Tip to Solve: Write DNA as A-G-C-T and RNA as A-G-C-U; compare only their differing last base.

10. 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 reduces a nitrile group, $-C \equiv N$, to $-CH_2NH_2$.
- Nitrile reduction retains the nitrile carbon in the carbon chain and produces a primary amine after work-up.

Step 1: Write the reduction of ethanenitrile Ethanenitrile is CH_3CN. Its carbon-nitrogen triple bond is reduced by lithium aluminium hydride, followed by hydrolysis:

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

The nitrile carbon becomes the methylene carbon bonded to the amino group.

Quick Tip to Solve: Count the carbon in the nitrile group too: CH3CN retains both carbons on reduction to ethylamine.

Step 2: Identify the product and exclude distractors The product contains two carbon atoms and is ethanamine, commonly called ethylamine. Propylamine would require three carbons, while methylamine would have only one. Ethanal contains an aldehyde group and is not the product of complete nitrile reduction with this reagent.

Step 3: Conclusion Ethylamine is formed. Hence, the correct option is (A).

Quick Tip to Solve: Count the carbon in the nitrile group too: CH3CN retains both carbons on reduction to ethylamine.

11. 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:

- Open-chain glucose is an aldohexose, represented as $\mathrm{CHO} - (\mathrm{CHOH})_4 - \mathrm{CH_2OH}$.
- Cyclic glucose has an anomeric carbon at C-1 and can exist as the α and β anomers.

Step 1: Test what the open chain explains Prolonged heating with HI gives n-hexane, consistent with the unbranched six-carbon skeleton. The aldehyde group explains oxime formation with hydroxylamine and oxidation by bromine water to gluconic acid. Thus, the observations in (A), (B) and (C) are compatible with the open-chain structure.

Step 2: Identify the need for a cyclic structure A single open-chain aldehyde structure does not account for two crystalline forms differing at C-1. Intramolecular hemiacetal formation between the aldehyde group and the C-5 hydroxyl group creates a new stereogenic anomeric carbon. The two configurations at this carbon give the α and β forms.

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

Quick Tip to Solve: Link alpha and beta glucose to the new anomeric centre created when the aldehyde closes into a ring.

12. 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:

- Amino acids form proteins through peptide linkages, $-CO-NH-$.
- This amide linkage forms by condensation of the carboxyl group of one amino acid with the amino group of another.

Step 1: Identify the joining groups The $-COOH$ group of one α-amino acid and the $-NH_2$ group of another eliminate water, forming a $-CO-NH-$ linkage. Repetition of this process produces the polypeptide backbone of a protein.

Step 2: Choose the specific linkage name A peptide bond is covalent, but option (B) gives the precise name of the linkage joining amino-acid residues. The general term in (A) does not identify this characteristic linkage. Glycosidic bonds join sugar units, whereas coordinate bonds are not the backbone linkages joining amino acids in proteins.

Step 3: Conclusion The characteristic linkage is a peptide bond. Hence, the correct option is (B).

Quick Tip to Solve: Recognise the CO-NH group between amino-acid residues and choose its specific name, peptide bond.

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13. 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 a common oxidation state.

Quick Tip to Solve: Check d-electron occupancy in both atom and common ion; a retained d10 configuration excludes Zn, Cd and Hg.

- Zinc, cadmium and mercury have filled d subshells, with the characteristic configuration d^{10}.

Step 1: Judge the assertion Zinc, cadmium and mercury do not meet the usual transition-element criterion. Although they belong to the d block, their d subshells remain completely occupied in their atoms and common ions. The assertion is true.

Step 2: Judge the reason Their atomic valence configurations are $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$, respectively. Loss of the outer s electrons in forming their common $+2$ ions leaves the filled d^{10} configuration. Thus the reason is true; the filled orbitals relevant here are the d orbitals.

Step 3: Check the explanatory connection The lack of an incompletely filled d subshell is precisely why these elements are excluded from the transition elements. Therefore the reason directly explains the assertion, rather than merely giving an unrelated property.

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

Quick Tip to Solve: Check d-electron occupancy in both atom and common ion; a retained d10 configuration excludes Zn, Cd and Hg.

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14. 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 in a single elementary reaction event.
- A reaction event involving two reactant molecules is bimolecular and has molecularity 2.

Step 1: Judge the assertion For the reaction event specified in the question, $2HI \longrightarrow H_2 + I_2$, two HI molecules participate together. Counting these reacting molecules gives molecularity 2, so the assertion is true.

Step 2: Judge the reason The stated simultaneous collision involves two molecules of the reactant, HI. This is the defining description of a bimolecular elementary event. Therefore the reason is true. The count concerns reactant molecules participating together, not the number of products formed.

Quick Tip to Solve: Use the two HI molecules in the stated simultaneous collision to identify the event as bimolecular.

Step 3: Link the reason to the assertion Because two reactant molecules participate in the event described, its molecularity is two. The reason therefore explains the assertion directly. Molecularity is assigned to such an elementary event; it should not in general be inferred just by adding coefficients in an overall multistep reaction.

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

Quick Tip to Solve: Use the two HI molecules in the stated simultaneous collision to identify the event as bimolecular.

15. 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:

- Bromine water is a mild oxidising agent that converts an aldehyde group, $-\mathrm{CHO}$, into a carboxyl group, $-\mathrm{COOH}$.
- Open-chain glucose is an aldohexose: it contains six carbon atoms and a terminal aldehyde group.

Step 1: Evaluate the assertion Bromine water oxidises glucose's aldehyde end without breaking its carbon chain:

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

The product is six-carbon gluconic acid. Assertion (A) is therefore true.

Step 2: Evaluate the reason The open-chain structure contains $-\mathrm{CHO}$, which includes a carbonyl bond, $\mathrm{C{=}O}$. Thus the statement that the carbonyl group is absent is false. Do not confuse the cyclic hemiacetal structure with the open-chain structure specified here.

Step 3: Check the explanatory link Oxidation occurs because an aldehyde group is present, not because it is absent. A false reason cannot explain the true assertion. Options (A) and (B) wrongly regard the reason as true, while (D) wrongly rejects the assertion.

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

Quick Tip to Solve: Write the open-chain aldehyde end of glucose first; bromine water changes only $-\mathrm{CHO}$ to $-\mathrm{COOH}$.

16. 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 forms primary aliphatic amines by alkylation of the phthalimide anion followed by hydrolysis.
- An aryl halide has its halogen directly attached to an aromatic ring; its carbon-halogen bond resists the substitution used in this synthesis.

Step 1: Evaluate the assertion The method requires the phthalimide anion to displace halide from the organic halide. Alkyl halides can undergo this reaction, but aryl halides do not under Gabriel synthesis conditions. Consequently, aromatic primary amines such as aniline, $C_6H_5NH_2$, cannot be prepared by this method. The assertion is false.

Step 2: Evaluate the reason In an aryl halide, resonance gives the carbon-halogen bond partial double-bond character, and the carbon bearing halogen is sp^2-hybridised. The ordinary nucleophilic displacement by the phthalimide anion does not occur. The reason is true in the context of this synthesis.

Step 3: Check the explanatory link The true reason explains the failure of the proposed aromatic-amine preparation; it does not support the assertion. Options (A) and (B) require a true assertion, while (C) requires a false reason, so each is excluded.

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

Quick Tip to Solve: Check the halide's carbon: an aryl carbon blocks the Gabriel substitution, whereas a suitable alkyl halide gives a primary aliphatic amine.

Section B (10 marks)

17. (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 ligand donor atoms directly bonded to the central metal atom or ion, rather than counting ligand molecules.
- A complex exhibits optical isomerism when it has non-superimposable mirror-image forms, called enantiomers.

Step 1: Define coordination number (a) The coordination number of a central metal atom or ion is the number of ligand donor atoms directly attached to it by coordinate bonds. A monodentate ligand contributes one donor atom, whereas a bidentate ligand contributes two. Counter-ions outside the coordination sphere are not included.

Step 2: Identify the ligand arrangement (b) In $[Co(en)_3]Cl_3$, en denotes ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$. Each en ligand binds through two nitrogen atoms. Three en ligands therefore provide six donor atoms around cobalt, giving an octahedral $[Co(en)_3]^{3+}$ ion. The three chloride ions are outside the coordination sphere.

Step 3: Identify the isomerism The three chelate rings can wind around cobalt in two opposite senses. These arrangements are mirror images but cannot be superimposed, giving the Δ and Λ optical isomers. With three identical bidentate en ligands, a separate cis-trans pair does not arise.

Step 4: Conclusion (a) Coordination number is the number of donor atoms directly bonded to the central metal. (b) $[Co(en)_3]Cl_3$ exhibits optical isomerism.

Quick Tip to Solve: Count two donor atoms per en ligand: three en ligands give coordination number six and an octahedral complex with optical isomers.

18. (a) Define Effective collision.

(b) Write the unit of (i) second order reaction and (ii) zero order reaction. [2 marks]

Solution:

Concept:

- Collision theory requires sufficient collision energy and a suitable molecular orientation for reactants to form products.
- For an overall reaction order n, a rate law has the dimensional form $r = kc^n$, where r is reaction rate, c represents concentration and k is the rate constant.

Step 1: Define an effective collision (a) An effective collision is a collision between reacting species that leads to product formation. The colliding species must possess energy at least equal to the activation-energy requirement and must approach with the proper orientation for bonds to break and

Quick Tip to Solve: Divide the rate units by concentration raised to the reaction order; zero order leaves the rate-constant units equal to rate units.

form. Merely colliding, or having sufficient energy with the wrong orientation, is not enough.

Step 2: Obtain the general units of the rate constant (b) The order-dependent units asked here are those of the rate constant. Reaction rate itself has units $\mathrm{mol\,L^{-1}\,s^{-1}}$ for every order. Taking concentration in $\mathrm{mol\,L^{-1}}$ and time in seconds,

$$[k] = \frac{[r]}{[c]^n} = (\mathrm{mol\,L^{-1}})^{1-n}\mathrm{s^{-1}}.$$

Step 3: Substitute each reaction order (i) For a second-order reaction, $n = 2$, so

$$[k] = \frac{\mathrm{mol\,L^{-1}\,s^{-1}}}{(\mathrm{mol\,L^{-1}})^2} = \mathrm{L\,mol^{-1}\,s^{-1}}.$$

(ii) For a zero-order reaction, $n = 0$, the rate law is $r = k$. Thus $[k] = \mathrm{mol\,L^{-1}\,s^{-1}}$.

Step 4: Conclusion An effective collision produces products and requires sufficient energy and correct orientation. The rate-constant units are (i) $\mathrm{L\,mol^{-1}\,s^{-1}}$ for second order and (ii) $\mathrm{mol\,L^{-1}\,s^{-1}}$ for zero order.

Quick Tip to Solve: Divide the rate units by concentration raised to the reaction order; zero order leaves the rate-constant units equal to rate units.

19. (a) Why are the second ionization enthalpies of chromium and copper exceptionally higher than those of their neighbouring elements?

(b) Why do transition elements form interstitial compounds? [2 marks]

Solution:

Concept:

- Second ionisation enthalpy is the energy required for $\mathrm{M^+(g) \longrightarrow M^{2+}(g) + e^-}$. It depends on the stability of the singly charged gaseous ion.
- Half-filled d^5 and completely filled d^{10} subshells have additional stability. Small atoms can occupy interstitial spaces in a metal crystal lattice.

Step 1: Examine chromium after first ionisation (a) Chromium has the configuration $[\mathrm{Ar}]3d^5 4s^1$. The first ionisation removes its $4s$ electron, producing $\mathrm{Cr^+}$ with the stable half-filled configuration $[\mathrm{Ar}]3d^5$. The second ionisation removes a $3d$ electron and produces $\mathrm{Cr^{2+}}$, $[\mathrm{Ar}]3d^4$. Disrupting the stable half-filled subshell requires unusually high energy compared with neighbouring elements.

Step 2: Examine copper after first ionisation Copper has the configuration $[\mathrm{Ar}]3d^{10}4s^1$, so $\mathrm{Cu^+}$ has the stable completely filled $[\mathrm{Ar}]3d^{10}$ subshell. The second ionisation gives $\mathrm{Cu^{2+}}$, $[\mathrm{Ar}]3d^9$, disturbing this filled subshell. This accounts for copper's exceptionally high second ionisation enthalpy relative to its neighbours.

Step 3: Explain interstitial-compound formation (b) Transition-metal crystal lattices contain interstitial spaces between the metal atoms. Small atoms such as hydrogen, carbon and nitrogen can fit into these spaces without substantially changing the metal framework. Their incorporation gives

Quick Tip to Solve: For second ionisation, write the configuration of the singly charged ion first; the decisive stable configurations here are d^5 and d^{10}.

interstitial compounds, which are commonly hard and often non-stoichiometric.

Step 4: Conclusion (a) Second ionisation disrupts the stable $3d^5$ configuration of Cr^+ and the stable $3d^{10}$ configuration of Cu^+. (b) Transition metals form interstitial compounds because small atoms can occupy voids in their crystal lattices.

Quick Tip to Solve: For second ionisation, write the configuration of the singly charged ion first; the decisive stable configurations here are d^5 and d^{10}.

20(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:

- For a first order reaction, the integrated rate law is $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial concentration and concentration remaining after time t.
- The concentration ratio is dimensionless. Hence, the unit of a first order rate constant is the reciprocal of the time unit used.

Step 1: Identify the remaining concentration The reactant concentration falls from $[R]_0 = 0.6\,\text{mol L}^{-1}$ to $[R]_t = 0.2\,\text{mol L}^{-1}$ in $t = 5\,\text{min}$. The final concentration is already the concentration remaining, so it is used directly in the denominator:

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

Step 2: Substitute into the first order equation Using the supplied value $\log 3 = 0.48$,

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

If time is expressed in seconds, divide this value by 60, giving $3.6848 \times 10^{-3}\,\text{s}^{-1}$. The positive value is consistent with a decreasing reactant concentration because the logarithm of the initial-to-final concentration ratio is positive.

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

Quick Tip to Solve: Use the concentration remaining, 0.2, in the denominator; using the concentration consumed, 0.4, would give the wrong first order ratio.

OR

20(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, $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]_t}$, where k is the rate constant and $[R]_t$ is the reactant concentration remaining at time t.
- If a fraction f decomposes, the fraction remaining is $1 - f$. The integrated rate equation uses the fraction remaining, not the fraction decomposed.

Step 1: Calculate the fraction remaining Three-fourth of the reactant has decomposed, so the remaining amount is

$$[R]_t = [R]_0 \left(1 - \frac{3}{4}\right) = \frac{[R]_0}{4}.$$

Therefore $[R]_0/[R]_t = 4$, irrespective of the initial concentration. This is why the initial concentration need not be supplied for this calculation.

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

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

The unit is seconds because the supplied rate constant is in s^{-1}. A remaining fraction of one-fourth also corresponds to two successive half-lives, which provides a useful check on the method.

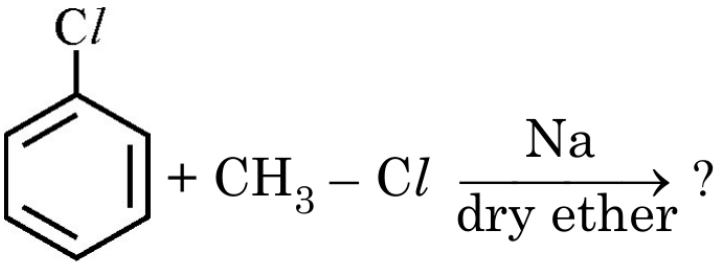
Step 3: Conclusion The time required is $\boxed{t \approx 544\,\text{s}}$, or approximately 9.07 min, using the supplied logarithm.

Quick Tip to Solve: For 75 percent decomposition, put 25 percent remaining in the rate law: the logarithm is $\log 4$, not $\log(4/3)$.

21. (a) Write the major product in the following reaction:

(b) What happens when 2-Bromobutane is made to react with alcoholic potassium hydroxide?

[2 marks]



Solution:

Concept:

- In the Wurtz–Fittig reaction, an aryl halide and an alkyl halide couple in the presence of sodium in dry ether to give an alkylbenzene.
- Alcoholic KOH promotes elimination of a hydrogen halide from a haloalkane. According to Saytzeff's rule, the more substituted alkene is the major product.

Step 1: Identify the coupling product in part (a) The printed reactants are chlorobenzene and chloromethane. Sodium in dry ether replaces the two carbon–chlorine bonds by a carbon–carbon bond between the phenyl group and the methyl group. The balanced Wurtz–Fittig equation is

$$C_6H_5Cl + CH_3Cl + 2\,Na \xrightarrow{\text{dry ether}} C_6H_5CH_3 + 2\,NaCl.$$

The organic product is toluene (methylbenzene); the benzene ring remains intact during this coupling.

Step 2: Apply elimination to part (b) On heating with alcoholic potassium hydroxide, 2-bromobutane loses a hydrogen atom from a carbon adjacent to the carbon bearing bromine, together with the bromide group. Thus, dehydrohalogenation gives mainly but-2-ene:

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

But-1-ene is a minor elimination product. But-2-ene predominates because it is the more substituted, more stable alkene. Alcoholic conditions favour elimination; aqueous hydroxide would instead favour substitution to an alcohol.

Step 3: Conclusion (a) The product is toluene, $C_6H_5CH_3$. (b) 2-Bromobutane undergoes dehydrohalogenation with alcoholic KOH, producing mainly but-2-ene, $CH_3CH{=}CHCH_3$.

Quick Tip to Solve: Spot sodium in dry ether for aryl–alkyl coupling; spot alcoholic KOH for elimination and choose the more substituted alkene.

Section C (21 marks)

22. 60 g of glucose is dissolved in 250 g of water. Calculate the freezing point of this solution. (molar mass of glucose = 180 g mol^{-1}, K_f for water = 1.86 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- Depression in freezing point is a colligative property: $\Delta T_f = iK_f m$, where K_f is the solvent's cryoscopic constant, m is molality and i is the van't Hoff factor.
- Glucose, $C_6H_{12}O_6$, is a nonelectrolyte that neither dissociates nor associates in water, so $i = 1$. Molality is moles of solute per kilogram of solvent.
- The freezing point of the solution is $T_f = T_f^\circ - \Delta T_f$, where pure water freezes at $T_f^\circ = 0\,^\circ$C or 273.15 K.

Step 1: Calculate the amount of glucose and solvent mass Divide the given solute mass by its molar mass:

$$n = \frac{60\,\text{g}}{180\,\text{g mol}^{-1}} = \frac{1}{3}\,\text{mol}.$$

The solvent is 250 g of water, hence its mass is $250/1000 = 0.250$ kg. The total solution mass is not used in the molality formula.

Step 2: Calculate the molality and freezing point depression The molality of the glucose solution is

$$m = \frac{1/3}{0.250} = \frac{4}{3}\,\text{mol kg}^{-1}.$$

Substitute this value and $K_f = 1.86$ K kg mol^{-1} into the colligative-property relation:

$$\Delta T_f = 1 \times 1.86 \times \frac{4}{3} = 2.48\,\text{K}.$$

The units kg mol^{-1} and mol kg^{-1} cancel, leaving a temperature difference in kelvin. A difference of 2.48 K equals a difference of $2.48\,^\circ$C.

Step 3: Subtract the depression from the solvent freezing point Dissolved glucose lowers water's freezing point, so subtract the positive depression:

$$T_f = 0 - 2.48 = -2.48\,^\circ\text{C}.$$

Equivalently, on the kelvin scale, $T_f = 273.15 - 2.48 = 270.67$ K. The negative Celsius value is physically consistent with freezing point depression.

Step 4: Conclusion The freezing point of the glucose solution is $\boxed{-2.48\,^\circ\text{C}}$, equivalent to 270.67 K.

Quick Tip to Solve: Use 0.250 kg of water in molality, not the combined mass of glucose and water; then subtract the depression from $0\,^\circ$C.

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 cathode reduction potential minus the anode reduction potential: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, in volts. Here n is the number of transferred electrons and Q is the reaction quotient.
- Pure solids have unit activity. The gas pressure is divided by its standard pressure of 1 bar, and dilute ion activities are approximated using their molar concentrations.

Step 1: Write the electrode reactions For the cell as written, tin is oxidised at the left electrode and hydrogen ions are reduced at the right electrode:

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

Adding these gives $\mathrm{Sn(s)} + 2\,\mathrm{H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}$. Thus $n = 2$; the hydrogen-ion concentration will appear squared in the reaction quotient.

Step 2: Calculate the standard emf and reaction quotient Both given electrode potentials are reduction potentials, so

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

With the gas at its standard pressure and solid tin omitted,

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

Concentrations here represent their numerical ratios to the standard concentration, making Q dimensionless.

Step 3: Apply the Nernst equation Substitute $n = 2$ and the supplied value $\log 10 = 1$:

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

Since $Q > 1$, the concentration correction lowers the emf below the standard value. Its positive sign is consistent with spontaneous operation in the written direction.

Step 4: Conclusion The emf of the cell at 298 K is $\boxed{E_{\text{cell}} \approx 0.110\,\mathrm{V}}$.

Quick Tip to Solve: Balance the hydrogen half-reaction first: two hydrogen ions give the squared denominator and two electrons give the factor $0.0591/2$.

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

(i) $2\,Na_2CrO_4 + 2\,H^+ \longrightarrow$ **?**

(ii) $5\,S^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow$ **?**

(b) Why is chemistry of actinoids complicated as compared to lanthanoids? [3 marks]

Solution:

Concept:

- Acidification converts yellow chromate ions to orange dichromate ions through an acid-base equilibrium; chromium remains in oxidation state $+6$.
- In acidic solution, permanganate is reduced from manganese(VII) to manganese(II). Oxidation and reduction half-reactions must exchange equal numbers of electrons.
- The range of accessible oxidation states depends on the relative energies and participation of the valence orbitals.

Step 1: Complete the chromate reaction in part (a)(i) The net ionic change is

$$2\,CrO_4^{2-} + 2\,H^+ \longrightarrow Cr_2O_7^{2-} + H_2O.$$

Retaining sodium in the form used in the question, the completed equation is

$$2\,Na_2CrO_4 + 2\,H^+ \longrightarrow Na_2Cr_2O_7 + 2\,Na^+ + H_2O.$$

Atoms and charge are balanced. Two sodium ions remain as spectator ions.

Step 2: Balance the redox reaction in part (a)(ii) Sulfide is oxidised to sulfur, whereas permanganate is reduced in the acidic medium:

$$S^{2-} \longrightarrow S + 2\,e^-,$$
$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O.$$

Multiply the first half-reaction by five and the second by two, then cancel ten electrons:

$$5\,S^{2-} + 2\,MnO_4^- + 16\,H^+ \longrightarrow 5\,S + 2\,Mn^{2+} + 8\,H_2O.$$

The atoms balance, and the net charges are equal: $-10 - 2 + 16 = +4$ on the left and $+4$ on the right.

Step 3: Explain the complexity of actinoid chemistry in part (b) The $5f$, $6d$ and $7s$ subshells of actinoids have comparable energies, so different numbers of their electrons can participate in bonding. Actinoids consequently exhibit a much wider range of oxidation states than lanthanoids, whose chemistry is dominated by the $+3$ state and whose $4f$ electrons are more deeply buried. This greater variability makes actinoid chemistry more complicated. Their radioactivity adds experimental difficulty to its study.

Step 4: Conclusion In (a)(i), the products are $Na_2Cr_2O_7 + 2\,Na^+ + H_2O$; in (a)(ii), they are $5\,S + 2\,Mn^{2+} + 8\,H_2O$. Actinoid chemistry is more complicated chiefly because closely spaced valence subshells permit a wider variety of oxidation states.

Quick Tip to Solve: For acidic permanganate, start with $MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O$, then match its five-electron gain to sulfide's two-electron loss.

25. (a) Explain why $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. [Atomic number of Fe = 26]

(b) On the basis of crystal field theory, write the electronic configuration for d^5 ion for which $\Delta_o < P$.

[3 marks]

Solution:

Concept:

- Paramagnetism arises from unpaired electrons. For n unpaired electrons, the spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\text{BM}$, where BM denotes Bohr magnetons.
- In an octahedral field, the five d orbitals split into lower-energy t_{2g} and higher-energy e_g sets. Their separation is Δ_o, while P is the energy required to pair electrons.
- If $\Delta_o < P$, occupation of higher orbitals is favoured over pairing, giving a high-spin complex. If $\Delta_o > P$, pairing in the lower orbitals is favoured, giving a low-spin complex.

Step 1: Find the iron oxidation states and electron count Water is neutral, so iron in $[Fe(H_2O)_6]^{3+}$ has oxidation state $+3$. For $[Fe(CN)_6]^{3-}$, each cyanide ligand has charge -1, giving $x - 6 = -3$, hence $x = +3$ again. Neutral iron has configuration $[\text{Ar}]\,3d^6 4s^2$; removal of two $4s$ electrons and one $3d$ electron gives Fe^{3+} the configuration $[\text{Ar}]\,3d^5$.

Step 2: Compare the ligand fields in part (a) Water is a weak-field ligand. In $[Fe(H_2O)_6]^{3+}$, $\Delta_o < P$, so the five electrons remain unpaired and occupy all five d orbitals:

$$(t_{2g})^3(e_g)^2, \qquad n = 5, \qquad \mu = \sqrt{35} \approx 5.92\,\text{BM}.$$

Cyanide is a strong-field ligand. In $[Fe(CN)_6]^{3-}$, $\Delta_o > P$, so electrons pair in the lower t_{2g} set before entering e_g:

$$(t_{2g})^5(e_g)^0, \qquad n = 1, \qquad \mu = \sqrt{3} \approx 1.73\,\text{BM}.$$

Thus the aqua complex has five unpaired electrons and is strongly paramagnetic; the cyanide complex has only one and is weakly paramagnetic. The latter is not diamagnetic because its odd electron count leaves one electron unpaired.

Step 3: Write the crystal-field configuration in part (b) For the specified d^5 ion, $\Delta_o < P$ means it costs less energy to occupy an e_g orbital than to pair in t_{2g}. The first three electrons singly occupy the three t_{2g} orbitals; the next two singly occupy the two e_g orbitals. The required high-spin configuration is therefore $(t_{2g})^3(e_g)^2$, with all five electrons unpaired.

Step 4: Conclusion (a) $[Fe(H_2O)_6]^{3+}$ has five unpaired electrons, whereas $[Fe(CN)_6]^{3-}$ has one, explaining their strong and weak paramagnetism respectively. (b) For d^5 with $\Delta_o < P$, the configuration is $\boxed{(t_{2g})^3(e_g)^2}$.

Quick Tip to Solve: Calculate the metal oxidation state before counting d electrons: both printed complexes contain Fe^{3+}, so both are d^5 despite their opposite overall charges.

26. (a) Write the IUPAC name of the given compound: $CH_3CH(CH_3)CH(Br)CH_3$

(b) Define Racemisation.

(c) The boiling points of the alkyl halides with the same alkyl group decrease in the given order: RI $>$ RBr $>$ RCl $>$ RF. Explain the above statement. [3 marks]

Solution:

Concept:

- IUPAC nomenclature selects the longest carbon chain and gives substituents the lowest possible locants. Alphabetical order breaks a tie between otherwise equivalent numberings.
- Enantiomers rotate plane-polarised light equally in opposite directions; an equimolar mixture has zero net optical rotation.
- For the same alkyl group, larger, more polarisable halogen atoms produce stronger London dispersion forces between alkyl halide molecules.

Step 1: (a) Choose and number the parent chain In $CH_3CH(CH_3)CH(Br)CH_3$, the longest continuous carbon chain contains four carbon atoms, so the parent is butane. There are bromo and methyl substituents. Numbering from either end gives the locant set $2, 3$; in this tie, bromo, which comes before methyl alphabetically, receives the lower locant. Thus bromine is on carbon 2 and methyl is on carbon 3.

Step 2: (b) Explain racemisation Racemisation is the conversion of an optically active compound into an equimolar mixture of its two enantiomers. The equal clockwise and anticlockwise optical rotations cancel, making the resulting racemic mixture optically inactive by external compensation. This is different from a molecule being achiral: each enantiomer in the mixture is still chiral.

Step 3: (c) Relate boiling point to intermolecular forces Keeping the alkyl group fixed, the size, number of electrons and polarisability of the halogen increase from fluorine to iodine. Consequently, the strength of intermolecular dispersion forces increases from RF to RI. More energy is required to separate the molecules of an alkyl iodide during boiling. The boiling-point order therefore follows the dispersion-force trend, even though the carbon–fluorine bond is more polar.

Step 4: Conclusion (a) The name is **2-bromo-3-methylbutane**. (b) Racemisation forms an optically inactive, equimolar mixture of enantiomers. (c) Increasing halogen polarisability and dispersion forces give $\mathrm{RI} > \mathrm{RBr} > \mathrm{RCl} > \mathrm{RF}$ in boiling point.

Quick Tip to Solve: For the tied locants $2, 3$, give bromo the lower number. For a fixed alkyl group, compare halogen polarisability rather than carbon–halogen bond polarity to rank boiling points.

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 by controlled catalytic hydrogenation.
- Cannizzaro reaction is disproportionation of an aldehyde without an α-hydrogen in concentrated alkali: one molecule is reduced and another oxidised.
- The Hell–Volhard–Zelinsky reaction introduces a halogen at the α-carbon of a carboxylic acid possessing an α-hydrogen.

Step 1: (a) Write the Rosenmund reduction Hydrogen is passed over an acyl chloride in the presence of palladium supported on barium sulphate, a poisoned catalyst. Its reduced activity prevents further reduction of the aldehyde to an alcohol. For example, ethanoyl chloride gives ethanal:

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

Thus the acyl chloride functional group is selectively reduced while the carbon skeleton remains unchanged.

Step 2: (b) Write the Cannizzaro reaction Benzaldehyde has no α-hydrogen and undergoes self-oxidation and self-reduction on treatment with concentrated aqueous sodium hydroxide:

$$\mathrm{2\,C_6H_5CHO + NaOH \xrightarrow{conc.} C_6H_5CH_2OH + C_6H_5COONa.}$$

One aldehyde molecule forms benzyl alcohol by reduction, while the other forms sodium benzoate by oxidation. The acid appears as its sodium salt because the reaction medium is strongly alkaline.

Step 3: (c) Write the Hell–Volhard–Zelinsky reaction A carboxylic acid containing an α-hydrogen reacts with bromine in the presence of a small amount of red phosphorus; hydrolysis gives the α-bromo acid. For example:

$$\mathrm{CH_3COOH + Br_2 \xrightarrow[\text{then } H_2O]{\text{red P}} BrCH_2COOH + HBr.}$$

Bromination occurs at the carbon adjacent to the carboxyl group, replacing an α-hydrogen. Chlorine can similarly give an α-chloro acid under the corresponding conditions.

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; Hell–Volhard–Zelinsky reaction gives an α-halo carboxylic acid.

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

28(A). (a) **Define the following terms:**

(i) **Invert Sugar**

(ii) **Polysaccharides**

(b) **On the basis of structure differentiate between fibrous and globular proteins.** [3 marks]

Solution:

Concept:

- Hydrolysis breaks glycosidic bonds in carbohydrates. Sucrose gives one molecule each of glucose and fructose.
- Polysaccharides contain many monosaccharide units joined by glycosidic linkages; hydrolysis releases their constituent monosaccharides.
- Protein shape depends on the arrangement and folding of its polypeptide chains. Extended fibres and compact globules are the two broad structural forms.

Step 1: (a)(i) Define invert sugar and explain the name Invert sugar is the equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose using dilute acid or the enzyme invertase:

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}.$$

Sucrose is dextrorotatory, whereas the resulting mixture is laevorotatory because the negative rotation of fructose is larger in magnitude than the positive rotation of glucose. The change in the sign of rotation is called inversion, giving invert sugar its name.

Step 2: (a)(ii) Define polysaccharides Polysaccharides are high-molecular-mass carbohydrates made of a large number of monosaccharide units linked by glycosidic bonds. On complete hydrolysis, they yield many monosaccharide molecules. The chains may be linear or branched. Starch, cellulose and glycogen are examples; each yields glucose on complete hydrolysis, though their linkages and branching differ.

Step 3: (b) Compare the structures of the proteins In fibrous proteins, polypeptide chains run approximately parallel and are held together by hydrogen bonds and, where present, disulphide bonds to form long, thread-like fibres. Examples include keratin and myosin. In globular proteins, polypeptide chains fold and coil into compact, approximately spherical shapes, as in insulin and albumin. Thus the structural distinction is an extended fibrous arrangement versus a tightly folded globular arrangement.

Step 4: Conclusion Invert sugar is the glucose–fructose mixture formed from sucrose. Polysaccharides are polymers of many monosaccharide units. Fibrous proteins have long, fibre-like arrangements, whereas globular proteins have compact, folded, approximately spherical structures.

Quick Tip to Solve: Remember that inversion refers to the sign of optical rotation. For the protein comparison, state the chain arrangement and overall shape because the question asks for a structural difference.

OR

28(B). (a) Why is glycogen known as animal starch?

(b) Differentiate between essential amino acids and non-essential amino acids.

(c) What is the effect of denaturation on the structure of proteins? [3 marks]

Solution:

Concept:

- Glycogen and starch are storage polysaccharides built from glucose units; glycogen is the principal carbohydrate reserve in animals.
- An essential amino acid must be supplied through food because the body cannot synthesise it in adequate amounts; a non-essential amino acid can be synthesised by the body.
- Protein function depends on its native three-dimensional conformation. Denaturation disturbs folding without normally breaking the peptide bonds of the primary structure.

Step 1: Explain why glycogen is animal starch Animals store excess glucose mainly as glycogen in the liver and muscles. Like starch in plants, glycogen is a reserve carbohydrate that can yield glucose when energy is needed. Both are polymers of α-D-glucose, but glycogen is more highly branched. Its storage role in animals is the reason for the name animal starch.

Step 2: Differentiate the two classes of amino acids Essential amino acids cannot be synthesised in sufficient amounts by the human body, so they must be obtained from the diet; valine and leucine are examples. Non-essential amino acids can be synthesised by the body, so a dietary supply of each such amino acid is not essential; glycine and alanine are examples. The distinction concerns the source of supply, not whether the amino acid is needed for protein formation.

Step 3: Describe the structural effect of denaturation Heating or a change in pH can disrupt the interactions that maintain the secondary and tertiary structures of a protein. The protein unfolds or loses its native spatial arrangement and hence its characteristic biological activity. In ordinary denaturation the amino-acid sequence and peptide bonds remain intact, so the primary structure is retained. Denaturation is therefore different from hydrolysis, which breaks peptide bonds.

Step 4: Conclusion (a) Glycogen is called animal starch because it is the storage polysaccharide of animals. (b) Essential amino acids must come from the diet, whereas non-essential ones can be synthesised in the body. (c) Denaturation disrupts secondary and tertiary structures while retaining the primary structure.

Quick Tip to Solve: For denaturation, distinguish loss of folding and activity from cleavage of peptide bonds: the latter is hydrolysis.

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). 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 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 explain, why IV fluids match blood's osmotic pressure, its 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, C is molarity, n is moles of solute, and V is solution volume.
- Using $n = w/M$, the required solute mass is $w = \pi VM/(iRT)$, where M is molar mass. Temperature must be in kelvin and volume units must agree with R.

Step 1: Convert temperature and identify the data The absolute temperature is $T = 27 + 273 = 300\,\text{K}$. For this dilute solution, use the given water volume as the solution volume: $V = 2.46\,\text{L}$. The other values are $\pi = 0.70\,\text{atm}$, $i = 2.59$, $R = 0.082\,\text{L atm K}^{-1}\,\text{mol}^{-1}$, and $M = 111\,\text{g mol}^{-1}$. The given factor already accounts for the effective increase in dissolved particles due to dissociation.

Step 2: Calculate moles and mass Rearranging the osmotic-pressure relation gives

$$n = \frac{\pi V}{iRT} = \frac{0.70 \times 2.46}{2.59 \times 0.082 \times 300} = 0.027027\,\text{mol}.$$

Convert the amount in moles into mass:

$$w = nM = 0.027027 \times 111 = 3.00\,\text{g}.$$

Using litres with the supplied gas constant makes the units consistent; no conversion to cubic metres is needed.

Step 3: Conclusion The required mass of $CaCl_2$ is $\boxed{3.0\,\text{g}}$ (approximately $0.0270\,\text{mol}$).

Quick Tip to Solve: Use the supplied value i = 2.59, not the ideal ion count of three, and convert 27 degrees Celsius to 300 K before substitution.

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 lower solute concentration to higher solute concentration.
- Entry of water into a cell or tissue by osmosis is called endosmosis.

Step 1: Compare the inside and outside solutions The cell sap inside a raisin contains dissolved sugars and other solutes, whereas the surrounding water has a lower solute concentration. The raisin cells therefore have a higher osmotic pressure than the surrounding water.

Step 2: Identify the direction of solvent movement Water passes inward through the semipermeable cell membranes. This inward movement increases the water content and volume of the raisin, which accounts for its swelling. It is solvent movement across a membrane, rather than simple diffusion of the sugar into water.

Step 3: Conclusion The phenomenon is endosmosis, that is, the inward movement of water by osmosis.

Quick Tip to Solve: For a raisin swelling in water, follow the water inward: inward osmosis is endosmosis.

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 non-electrolyte solution, where C is molarity and T is absolute temperature.
- A colligative property is useful experimentally when its change is measurable under conditions that do not damage the solute.

Step 1: Compare the measurable effects Even very dilute solutions can have an appreciable osmotic pressure that is measured accurately. For such solutions, elevation of boiling point and depression of freezing point may be too small for equally convenient measurement.

Step 2: Explain the temperature advantage Osmotic pressure can be measured at room temperature. Heating to the boiling point is unnecessary, so heat-sensitive macromolecules such as proteins do not need to be exposed to conditions that may denature them. This makes the method especially useful for determining high molar masses.

Step 3: Conclusion Osmotic pressure is advantageous because it is appreciable even in very dilute solutions and can be measured at room temperature, especially for molar-mass determination of heat-sensitive macromolecules.

Quick Tip to Solve: For the advantage over other colligative properties, mention a measurable dilute-solution effect and room-temperature measurement.

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

Solution:

Concept:

- Normal osmosis carries solvent through a semipermeable membrane towards the solution of higher solute concentration.
- Applying pressure greater than the osmotic pressure to the concentrated solution reverses this solvent flow.

Step 1: Apply pressure on the seawater side Seawater contains dissolved salts and has a higher osmotic pressure than pure water. In desalination, an external pressure exceeding its osmotic pressure is applied on the seawater side of a semipermeable membrane.

Step 2: Describe the separation The applied pressure forces water molecules through the membrane towards the fresh-water side, against the direction of spontaneous osmosis. Dissolved salts are largely retained on the seawater side, so the collected water has a much lower salt concentration.

Step 3: Conclusion The phenomenon responsible for desalination of seawater is reverse osmosis.

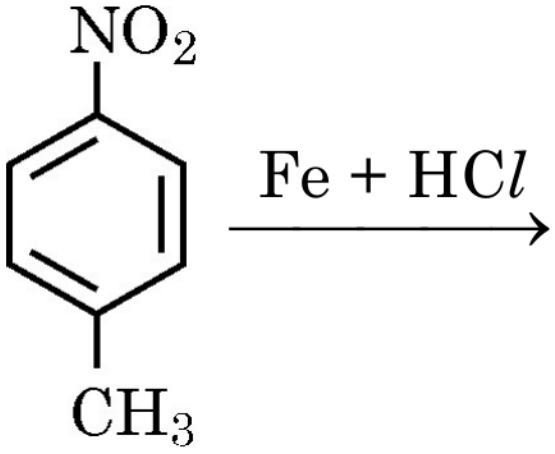
Quick Tip to Solve: Remember the direction and condition together: pressure greater than osmotic pressure drives water out of the salty solution.

30. 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. [4 marks]

30(a). Complete the following equations:

(i) $CH_3CONH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$ **?** [2 marks]

(ii)



Solution:

Concept:

- Lithium aluminium hydride, $LiAlH_4$, reduces an amide group $-CONH_2$ to $-CH_2NH_2$; the number of carbon atoms is retained.
- Iron and hydrochloric acid reduce an aromatic nitro group $-NO_2$ to an amino group $-NH_2$, without removing a methyl group attached to the ring.

Step 1: Reduce the amide in part (i) The starting compound is ethanamide, CH_3CONH_2. Reduction changes its carbonyl carbon into a methylene carbon; hydrolysis in the second stage releases the amine. The product is ethanamine (ethylamine):

$$CH_3CONH_2 \xrightarrow[\text{(ii) H2O}]{\text{(i) LiAlH4}} CH_3CH_2NH_2.$$

Thus both carbon atoms remain in the product. This reaction must not be confused with the Hofmann bromamide reaction, which gives an amine containing one fewer carbon atom.

Step 2: Reduce the nitro group in part (ii) The printed structure is para-nitrotoluene. Iron and hydrochloric acid convert its nitro group to an amino group while preserving the para relationship to the methyl substituent. The organic product is para-toluidine, also called 4-methylaniline. Using [H] to denote reducing hydrogen, the balanced reduction is

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

In the acidic reaction mixture the amine is protonated; the displayed product is the free amine obtained on isolation.

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

Quick Tip to Solve: For $LiAlH_4$, replace CO in an amide by CH_2; for Fe/HCl, replace only NO_2 by NH_2.

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 require more heat.
- Intermolecular hydrogen bonding between amine molecules requires a hydrogen bonded directly to nitrogen and a nitrogen lone pair on a neighbouring molecule.

Step 1: Examine primary amines A primary amine has the form RNH_2, so it has two $N-H$ bonds. Its molecules associate through intermolecular hydrogen bonds, $N-H\cdots N$, in addition to other molecular attractions.

Step 2: Compare tertiary amines A tertiary amine has the form R_3N and no hydrogen attached to nitrogen. Although nitrogen has a lone pair, these molecules cannot donate the hydrogen needed

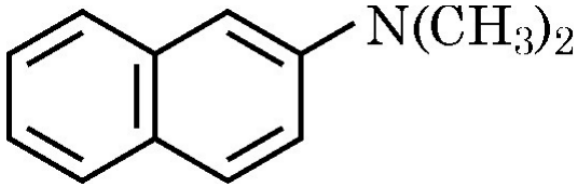
Quick Tip to Solve: Count the $N-H$ bonds when comparing pure amines: a lone pair alone cannot create self-association by hydrogen bonding.

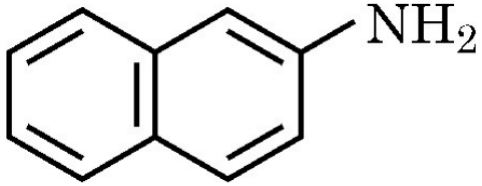
for hydrogen bonding among themselves. For comparable isomeric amines, less energy is therefore needed to separate tertiary-amine molecules during boiling.

Step 3: Conclusion Primary amines have higher boiling points than comparable tertiary amines because primary amines form intermolecular hydrogen bonds, whereas tertiary amines cannot hydrogen-bond among themselves.

Quick Tip to Solve: Count the $\mathrm{N-H}$ bonds when comparing pure amines: a lone pair alone cannot create self-association by hydrogen bonding.

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

(i) 

(ii) 

Solution:

Concept:

- An amine is classified by the number of carbon groups directly bonded to its nitrogen atom, not by the number of rings or carbon atoms in the molecule.
- The patterns $\mathrm{RNH_2}$, $\mathrm{R_2NH}$, and $\mathrm{R_3N}$ denote primary, secondary, and tertiary amines, respectively; the carbon groups may be alkyl or aryl.

Step 1: Count nitrogen substituents in structure (i) The group is $-\mathrm{N(CH_3)_2}$ attached to the naphthalene framework. Nitrogen is bonded directly to two methyl groups and one aryl group. There are three carbon groups and no $\mathrm{N-H}$ bond, so its pattern is $\mathrm{R_3N}$.

Step 2: Count nitrogen substituents in structure (ii) The group is $-\mathrm{NH_2}$ attached to the naphthalene framework. Nitrogen is bonded to one aryl group and two hydrogen atoms, giving the pattern $\mathrm{RNH_2}$. The two fused rings together do not count as two separate substituents on nitrogen.

Step 3: Conclusion Structure (i) is a tertiary (3°) amine; structure (ii) is a primary (1°) amine.

Quick Tip to Solve: Focus on the three bonds from nitrogen: two methyl groups plus one aryl group make structure (i) tertiary.

OR

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

Solution:

Concept:

- The passage compares the solubility of amines and alcohols in terms of hydrogen bonding with water.
- Oxygen is more electronegative than nitrogen, so alcohols form stronger hydrogen bonds with water than analogous amines in the comparison given.

Step 1: Compare the hydrocarbon portions Butan-1-amine, $CH_3CH_2CH_2CH_2NH_2$, and butan-1-ol, $CH_3CH_2CH_2CH_2OH$, both have a straight four-carbon chain. The comparison in the passage therefore centres on the $-NH_2$ and $-OH$ groups and their interaction with water.

Step 2: Apply the passage's hydrogen-bonding comparison Both functional groups can form hydrogen bonds with water. The more electronegative oxygen atom makes the alcohol group better able to establish the strong hydrogen-bonding interactions used in the passage's explanation. Hence the passage places the corresponding alcohol above the amine in water solubility.

Step 3: Conclusion According to the comparison stated in the passage, butan-1-ol is more soluble in water than butan-1-amine.

Quick Tip to Solve: With the same four-carbon chain in this passage-based comparison, use the stronger hydrogen bonding of the $-OH$ group.

Section E (15 marks)

31(A). (a) The conductivity of 0.1 mol L^{-1} solution of NaCl is 1.06 $\times$ 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 $\Lambda_m = 1000\kappa/c$, where κ is conductivity in S cm^{-1} and c is concentration in mol L^{-1}.
- Kohlrausch's law gives $\Lambda^{\circ}_m = \lambda^{\circ}_{Na^+} + \lambda^{\circ}_{Cl^-}$. The conductivity ratio used in this calculation is $\alpha = \Lambda_m/\Lambda^{\circ}_m$.
- Oxidation occurs at the anode and reduction at the cathode. External conventional current flows opposite to the flow of electrons.

Quick Tip to Solve: Use the factor 1000 when concentration is in mol L^{-1}. First trace electrons from the oxidised metal to the reduced ion, then reverse that arrow for conventional current.

- Primary batteries cannot be recharged for repeated use; secondary batteries have cell reactions that can be reversed by an external electrical supply.

Step 1: (a) Calculate the molar conductivity Substitute the given conductivity and concentration. The factor 1000 converts the litre-based concentration to the cubic-centimetre convention used with conductivity:

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

Step 2: (a) Calculate the conductivity ratio One formula unit of NaCl gives one Na^+ and one Cl^-, so their limiting ionic conductivities are added without extra coefficients:

$$\Lambda_m^\circ = 50.1 + 76.5 = 126.6\,\text{S cm}^2\ \text{mol}^{-1}.$$

Hence the degree of dissociation obtained by the stated conductivity method is

$$\alpha = \frac{106}{126.6} = 0.8373, \qquad \alpha \times 100 = 83.73\%.$$

For a strong electrolyte such as NaCl, this ratio is an apparent degree of dissociation: interionic effects also lower molar conductivity at finite concentration.

Step 3: (b)(i) Identify the electrodes and current direction The half-reactions for the spontaneous galvanic-cell reaction are

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

Zinc releases electrons and is the negative electrode; silver receives electrons and is the positive electrode. Thus electrons pass through the external wire from zinc to silver, while conventional current passes from silver to zinc. The positive standard cell potential is consistent with this spontaneous direction.

Step 4: (b)(ii) Distinguish the battery types A primary battery operates through a cell reaction that is not practically reversible by passing current; it is used until its reactants are consumed and cannot be recharged. A dry cell is an example. In a secondary battery, the discharge reaction can be reversed by supplying electrical energy, so the battery can be recharged and used repeatedly. A lead storage battery is an example.

Step 5: Conclusion (a) $\Lambda_m = 106\,\text{S cm}^2\ \text{mol}^{-1}$ and the calculated conductivity ratio gives $\alpha = 0.837$, or approximately 83.7%. (b)(i) Conventional current flows externally from the silver electrode to the zinc electrode. (ii) Primary batteries are not rechargeable; secondary batteries are rechargeable because their cell reactions are reversible.

Quick Tip to Solve: Use the factor 1000 when concentration is in mol L^{-1}. First trace electrons from the oxidised metal to the reduced ion, then reverse that arrow for conventional current.

OR

31(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 $\times$ 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:

- For a conductivity cell, $\kappa = G(l/A) = (l/A)/R$, where R is resistance, $G = 1/R$ is conductance and l/A is the cell constant. The same cell has the same cell constant.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ for κ in S cm^{-1} and concentration c in mol L^{-1}.
- A fuel cell continuously converts the chemical energy of supplied fuel and oxidant directly into electrical energy.
- The Nernst equation relates cell potential to the reaction quotient. Constant activities of the substances in the net cell reaction give a constant potential at fixed temperature.

Step 1: (a) Determine the cell constant from the standard solution The $0.1\,\mathrm{M\ KCl}$ solution has known conductivity and resistance. Rearranging $\kappa = (l/A)/R$ gives

$$\frac{l}{A} = \kappa_1 R_1 = (1.29 \times 10^{-2})(100) = 1.29\,\mathrm{cm^{-1}}.$$

This geometric factor is unchanged when the solution in the cell is replaced.

Step 2: (a) Calculate the conductivity of the dilute solution With $0.01\,\mathrm{mol\ L^{-1}\ KCl}$, the resistance is $300\,\Omega$. Therefore

$$\kappa_2 = \frac{l/A}{R_2} = \frac{1.29}{300} = 4.30 \times 10^{-3}\,\mathrm{S\ cm^{-1}}.$$

As a check, tripling the resistance in the same cell reduces conductivity to one-third of its original value.

Step 3: (a) Convert conductivity to molar conductivity Use the concentration of the dilute solution, not the concentration used for calibration:

$$\Lambda_{m,2} = \frac{1000\kappa_2}{c_2} = \frac{1000(4.30 \times 10^{-3})}{0.01} = 430\,\mathrm{S\ cm^2\ mol^{-1}}.$$

The litre-to-cubic-centimetre conversion produces the factor 1000.

Step 4: (b)(i) Give two advantages of the hydrogen-oxygen fuel cell First, the H_2-O_2 fuel cell has high electrical conversion efficiency because it converts chemical energy directly into electrical energy. Second, its operating reaction forms water as the product, so it does not release combustion pollutants such as carbon dioxide or smoke at the cell:

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

Quick Tip to Solve: For the same conductivity cell, $\kappa_1 R_1 = \kappa_2 R_2$. Then use the new solution's concentration when calculating its molar conductivity.

Step 5: (b)(ii) Explain the constant potential of a mercury cell The electrode reactions in the alkaline mercury cell are

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

Adding them cancels water, hydroxide ions and electrons, giving

$$\mathrm{Zn(Hg) + HgO\,(s) \longrightarrow ZnO\,(s) + Hg\,(l)}.$$

No electrolyte ion appears in the overall reaction, so no changing electrolyte concentration enters the cell reaction quotient. The activities of the solid and liquid phases remain effectively constant during normal discharge; hence the cell potential remains nearly constant throughout its useful life.

Step 6: Conclusion (a) The conductivity is $4.30 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ and the molar conductivity is $430\,\mathrm{S\,cm^2\,mol^{-1}}$. (b)(i) The fuel cell offers high electrical efficiency and clean operation with water as its product. (ii) The mercury cell has constant potential because its net reaction does not involve a changing electrolyte-ion concentration.

Quick Tip to Solve: For the same conductivity cell, $\kappa_1 R_1 = \kappa_2 R_2$. Then use the new solution's concentration when calculating its molar conductivity.

32(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:

- Alcohols contain an O–H bond and react with sodium to form sodium alkoxides with liberation of hydrogen; ethers lack this acidic hydrogen.
- Ethanol gives the iodoform test with iodine and aqueous sodium hydroxide. The characteristic yellow precipitate is iodoform, CHI_3.
- Concentrated H_2SO_4 at $413\,\mathrm{K}$ causes intermolecular dehydration of ethanol to ethoxyethane. Excess HI cleaves the ether and converts the alcohol formed into an alkyl iodide.

Step 1: Identify A and its reaction with sodium The molecular formula C_2H_6O allows ethanol, CH_3CH_2OH, and dimethyl ether, CH_3OCH_3. Liberation of hydrogen with sodium establishes the presence of an O–H bond, so A is ethanol. Sodium replaces the hydrogen of the hydroxyl group; B is sodium ethoxide, CH_3CH_2ONa:

$$\mathrm{2\,CH_3CH_2OH + 2\,Na \longrightarrow 2\,CH_3CH_2ONa + H_2\uparrow}.$$

The two alcohol molecules supply the two hydrogen atoms needed to form one molecule of hydrogen gas.

Quick Tip to Solve: Use sodium to distinguish ethanol from its ether isomer, then use $413\,\mathrm{K}$ to select ether formation. With excess HI, continue the cleavage until both ethyl groups become iodoethane.

Step 2: Identify C through the iodoform reaction In alkaline iodine, ethanol is first oxidised to ethanal. Its methyl carbon is then iodinated and cleavage gives iodoform as a yellow precipitate, together with sodium methanoate. Thus C is CHI_3. The balanced overall reaction is

$$\begin{aligned} &CH_3CH_2OH + 4\,I_2 + 6\,NaOH \\ &\quad\longrightarrow CHI_3\downarrow + HCOONa + 5\,NaI + 5\,H_2O. \end{aligned}$$

The formation of iodoform independently supports the identification of A as ethanol.

Step 3: Identify D from dehydration at 413 K At $413\,K$, two molecules of ethanol undergo acid-catalysed intermolecular dehydration, losing one molecule of water and forming ethoxyethane (diethyl ether):

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

Hence D is $CH_3CH_2OCH_2CH_3$, whose molecular formula is $C_4H_{10}O$, exactly as specified. The stated temperature favours ether formation rather than the higher-temperature dehydration to ethene.

Step 4: Identify E by cleavage with excess HI Protonation of the ether oxygen makes the carbon–oxygen bond susceptible to attack by iodide. Initial cleavage gives iodoethane and ethanol; excess HI also converts this ethanol to iodoethane:

$$\begin{aligned} &CH_3CH_2OCH_2CH_3 + HI \longrightarrow CH_3CH_2I + CH_3CH_2OH, \\ &CH_3CH_2OH + HI \longrightarrow CH_3CH_2I + H_2O. \end{aligned}$$

Combining the two stages gives

$$CH_3CH_2OCH_2CH_3 + 2\,HI \longrightarrow 2\,CH_3CH_2I + H_2O.$$

Step 5: Conclusion A is ethanol, CH_3CH_2OH; B is sodium ethoxide, CH_3CH_2ONa; C is iodoform, CHI_3; D is ethoxyethane, $CH_3CH_2OCH_2CH_3$; and E is iodoethane, CH_3CH_2I.

Quick Tip to Solve: Use sodium to distinguish ethanol from its ether isomer, then use $413\,K$ to select ether formation. With excess HI, continue the cleavage until both ethyl groups become iodoethane.

OR

32(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 activates the phenol ring towards electrophilic substitution at its ortho and para positions; bromine water gives substitution at all three available activated positions.
- Hydroboration–oxidation converts an alkene into an anti-Markovnikov alcohol. A ketone is reduced to a secondary alcohol by a hydride reducing agent such as $NaBH_4$.
- Acid-catalysed hydration involves protonation of the alkene, nucleophilic attack of water on the carbocation, and deprotonation of the oxonium ion. The acid catalyst is regenerated.

Step 1: (a)(i) Brominate phenol Use bromine water, $Br_2(aq)$, at room temperature. The strongly activating $-OH$ group directs substitution to positions 2, 4 and 6, giving a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3\,Br_2 \longrightarrow C_6H_2Br_3OH\downarrow + 3\,HBr.$$

A Lewis acid catalyst is unnecessary because the phenol ring is already activated.

Step 2: (a)(ii) Convert propene to propan-1-ol Use hydroboration followed by oxidation: first BH_3 in tetrahydrofuran (THF), then H_2O_2 in aqueous NaOH. The net conversion is

$$CH_3CH{=}CH_2 \xrightarrow[2.\ H_2O_2,\ OH^-]{1.\ BH_3/THF} CH_3CH_2CH_2OH.$$

Boron initially bonds to the less substituted terminal carbon; oxidation replaces the carbon–boron bond by a carbon–oxygen bond. The hydroxyl group therefore appears on carbon 1. Acid-catalysed hydration would instead give propan-2-ol and is unsuitable for this conversion.

Step 3: (a)(iii) Reduce butan-2-one Use $NaBH_4$, followed by aqueous work-up. Reduction adds hydrogen across the carbonyl group while retaining the carbon skeleton:

$$CH_3COCH_2CH_3 + 2\,[H] \xrightarrow{NaBH_4} CH_3CH(OH)CH_2CH_3.$$

The ketone carbonyl becomes a secondary alcohol group. $LiAlH_4$ in dry ether followed by hydrolysis is an alternative reagent sequence.

Step 4: (b) Protonate the alkene to form a carbocation Use propene to illustrate hydration in dilute aqueous acid. The electron-rich π bond accepts a proton from hydronium, producing the more stable secondary carbocation:

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

Quick Tip to Solve: For propan-1-ol from propene, choose hydroboration–oxidation. For the acid-hydration mechanism, track the positive charge from carbon to oxygen and finally regenerate H_3O^+.

The π electrons form the new carbon–hydrogen bond as the hydronium oxygen–hydrogen bond breaks towards oxygen. Proton addition at the terminal carbon leaves positive charge on carbon 2, rather than forming a less stable primary carbocation.

Step 5: Allow water to attack the carbocation A lone pair on the oxygen atom of water attacks the positively charged carbon, forming a carbon–oxygen bond and a protonated alcohol (oxonium ion):

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

Oxygen now has three bonds and carries the positive charge. The abundant water acts as the nucleophile.

Step 6: Remove a proton and regenerate the acid Another water molecule removes a proton from the oxonium ion. The electrons of its oxygen–hydrogen bond remain on the alcohol oxygen:

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

Hydronium is regenerated, so acid is a catalyst. Overall, water adds across the alkene double bond, with the hydroxyl group at the more substituted carbon in this example.

Step 7: Conclusion The reagents are (i) bromine water, (ii) BH_3/THF followed by alkaline H_2O_2, and (iii) $NaBH_4$ followed by aqueous work-up. Acid-catalysed hydration proceeds through a carbocation and oxonium ion to the alcohol; propene gives propan-2-ol by this mechanism.

Quick Tip to Solve: For propan-1-ol from propene, choose hydroboration–oxidation. For the acid-hydration mechanism, track the positive charge from carbon to oxygen and finally regenerate H_3O^+.

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

(i) Propanone to Propene

(ii) Benzoic acid to Benzaldehyde

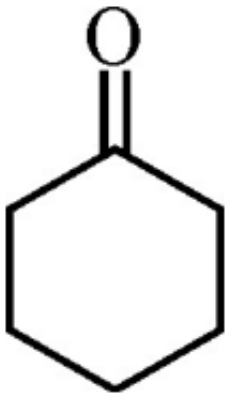
(iii) Benzene to *m*-Nitroacetophenone

(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:

- Reduction of a ketone gives a secondary alcohol, whose dehydration gives an alkene. Rosenmund reduction converts an acid chloride into an aldehyde.
- The acetyl group is meta-directing in electrophilic aromatic substitution. The order of acylation and nitration therefore determines the required aromatic product.
- Addition of CN^- to a carbonyl group is favoured by low steric hindrance and high electrophilicity. Aldol condensation requires at least one α-hydrogen on an aldehyde or ketone.

Step 1: (a)(i) Reduce propanone and dehydrate the alcohol First reduce the carbonyl group using sodium borohydride, followed by aqueous work-up, to obtain propan-2-ol. Heat this alcohol with concentrated sulphuric acid to eliminate water and form propene:

$$CH_3COCH_3 \xrightarrow[\text{work-up}]{NaBH_4} CH_3CH(OH)CH_3$$

$$CH_3CH(OH)CH_3 \xrightarrow[\text{heat}]{\text{conc}\cdot\ H_2SO_4} CH_3CH{=}CH_2 + H_2O$$

Direct complete reduction of the ketone would give an alkane, so the alcohol intermediate is essential in this route.

Step 2: (a)(ii) Form benzoyl chloride and reduce it selectively Treat benzoic acid with thionyl chloride. Then carry out Rosenmund reduction using hydrogen and poisoned palladium supported on barium sulphate:

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

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

The poisoned catalyst limits further reduction, allowing benzaldehyde to be obtained.

Step 3: (a)(iii) Acylate benzene before nitration Friedel–Crafts acylation with acetyl chloride and anhydrous aluminium chloride forms acetophenone. Nitration then introduces the nitro group predominantly at the meta position because the acetyl group withdraws electrons:

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

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

Nitrating first is unsuitable: nitrobenzene is strongly deactivated and does not undergo ordinary Friedel–Crafts acylation.

Step 4: (b)(i) Compare steric hindrance and electron donation The two tert-butyl groups strongly crowd the carbonyl carbon and donate electron density, making their ketone least reactive. Propanone has two smaller methyl groups. Ethanal has only one alkyl group and one hydrogen, so nucleophilic attack is easiest. Thus the increasing reactivity towards hydrogen cyanide is

$$((CH_3)_3C)_2CO < (CH_3)_2CO < CH_3CHO.$$

Step 5: (b)(ii) Locate the alpha hydrogens Ethanal, CH_3CHO, has α-hydrogens on its methyl

Quick Tip to Solve: For the benzene conversion, install the meta-directing acetyl group first. For aldol condensation, inspect the carbon next to the carbonyl, not the aldehydic hydrogen.

carbon. The cyclic ketone shown is cyclohexanone; its two carbons adjacent to the carbonyl group are methylene groups and also bear α-hydrogens. Both can form an enolate and undergo aldol condensation. Methanal, $HCHO$, has no adjacent carbon, while benzaldehyde, C_6H_5CHO, has no α-hydrogen; neither undergoes self-aldol condensation.

Step 6: Conclusion The conversions proceed through propan-2-ol, benzoyl chloride and acetophenone, respectively. HCN reactivity increases from the di-tert-butyl ketone to propanone to ethanal. The compounds undergoing aldol condensation are ethanal and cyclohexanone.

Quick Tip to Solve: For the benzene conversion, install the meta-directing acetyl group first. For aldol condensation, inspect the carbon next to the carbonyl, not the aldehydic hydrogen.

OR

33(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:

- Methyl ketones, $CH_3C(=O)R$, where R is an alkyl or aryl group, give the iodoform test with iodine and aqueous alkali, producing yellow CHI_3.
- Aldehydes reduce Tollens' reagent, the alkaline diamminesilver(I) complex, to metallic silver; simple ketones do not.
- Electron-withdrawing substituents strengthen carboxylic acids by stabilising their carboxylate ions. Boiling point depends on the strength of intermolecular attractions.

Step 1: (a)(i) Apply the iodoform test to the aromatic ketones Warm separate samples with iodine and aqueous sodium hydroxide. Acetophenone contains the methyl ketone group and gives a yellow precipitate of iodoform. Benzophenone has two phenyl groups attached to its carbonyl carbon and gives no yellow precipitate under these conditions.

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

Both compounds are ketones, so Tollens' reagent would not distinguish this pair.

Step 2: (a)(ii) Use Tollens' reagent for propanal and propanone Warm the samples separately with freshly prepared Tollens' reagent. Propanal is oxidised to propanoate and reduces silver(I) to metallic

Quick Tip to Solve: Check for a methyl group directly bonded to the carbonyl carbon before choosing iodoform. For boiling points in this set, rank nonpolar, ether, carbonyl and hydrogen-bonded liquids in that order.

silver, giving a silver mirror. Propanone is a ketone and does not produce a silver mirror.

$$\begin{aligned}&\mathrm{CH_3CH_2CHO} + 2\,[\mathrm{Ag(NH_3)_2}]^{+} + 3\,\mathrm{OH^-}\\ &\longrightarrow \mathrm{CH_3CH_2COO^-} + 2\,\mathrm{Ag}\downarrow + 4\,\mathrm{NH_3} + 2\,\mathrm{H_2O}\end{aligned}$$

The positive observation identifies the aldehyde because its carbonyl group is readily oxidised under these mild conditions.

Step 3: (a)(iii) Test the two pentanones with alkaline iodine Pentan-2-one, $\mathrm{CH_3COCH_2CH_2CH_3}$, is a methyl ketone and gives a yellow iodoform precipitate on warming with iodine and aqueous sodium hydroxide. Pentan-3-one, $\mathrm{CH_3CH_2COCH_2CH_3}$, has an ethyl group on each side of the carbonyl and gives no iodoform precipitate.

$$\begin{aligned}&\mathrm{CH_3CH_2CH_2COCH_3} + 3\,\mathrm{I_2} + 4\,\mathrm{NaOH}\\ &\longrightarrow \mathrm{CH_3CH_2CH_2COONa} + \mathrm{CHI_3}\downarrow + 3\,\mathrm{NaI} + 3\,\mathrm{H_2O}\end{aligned}$$

Step 4: (b)(i) Compare the stability of the conjugate bases Fluoroacetic acid, $\mathrm{CH_2FCOOH}$, is stronger than ethanoic acid, $\mathrm{CH_3COOH}$. The highly electronegative fluorine atom withdraws electron density through sigma bonds by its negative inductive effect. This stabilises the negative charge in the fluoroacetate ion, $\mathrm{CH_2FCOO^-}$, and favours ionisation. The methyl group's positive inductive effect in ethanoic acid instead destabilises the carboxylate ion relative to an electron-withdrawing substituent.

Step 5: (b)(ii) Rank the intermolecular attractions Propane is nonpolar and has only London dispersion forces. Dimethyl ether is polar and has dipole–dipole attractions; ethanal has a stronger carbonyl dipole, giving stronger attractions than the ether. Ethanol molecules form intermolecular hydrogen bonds through their hydroxyl groups, so ethanol has the highest boiling point in this set. The increasing order is

$$\mathrm{CH_3CH_2CH_3} < \mathrm{CH_3OCH_3} < \mathrm{CH_3CHO} < \mathrm{CH_3CH_2OH}.$$

Ether and ethanal can accept hydrogen bonds from water, but neither can form the alcohol-like hydrogen-bond network in its own pure liquid.

Step 6: Conclusion Use the iodoform test for acetophenone/benzophenone and pentan-2-one/pentan-3-one; only the first compound in each pair gives yellow iodoform. Propanal alone gives Tollens' silver mirror. Fluoroacetic acid is stronger, and boiling points increase as propane, dimethyl ether, ethanal, ethanol.

Quick Tip to Solve: Check for a methyl group directly bonded to the carbonyl carbon before choosing iodoform. For boiling points in this set, rank nonpolar, ether, carbonyl and hydrogen-bonded liquids in that order.