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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is NOT allowed.

Section A (16 marks)

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

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

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

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

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

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

Solution:

Concept:

- The open-chain formula of glucose is $CHO - (CHOH)_4 - CH_2OH$; it contains an aldehyde group and an unbranched six-carbon chain.
- The cyclic hemiacetal forms have different configurations at the anomeric carbon, C-1, giving the α and β forms.

Step 1: Check reactions supported by the open chain Prolonged heating with HI converts glucose into n-hexane, supporting its straight six-carbon skeleton, so (A) is explained. The aldehyde group reacts with hydroxylamine to give an oxime, explaining (B). Bromine water oxidises the aldehyde group to a carboxyl group, producing gluconic acid, so (C) is also explained.

Step 2: Identify the limitation A single open-chain aldehyde structure does not account for two crystalline anomers. Ring formation creates a new stereogenic centre at C-1, and the two configurations of this centre explain the α and β forms in option (D).

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

Quick Tip to Solve: For glucose, separate evidence for the aldehyde and carbon chain from evidence for cyclic anomers.

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

(A) Covalent Bond

(B) Peptide Bond

(C) Glycosidic Bond

(D) Coordinate Bond

Correct Answer: (B) Peptide Bond

Solution:

Concept:

- A peptide linkage is the amide group $-CO-NH-$ formed between two amino acids.
- Condensation joins the carboxyl group of one amino acid to the amino group of another, eliminating water.

Quick Tip to Solve: Look for the specific linkage name: amino acids form peptide bonds; sugar units form glycosidic bonds.

Step 1: Identify the joining groups In a protein chain, the $-COOH$ group of one α-amino acid reacts with the $-NH_2$ group of another. Loss of H_2O forms the covalent amide linkage $-CO-NH-$, specifically called a peptide bond.

Step 2: Compare the options Option (B) gives the specific name of the linkage. A peptide bond is covalent, but (A) is a broad bond category rather than the characteristic linkage requested. Glycosidic bonds in (C) join sugar units, while coordinate bonds in (D) involve donation of an electron pair and do not define the protein backbone.

Step 3: Conclusion The amino-acid units are joined by peptide bonds. Hence, the correct option is (B).

Quick Tip to Solve: Look for the specific linkage name: amino acids form peptide bonds; sugar units form glycosidic bonds.

3. 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 adenine, guanine, cytosine and thymine as its nitrogenous bases.
- RNA contains adenine, guanine, cytosine and uracil; uracil replaces thymine in its standard base set.

Step 1: Compare the base sets Write the standard base sets as DNA: A, G, C, T, and RNA: A, G, C, U. Adenine, guanine and cytosine occur in both nucleic acids, whereas thymine belongs to the DNA set.

Step 2: Eliminate the shared bases Guanine in (A), cytosine in (B), and adenine in (D) cannot be the answer because all three occur in RNA as well as DNA. Thymine in (C) is the distinguishing base in DNA; RNA uses uracil in its place.

Step 3: Conclusion The required base is thymine. Hence, the correct option is (C).

Quick Tip to Solve: Compare the final letters of AGCT and AGCU: DNA has thymine, while RNA has uracil.

4. 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 $R - C \equiv N$ to a primary amine $R - CH_2 - NH_2$, after work-up.
- The nitrile carbon remains in the product, so the number of carbon atoms does not change.

Step 1: Write the nitrile reduction Ethanenitrile is CH_3CN, containing two carbon atoms. Complete reduction of its nitrile group gives

$$CH_3CN + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2NH_2.$$

Here $[H]$ denotes reducing hydrogen equivalents, with aqueous work-up completing formation of the amine.

Step 2: Name the product and reject alternatives The product $CH_3CH_2NH_2$ is ethylamine, also called ethanamine. Ethanal in (B) is an aldehyde rather than the complete-reduction product. Propylamine in (C) has three carbons and methylamine in (D) has only one; neither conserves the two-carbon skeleton.

Step 3: Conclusion Ethanenitrile gives ethylamine on reduction with lithium aluminium hydride. Hence, the correct option is (A).

Quick Tip to Solve: Retain the nitrile carbon when converting a nitrile into an amine: the carbon count stays the same.

5. 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 associate through intermolecular hydrogen bonding involving their hydroxyl groups.

Quick Tip to Solve: First order the straight-chain primary alcohols by size, then place butan-2-ol just below butan-1-ol.

- Within comparable alcohols, a larger carbon chain increases dispersion forces; for the two butanol isomers, butan-1-ol has the higher boiling point.

Step 1: Compare the carbon-chain lengths All four compounds contain one hydroxyl group and can form hydrogen bonds. For the straight-chain primary alcohols, increasing molecular size strengthens dispersion forces, giving propan-1-ol below butan-1-ol below pentan-1-ol.

Step 2: Place the secondary butanol Butan-2-ol boils below butan-1-ol because its more compact structure and less accessible hydroxyl group reduce intermolecular association relative to the primary isomer. Its extra carbon compared with propan-1-ol still gives a higher boiling point. Thus the increasing order is

$$\text{propan-1-ol} < \text{butan-2-ol} < \text{butan-1-ol} < \text{pentan-1-ol}.$$

(A) reverses the two butanols; (B) places pentan-1-ol first; (D) incorrectly places propan-1-ol above both butanols.

Step 3: Conclusion The correct 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: First order the straight-chain primary alcohols by size, then place butan-2-ol just below butan-1-ol.

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

(A) Propan-2-ol

(B) Butan-2-ol

(C) 1-Bromobutane

(D) 2-Bromopropane

Correct Answer: (B) Butan-2-ol

Solution:

Concept:

- A tetrahedral carbon bonded to four different groups is a stereogenic centre.
- A molecule with one such centre is chiral when its mirror image is non-superimposable on it.

Step 1: Inspect butan-2-ol In $CH_3 - CH(OH) - CH_2CH_3$, carbon-2 is bonded to $-OH$, $-H$, $-CH_3$ and $-CH_2CH_3$. All four groups differ, so this carbon is stereogenic and butan-2-ol is chiral.

Step 2: Check the other molecules Propan-2-ol in (A) has two identical methyl groups on the hydroxyl-bearing carbon. In 1-bromobutane, (C), the bromine-bearing carbon has two hydrogens and no other carbon has four different substituents. In 2-bromopropane, (D), the bromine-bearing carbon has two identical methyl groups. These molecules lack the required stereogenic centre.

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

Quick Tip to Solve: At the candidate carbon, list all four attached groups; two identical groups immediately rule out chirality here.

7. 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 homoleptic complex contains only one kind of ligand attached to the central metal.
- A heteroleptic complex contains more than one kind of ligand; ligand identity matters, not simply ligand count.

Step 1: Check the single-ligand complexes The cobalt complex in (A) and chromium complex in (B) each contain six ammine ligands, NH_3, and no second ligand type. The nickel complex in (C) contains six aqua ligands, H_2O. Each is therefore homoleptic despite the different metals and charges.

Step 2: Identify the mixed-ligand complex In $[Co(NH_3)_4Cl_2]^{+}$, the central cobalt is coordinated to four ammine ligands and two chlorido ligands. Because NH_3 and Cl^{-} are two distinct ligand types, the complex is heteroleptic. The overall charge does not change this classification.

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

Quick Tip to Solve: Count distinct ligand types inside the coordination brackets, rather than the number of ligands or the charge.

8. 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:

- Neutral ligands do not contribute to the charge of a complex; each chlorido ligand has charge -1.
- Ligand names precede the metal name in alphabetical order, ignoring multiplying prefixes such as di.

Step 1: Determine the oxidation state The complex is neutral. If the oxidation state of platinum is x, then $x + 2(0) + 2(-1) = 0$, so $x = +2$. Thus the Roman numeral must be (II), ruling out options (A) and (C).

Step 2: Arrange the ligand names The ligand NH_3 is called ammine and Cl^{-} is called chlorido.

Quick Tip to Solve: First calculate the metal oxidation state, then alphabetise ligand names without their prefixes.

Alphabetically, ammine precedes chlorido; the prefix di does not affect this ordering. There are two of each ligand, so diamminedichlorido precedes platinum. Option (D) reverses the required ligand order.

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

Quick Tip to Solve: First calculate the metal oxidation state, then alphabetise ligand names without their prefixes.

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

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

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

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

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

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

Solution:

Concept:

- Chromium has atomic number $Z = 24$; the argon core contains 18 electrons.
- The ground state is determined by the total energy; a half-filled $3d^5$ subshell has enhanced stability.

Step 1: Count the electrons beyond argon Chromium has $24 - 18 = 6$ electrons outside the argon core. Therefore the occupations of the $3d$ and $4s$ subshells must add to six. Options (A) and (D) give five and seven electrons respectively and cannot describe neutral chromium.

Step 2: Use the observed ground-state arrangement The simple filling prediction is $[\mathrm{Ar}]3d^4 4s^2$, option (B). However, the actual lower-energy ground state redistributes one electron from $4s$ to $3d$, giving a half-filled $3d^5$ subshell. This arrangement is associated with exchange-energy stabilisation and the close energies of the two subshells.

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

Quick Tip to Solve: For chromium, remember the six outer electrons as five in 3d and one in 4s.

10. 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 a rate law $r = k[A]^m[B]^n$, the overall order is $m + n$.
- Reaction order comes from the experimentally established rate law, not from the coefficients of the balanced equation.

Step 1: Read the powers in the rate law The supplied rate law is $r = k[A]^{1/2}[B]^1$. Thus the reaction is half order with respect to A and first order with respect to B. The coefficient 2 before B in the reaction equation does not replace the exponent 1 in the rate expression.

Step 2: Add the partial orders The overall order is $\frac{1}{2} + 1 = \frac{3}{2} = 1.5$. Option (B) uses only the power of B, while option (C) uses only the power of A. Option (D) incorrectly assigns a whole-number order or uses the coefficient of B rather than adding the rate-law exponents.

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

Quick Tip to Solve: Underline the concentration exponents in the rate law and add them, ignoring equation coefficients.

11. 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 is the number of reacting species participating in a single elementary step.
- It is a positive integer; experimental rate-law exponents instead determine reaction order.

Step 1: Identify the scope of molecularity A complex reaction proceeds through several elementary steps. Each step can have its own molecularity, but assigning one molecularity to the overall complex reaction has no meaning. Its overall equation does not specify a single molecular collision.

Step 2: Check the remaining statements Option (A) confuses molecularity with experimentally

Quick Tip to Solve: Associate molecularity with an elementary step and order with the measured rate law.

determined reaction order. Option (C) is false because a count of species in an elementary reaction cannot be zero or fractional. Option (D) is false because simultaneous effective collisions of many species are very improbable; molecularity greater than three is not common.

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

Quick Tip to Solve: Associate molecularity with an elementary step and order with the measured rate law.

12. Consider the following reaction:

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

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

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

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

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

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

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

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

Solution:

Concept:

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

Step 1: Determine the electron transfer and potential difference Zinc changes from oxidation state 0 to +2, releasing two electrons: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$. The two silver atoms are reduced from +1 to 0 and together receive two electrons. Thus $n = 2$. Using the reduction-potential values supplied in the question, $E^\circ_{\text{cell}} = 0.80 - (-0.76) = 1.56\,\text{V}$.

Step 2: Calculate the Gibbs energy change Substituting the supplied data gives

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

The positive value in option (B) has the wrong sign; options (C) and (D) do not match this product. The printed cathode datum is labelled Ag^+/Ag, so this numerical choice follows the potential values supplied, rather than a separately determined $\text{Ag}_2\text{O}/\text{Ag}$ electrode potential.

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

Quick Tip to Solve: Count electrons from zinc oxidation, subtract the signed potentials, then convert joules to kilojoules.

13. Assertion (A): Glucose gets oxidized to six carbon gluconic acid on reaction with bromine water.
Reason (R): The carbonyl group is absent in the open chain structure of glucose. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Open-chain glucose is an aldohexose with an aldehyde group $-\mathrm{CHO}$.
- Bromine water mildly oxidises an aldehyde to a carboxylic acid without changing the carbon skeleton.

Step 1: Judge the assertion Glucose reacts with bromine water to give gluconic acid. Its terminal aldehyde group becomes $-\mathrm{COOH}$, while all six carbon atoms remain in the chain. Consequently, the assertion that a six-carbon gluconic acid forms is true.

Step 2: Judge the reason The open-chain structure is $\mathrm{CHO}-(\mathrm{CHOH})_4-\mathrm{CH_2OH}$. The $-\mathrm{CHO}$ group contains a carbonyl bond, $\mathrm{C}=\mathrm{O}$. Therefore the claim that the carbonyl group is absent from open-chain glucose is false.

Step 3: Check the proposed explanation The oxidation is explained by the presence of an aldehyde carbonyl group, not its absence. Thus the reason cannot explain the true assertion. Options (A) and (B) wrongly call the reason true, and option (D) wrongly calls the assertion false.

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

Quick Tip to Solve: For mild oxidation of glucose, track only the terminal CHO group becoming COOH.

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

[1 mark]

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

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

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

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

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

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines through alkylation of the phthalimide anion followed by hydrolysis.
- Ordinary aryl halides do not undergo the required nucleophilic substitution with the phthalimide anion.

Step 1: Judge the assertion The phthalimide anion substitutes a suitable alkyl halide to form an N-alkylphthalimide; hydrolysis then releases a primary aliphatic amine. The same route does not prepare aromatic primary amines such as aniline from ordinary aryl halides. The assertion is therefore false.

Step 2: Judge the reason In an aryl halide, the carbon bonded to the halogen is sp^2-hybridised and the carbon-halogen bond has partial double-bond character through resonance. The aryl halide does not undergo the usual nucleophilic substitution with the phthalimide anion. The reason is true in the context of Gabriel synthesis.

Step 3: Relate the statements to the options The true reason accounts for why aromatic primary amines cannot be obtained by this synthesis, directly contradicting the assertion. Options (A), (B) and (C) all incorrectly classify the assertion as true; only option (D) matches the two truth values.

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

Quick Tip to Solve: In Gabriel synthesis, check whether the halide is alkyl or aryl before predicting the amine.

15. 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 at least one common oxidation state.
- A filled d^{10} subshell does not satisfy this definition.

Step 1: Judge the assertion Zinc, cadmium and mercury belong to the d-block, but their atoms and common ions have filled d subshells. Consequently, the assertion is true.

Step 2: Judge the reason The relevant configurations are $\mathrm{Zn} : 3d^{10}4s^2$, $\mathrm{Cd} : 4d^{10}5s^2$ and $\mathrm{Hg} : 5d^{10}6s^2$. Their common $+2$ ions lose the outer s electrons and retain d^{10}. The printed statement about filled orbitals refers to these d orbitals; the reason is true.

Step 3: Connect the reason to the assertion The absence of a partially filled d subshell is precisely why these elements are excluded from transition elements. Thus the reason explains the assertion; options (B), (C) and (D) respectively deny this explanation or incorrectly declare one statement false.

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

Quick Tip to Solve: Check the d subshell in both the atom and common ions, rather than using membership of the d-block alone.

16. 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 one elementary collision step.
- A collision involving two reactant molecules is bimolecular.

Step 1: Judge the assertion For the stated bimolecular decomposition $2HI \rightarrow H_2 + I_2$, two HI molecules participate in the reacting collision. Its molecularity is therefore two, so A is true.

Step 2: Judge the reason The reason identifies the simultaneous encounter of two reactant molecules. This is exactly a bimolecular event, so R is true in the elementary-reaction interpretation used here.

Step 3: Check the explanation Counting the two colliding molecules gives molecularity two directly. Hence R explains A. Option (B) wrongly denies the explanatory link; (C) and (D) wrongly classify one of the statements as false. In general, molecularity belongs to an elementary step and should not be inferred merely from an arbitrary overall balanced equation.

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

Quick Tip to Solve: Count molecules in the elementary collision; distinguish this count from reaction order, which is obtained experimentally.

Section B (10 marks)

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

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

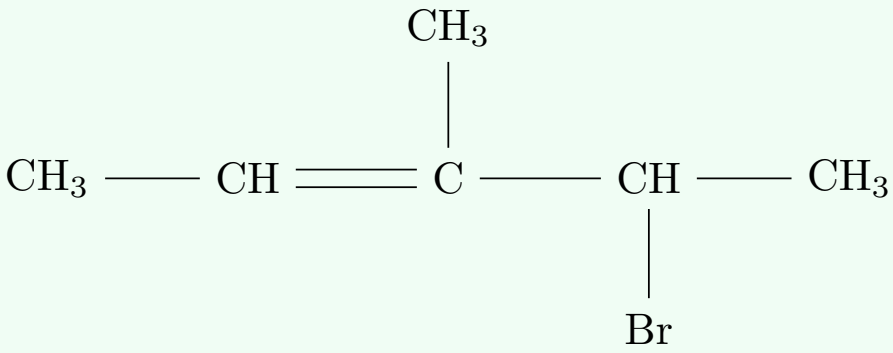
Solution:

Concept:

- In an IUPAC name, the parent chain fixes the carbon skeleton and locants fix the positions of the double bond and substituents.
- Aqueous KOH supplies OH^-, which replaces halide in a haloalkane by nucleophilic substitution.

Quick Tip to Solve: Place the double bond before adding substituents, and associate aqueous KOH with replacement of halogen by OH.

Step 1: (a) Build the named structure Use a five-carbon chain and place its double bond between C2 and C3, as required by pent-2-ene. Attach a methyl group at C3 and bromine at C4. C3 therefore has no hydrogen: its bonds are a double bond to C2 and single bonds to C4 and the methyl substituent. The labelled structural formula is shown below.



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

Step 2: (b) React chloroethane with aqueous potassium hydroxide The hydroxide ion replaces chlorine in chloroethane, giving ethanol. Chloride combines with potassium to give potassium chloride:

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

This is nucleophilic substitution (hydrolysis). The aqueous medium favours alcohol formation; the alcoholic-KOH elimination condition is not the reagent specified in the question.

Step 3: Conclusion (a) The structure is $CH_3CH = C(CH_3)CH(Br)CH_3$. (b) Chloroethane forms ethanol and potassium chloride with aqueous KOH.

Quick Tip to Solve: Place the double bond before adding substituents, and associate aqueous KOH with replacement of halogen by OH.

18. (a) Define Collision frequency.

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

Solution:

Concept:

- Collision frequency is the number of molecular collisions occurring per unit time per unit volume of the reaction mixture.
- For $r = k[A]^n$, the units of k are $(\text{mol L}^{-1})^{1-n}\text{s}^{-1}$, where n is the reaction order.

Step 1: (a) Define collision frequency Collision frequency measures how many collisions between molecules occur in unit volume in unit time. Its volume basis is essential: a larger reaction volume can contain more collisions without having a larger collision frequency. All collisions are counted; only collisions with sufficient energy and suitable orientation are effective in producing reaction.

Step 2: (b) Obtain the requested units The question asks for the characteristic rate-constant units for

Quick Tip to Solve: Divide rate units by concentration raised to the reaction order; rate units themselves do not change with order.

the stated orders. Rate itself always has concentration-per-time units. For first order, $r = k[A]$, so

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

For zero order, $r = k[A]^0 = k$, and thus

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

These units use seconds as the time unit; a consistently chosen alternative time unit is also possible.

Step 3: Conclusion (a) Collisions per unit volume per unit time. (b) Rate-constant units: (i) first order, s^{-1}; (ii) zero order, $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Quick Tip to Solve: Divide rate units by concentration raised to the reaction order; rate units themselves do not change with order.

19. (a) Why is third ionization enthalpy of manganese very high?
(b) Why Zn, Cd and Hg are not regarded as transition elements? [2 marks]

Solution:

Concept:

- Ionization enthalpy is the energy required to remove an electron from an isolated gaseous species.
- Half-filled d^5 subshells have additional stability; a transition element must have an incompletely filled d subshell in its atom or a common ion.

Step 1: (a) Examine the third electron removed from manganese Manganese has the configuration $[\text{Ar}]3d^5 4s^2$. The first two ionizations remove the two $4s$ electrons, leaving Mn^{2+} with the particularly stable half-filled $3d^5$ configuration. The third ionization is

$$\text{Mn}^{2+}(\text{g}) \longrightarrow \text{Mn}^{3+}(\text{g}) + \text{e}^-.$$

It removes a $3d$ electron and produces $3d^4$, disrupting the half-filled subshell. This loss of extra stability makes the third ionization enthalpy very high.

Step 2: (b) Apply the transition-element definition Zn, Cd and Hg have configurations ending in $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$, respectively. Their common $+2$ ions retain the corresponding filled d^{10} subshell after losing the two outer s electrons. Thus neither their atoms nor their common ions have a partially filled d subshell, and they do not satisfy the definition of a transition element.

Step 3: Conclusion (a) Third ionization breaks the stable $3d^5$ configuration of Mn^{2+}. (b) Zn, Cd and Hg have fully filled d subshells in their atoms and common ions.

Quick Tip to Solve: Write the configuration of the ion before removal: for third ionization of Mn, start from Mn(II), not neutral Mn.

20. (a) Define didendate ligand. Give an example.

(b) Indicate the type of isomerism exhibited by the given complex: $[Pt(NH_3)(H_2O)Cl_2]$ [2 marks]

Solution:

Concept:

- A ligand donates an electron pair to a central metal atom or ion. Denticity is the number of donor atoms of one ligand that bind to the same metal centre.
- For a square-planar complex, geometrical isomerism arises when ligands can occupy different relative positions without changing the coordination formula.

Step 1: Define a bidentate ligand and give an example A bidentate ligand has two donor atoms and coordinates to the same metal atom or ion through both of them, forming two coordinate bonds. For example, ethane-1,2-diamine (en), $H_2NCH_2CH_2NH_2$, binds through the lone pairs on its two nitrogen atoms. The two donors belong to one ligand molecule.

Step 2: Identify the isomerism of the platinum complex In $[Pt(NH_3)(H_2O)Cl_2]$, ammonia and water are neutral and the two chloride ligands each have charge -1. Thus platinum is in the $+2$ oxidation state. This Pt(II) complex is square planar. The two chloride ligands can lie next to each other (cis, an angle of $90°$) or opposite each other (trans, an angle of $180°$). These arrangements have the same formula but different spatial arrangements.

Step 3: Conclusion (a) A bidentate ligand binds through two donor atoms; ethane-1,2-diamine is an example. (b) The complex exhibits geometrical (cis-trans) isomerism.

Quick Tip to Solve: For a square-planar complex with two identical ligands, compare their adjacent and opposite positions to identify cis-trans isomerism.

21(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, $k = \dfrac{2.303}{t}\log\left(\dfrac{[R]_0}{[R]_t}\right)$, where $[R]_0$ and $[R]_t$ are the initial and remaining concentrations at time t.
- The concentration ratio is dimensionless. A first-order rate constant has units of inverse time, with the time unit fixed by the unit used for t.

Step 1: Form the concentration ratio The initial concentration is $[R]_0 = 0.6\,\text{mol}\,\text{L}^{-1}$ and the concentration remaining after $t = 5\,\text{min}$ is $[R]_t = 0.2\,\text{mol}\,\text{L}^{-1}$. Hence $[R]_0/[R]_t = 0.6/0.2 = 3$. The final concentration, rather than the amount consumed, belongs in the denominator of the integrated first-order equation.

Step 2: Substitute in the integrated rate law Using the supplied value $\log 3 = 0.48$,

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

Quick Tip to Solve: Use the initial-to-remaining concentration ratio, and keep minutes in the answer unless you explicitly convert the time to seconds.

Equivalently, dividing by 60 to express inverse minutes in inverse seconds gives $k = 3.6848 \times 10^{-3}\,\text{s}^{-1}$. Both values represent the same rate constant.

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

Quick Tip to Solve: Use the initial-to-remaining concentration ratio, and keep minutes in the answer unless you explicitly convert the time to seconds.

OR

21(B). Rate constant *k* for the first order reaction is 2.54×10^{-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, $t = \dfrac{2.303}{k} \log\left(\dfrac{[R]_0}{[R]_t}\right)$. Here 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 remaining fraction, not the decomposed fraction, is used in the integrated rate law.

Step 1: Determine the fraction remaining Three-fourth of the reactant decomposes, so one-fourth remains. Therefore $[R]_t = [R]_0/4$, and the ratio in the first-order equation is $[R]_0/[R]_t = 4$. The actual starting concentration cancels and need not be known.

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

$$\begin{aligned} t &= \frac{2.303}{2.54 \times 10^{-3}} \log 4 \\ &= \frac{2.303 \times 0.60}{2.54 \times 10^{-3}} \\ &= 544.0\,\text{s}. \end{aligned}$$

Because the rate constant is in inverse seconds, this result is in seconds. Dividing by 60 gives approximately 9.07 min. Reaching one-fourth of the initial concentration corresponds to two half-lives.

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

Quick Tip to Solve: Convert the decomposed fraction to the remaining fraction first: three-fourth decomposed means one-fourth remains, so the logarithm is of 4.

Section C (21 marks)

22. A solution containing 8.0 g of a non-volatile solute in 100 g of diethyl ether boils at 36.86°C whereas pure diethyl ether boils at 35.60°C. Determine the molar mass of the solute. (K_b for diethyl ether = 2.02 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- For a dilute solution of a non-volatile solute, the boiling-point elevation is $\Delta T_b = K_b m$, where K_b is the molal elevation constant and m is moles of solute per kilogram of solvent.
- If w_2 grams of solute of molar mass M_2 are dissolved in w_1 grams of solvent, then $m = \dfrac{1000 w_2}{M_2 w_1}$. Thus $M_2 = \dfrac{1000 K_b w_2}{\Delta T_b w_1}$.
- A difference between two temperatures in degrees Celsius has the same numerical value in kelvin. Use solvent mass, not total solution mass, to calculate molality.

Step 1: Find the boiling-point elevation The solution boils at $36.86\,^\circ$C while the pure solvent boils at $35.60\,^\circ$C. Hence

$$\Delta T_b = 36.86 - 35.60 = 1.26\,\text{K}.$$

The increase is positive, as expected on adding a non-volatile solute. The solute lowers the vapour pressure, so a higher temperature is required for the solution to boil.

Step 2: Calculate molality and the moles of solute Using $K_b = 2.02\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_b}{K_b} = \frac{1.26}{2.02} = 0.62376\,\text{mol kg}^{-1}.$$

The solvent mass is $100\,\text{g} = 0.100\,\text{kg}$. Consequently, the amount of solute is

$$n_2 = m \times 0.100 = 0.062376\,\text{mol}.$$

The $8.0\,\text{g}$ solute mass is not added to the solvent mass when calculating molality.

Step 3: Determine the molar mass Molar mass is the mass of solute divided by its amount:

$$\begin{aligned} M_2 &= \frac{8.0}{0.062376} \\ &= \frac{2.02 \times 8.0 \times 1000}{1.26 \times 100} \\ &= 128.25\,\text{g mol}^{-1}. \end{aligned}$$

As a check, $8.0/128.25$ moles in $0.100\,\text{kg}$ solvent gives a molality of about $0.624\,\text{mol kg}^{-1}$; multiplying by 2.02 reproduces the observed $1.26\,\text{K}$ elevation.

Step 4: Conclusion The molar mass of the solute is $\boxed{M_2 \approx 128.3\,\text{g mol}^{-1}}$ (about $1.3 \times 10^2\,\text{g mol}^{-1}$ to two significant figures).

Quick Tip to Solve: Convert the solvent mass from grams to kilograms before using molality; the Celsius temperature difference can be used directly as a kelvin difference.

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 standard cell potential is the cathode reduction potential minus the anode reduction potential: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At 298 K, $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the electron count and Q the reaction quotient. Pure solids have unit activity.

Step 1: Write the cell reaction Tin is oxidised at the left electrode and hydrogen ions are reduced at the right electrode:

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

Adding these gives $\mathrm{Sn(s)} + 2\mathrm{H^+(aq)} \rightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}$, with $n = 2$. The coefficient of hydrogen ions is two, so their concentration must be squared in the reaction quotient.

Step 2: Calculate the standard potential and reaction quotient Using the supplied reduction potentials,

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

With concentrations relative to 1 M and hydrogen pressure relative to 1 bar,

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

Tin metal contributes unit activity, while platinum is only an inert conducting electrode and does not enter the quotient.

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

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

Because $Q > 1$, the concentration correction decreases the emf below its standard value, consistent with the sign in the Nernst equation.

Step 4: Conclusion The emf at 298 K is $\boxed{0.11045\,\mathrm{V} \simeq 0.110\,\mathrm{V}}$.

Quick Tip to Solve: Balance the hydrogen half-reaction first: its coefficient 2 puts $[\mathrm{H^+}]^2$ in the denominator of Q.

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

(i) $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow$?

(ii) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow$?

(b) Explain why actinoid contraction is greater from element to element than lanthanoid contraction.

[3 marks]

Solution:

Concept:

- In oxidative roasting, chromium in chromite is oxidised from $+3$ to $+6$, producing sodium chromate; iron forms iron(III) oxide.
- In acidic solution, permanganate is reduced from Mn($+7$) to Mn($+2$); each Fe^{2+} loses one electron.
- Contraction across an f-block series results from increasing effective nuclear charge because f electrons shield the nuclear charge poorly.

Step 1: (a)(i) Complete the oxidative roasting reaction The products are sodium chromate, iron(III) oxide and carbon dioxide. The completed equation is

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

There are 4 iron, 8 chromium, 16 sodium and 8 carbon atoms on each side. Oxygen also balances: the left side has $16 + 24 + 14 = 54$ oxygen atoms, and the right side has $32 + 6 + 16 = 54$. Thus the given reactant coefficients yield the displayed product coefficients.

Step 2: (a)(ii) Complete the acidic permanganate reaction The reduction and oxidation half-reactions are

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O,$$
$$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-.$$

Adding them cancels the five electrons:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O.$$

Both sides have total charge $+17$, and the four oxygen atoms and eight hydrogen atoms form four water molecules.

Step 3: (b) Explain the greater actinoid contraction Across the actinoid series, successive electrons enter the $5f$ subshell while the nuclear charge increases. The $5f$ electrons shield the increasing nuclear charge less effectively than the $4f$ electrons do in lanthanoids. Consequently the effective nuclear charge felt by the outer electrons increases more strongly, drawing them inward. This causes a greater decrease in atomic or ionic size from one actinoid to the next.

Step 4: Conclusion The products are (i) $8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$ and (ii) $5Fe^{3+} + Mn^{2+} + 4H_2O$. Greater actinoid contraction is due to poorer shielding by $5f$ electrons than by $4f$ electrons.

Quick Tip to Solve: For acidic permanganate, remember the half-reaction consumes five electrons and eight hydrogen ions and forms four water molecules.

25. (a) $[Fe(H_2O)_6]^{2+}$ is paramagnetic whereas $[Fe(CO)_5]$ is diamagnetic. Justify the statement. [Atomic number of Fe = 26]

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

Solution:

Concept:

- A complex is paramagnetic when it contains unpaired electrons and diamagnetic when all electrons are paired. Neutral iron has configuration $[\mathrm{Ar}]\,3d^6 4s^2$; Fe^{2+} is $3d^6$.
- Water is a weak-field ligand whereas CO is a strong-field ligand that promotes electron pairing.
- In an octahedral field, t_{2g} orbitals lie below e_g. When the splitting Δ_o is less than the pairing energy P, a high-spin configuration is favoured.

Step 1: (a) Explain the magnetism of the aqua complex Water is neutral, so the oxidation state of iron in $[Fe(H_2O)_6]^{2+}$ is $+2$. Removal of the two $4s$ electrons gives Fe^{2+} the configuration $3d^6$. The weak-field water ligands produce a high-spin octahedral complex, with occupancy $t_{2g}^4 e_g^2$. Three electrons first occupy the three lower orbitals singly, the next two occupy the upper orbitals, and the sixth pairs in a lower orbital. Four electrons remain unpaired, so the complex is paramagnetic.

Step 2: (a) Explain the magnetism of iron pentacarbonyl All five CO ligands are neutral and the complex has no overall charge; therefore iron has oxidation state zero in $[Fe(CO)_5]$. CO is a strong-field ligand. In the valence-bond description, the iron valence electrons rearrange and pair in the $3d$ orbitals, leaving one vacant $3d$ orbital available for dsp^3 hybridisation. The five CO ligands donate electron pairs into the five hybrid orbitals, giving a trigonal-bipyramidal complex. The resulting complex contains no unpaired electrons and is therefore diamagnetic. Its five-coordinate geometry should not be assigned an octahedral t_{2g}/e_g configuration.

Step 3: (b) Fill the octahedral orbitals for the stated inequality For a d^4 ion with $\Delta_o < P$, moving an electron into an upper e_g orbital costs less energy than pairing it in an occupied t_{2g} orbital. The first three electrons therefore occupy the three t_{2g} orbitals singly and the fourth enters an e_g orbital. The high-spin electronic configuration is $t_{2g}^3 e_g^1$, containing four unpaired electrons.

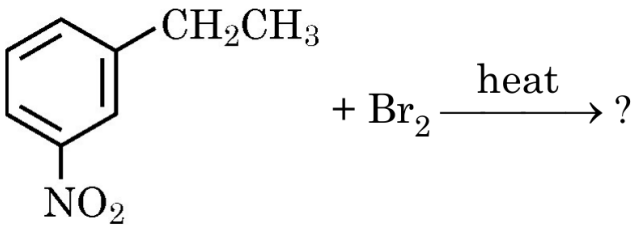
Step 4: Conclusion $[Fe(H_2O)_6]^{2+}$ is paramagnetic with four unpaired electrons; $[Fe(CO)_5]$ is diamagnetic with all electrons paired. For the octahedral d^4 ion when $\Delta_o < P$, $\boxed{t_{2g}^3 e_g^1}$.

Quick Tip to Solve: Determine the metal oxidation state before counting d electrons: Fe is $+2$ in the aqua ion but zero in the neutral carbonyl.

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

(b) Define Chirality.

(c) Why does racemisation occur in S_N1 reaction? [3 marks]



Solution:

Concept:

- Heating an alkylbenzene with Br_2 favours free-radical substitution at a benzylic carbon, whose radical is resonance-stabilised by the benzene ring.
- Chirality is non-superimposability of a molecule on its mirror image. An asymmetric carbon bonded to four different groups is a common source of chirality.
- An S_N1 reaction proceeds through a planar, sp^2-hybridised carbocation, which can be attacked from either face.

Step 1: (a) Identify the bromination site The ethyl and nitro substituents in the printed substrate are meta to each other. Bromine under heat replaces a hydrogen on the benzylic $-CH_2-$ group, where radical formation is favoured by resonance stabilisation. The ring substituents retain their relative positions. The major product is 1-(1-bromoethyl)-3-nitrobenzene:

$$\mathrm{m-NO_2C_6H_4CH_2CH_3 + Br_2 \xrightarrow{heat} m-NO_2C_6H_4CHBrCH_3 + HBr.}$$

The terminal methyl group is not the preferred site, and these conditions favour side-chain bromination.

Step 2: (b) Define chirality Chirality is the property of a molecule that makes it non-superimposable on its mirror image. The two mirror-image forms are called enantiomers. A tetrahedral carbon attached to four different groups commonly provides chirality, provided the molecule has no internal symmetry that makes the entire structure achiral.

Step 3: (c) Explain racemisation Loss of the leaving group from an optically active substrate converts the initially tetrahedral stereogenic carbon into a trigonal planar carbocation. The nucleophile can attack its vacant p orbital from either face. Attack from one side leads to retention of configuration and attack from the other leads to inversion. Both enantiomers therefore form and optical purity is lost; this is racemisation. Equal amounts give an optically inactive racemic mixture. In practice ion-pair effects can give some excess of the inverted product.

Step 4: Conclusion (a) The major product is $\mathrm{m-NO_2C_6H_4CHBrCH_3}$. (b) Chirality means non-superimposability on the mirror image. (c) Attack on both faces of the planar carbocation causes racemisation in S_N1.

Quick Tip to Solve: With bromine and heat on an alkylbenzene, locate the benzylic hydrogen first and retain the printed ring-substituent positions.

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

Step 1: (a) Rosenmund reduction An acid chloride undergoes catalytic hydrogenation with H_2 over $Pd/BaSO_4$. The catalyst is poisoned to restrict further reduction of the aldehyde to an alcohol. For example, acetyl chloride gives ethanal:

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

In general the carbon skeleton is retained as $RCOCl \rightarrow RCHO$.

Step 2: (b) Cannizzaro reaction An aldehyde lacking an alpha hydrogen reacts with concentrated aqueous alkali to form an alcohol and a carboxylate salt. Benzaldehyde gives benzyl alcohol and sodium benzoate:

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

One aldehyde molecule accepts hydrogen and is reduced to the alcohol; the other is oxidised to the carboxylate. The acid would be obtained only after subsequent acidification.

Step 3: (c) Hell–Volhard–Zelinsky reaction A carboxylic acid containing at least one alpha hydrogen undergoes alpha halogenation with bromine or chlorine in the presence of a small amount of red phosphorus. For example:

$$CH_3COOH + Br_2 \xrightarrow{red\ P} BrCH_2COOH + HBr.$$

The product is bromoacetic acid. The halogen replaces a hydrogen on the carbon immediately adjacent to the carboxyl group; the carboxyl group remains in the final product.

Step 4: Conclusion Rosenmund reduction: acyl chloride to aldehyde. Cannizzaro reaction: aldehyde without α-H to alcohol plus carboxylate. HVZ reaction: carboxylic acid with α-H to an α-halo acid.

Quick Tip to Solve: Match the starting functional group and reagent first: acid chloride with hydrogen, aldehyde with concentrated alkali, or acid with halogen/red phosphorus.

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

(i) Denaturation as related to proteins

(ii) Oligosaccharides

(b) On the basis of structure differentiate between Amylose and Amylopectin. [3 marks]

Solution:

Concept:

- Protein activity depends on its native secondary and tertiary structure; denaturation disrupts this conformation without hydrolysing its peptide backbone.
- Oligosaccharides yield two to ten monosaccharide units on hydrolysis.
- Amylose and amylopectin are starch components made from α-D-glucose, but differ in chain architecture and glycosidic linkage positions.

Step 1: (a)(i) Define denaturation Denaturation is the loss of a proteiń native conformation and biological activity when it is exposed to agents such as heat or a change in pH. Hydrogen bonds and other interactions maintaining secondary and tertiary structure are disrupted. The protein unfolds, but the peptide bonds and therefore its primary structure remain intact. For example, boiling causes the albumin of egg white to coagulate.

Step 2: (a)(ii) Define oligosaccharides Oligosaccharides are carbohydrates which on hydrolysis yield two to ten monosaccharide units. Their constituent units are joined by glycosidic bonds. Disaccharides are included in this class: sucrose, for example, gives one molecule each of glucose and fructose on hydrolysis. Thus the classification depends on the number of monosaccharide units released, rather than merely whether a carbohydrate tastes sweet.

Step 3: (b) Compare the structures Amylose is an essentially unbranched polymer of α-D-glucose. Its units are linked by $\alpha(1 \to 4)$ glycosidic bonds, and the chain coils into a helix. Amylopectin is a branched polymer of α-D-glucose. It has $\alpha(1 \to 4)$ bonds along its chains and additional $\alpha(1 \to 6)$ bonds at branch points. Hence the key structural distinction is linear helical chains in amylose versus branched chains in amylopectin; both share the same glucose monomer.

Step 4: Conclusion Denaturation destroys the native protein conformation and activity while retaining primary structure. Oligosaccharides yield two to ten monosaccharides. Amylose is unbranched with $\alpha(1 \to 4)$ links; amylopectin has these links plus $\alpha(1 \to 6)$ branch links.

Quick Tip to Solve: For the starch comparison, state both chain shape and linkage: 1-to-4 along chains, with 1-to-6 only at amylopectin branch points.

OR

28(B). (a) What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?

(b) How will you explain the presence of five -OH groups in glucose molecule which are attached to different carbon atoms?

(c) Write the reaction of glucose with HCN. [3 marks]

Solution:

Concept:

- A DNA nucleotide contains a nitrogenous base, 2-deoxy-D-ribose and a phosphate group. Complete hydrolysis separates these components.
- Acetylation converts each alcohol group, $-OH$, into an acetate ester, $-OCOCH_3$. The number of acetyl groups measures the number of hydroxyl groups.
- An aldehyde reacts with hydrogen cyanide by nucleophilic addition to form a cyanohydrin: $RCHO + HCN \rightarrow RCH(OH)CN$.

Step 1: (a) Hydrolyse the thymine nucleotide Complete hydrolysis breaks the phosphate ester bond and the bond between the sugar and the nitrogenous base. Since the nucleotide belongs to DNA, its sugar is 2-deoxy-D-ribose, not ribose. The base specified in the question is thymine. Therefore the hydrolysis products are thymine, 2-deoxy-D-ribose and phosphoric acid (H_3PO_4).

Step 2: (b) Use acetylation evidence Glucose reacts with acetic anhydride to form glucose pentaacetate. Each hydroxyl group gives one acetate ester, so formation of the pentaacetate establishes the presence of five $-OH$ groups. The stable nature of glucose supports their attachment to five different carbon atoms: two hydroxyl groups on the same carbon would give a generally unstable geminal diol arrangement. In the open-chain formula $CHO - (CHOH)_4 - CH_2OH$, four hydroxyl groups occur at C-2 to C-5 and the fifth occurs at C-6.

Step 3: (c) Add HCN to the aldehyde group The open-chain form of glucose contains an aldehyde group at C-1. Cyanide adds to its carbonyl carbon and protonation of the oxygen produces the cyanohydrin. The remaining chain is unchanged:

$$\mathrm{CHO - (CHOH)_4 - CH_2OH + HCN \longrightarrow NC - CH(OH) - (CHOH)_4 - CH_2OH.}$$

The product has a new carbon-carbon bond to the cyanide carbon and an additional hydroxyl group at the former carbonyl carbon.

Step 4: Conclusion (a) Thymine, 2-deoxy-D-ribose and phosphoric acid; (b) formation of stable glucose pentaacetate establishes five hydroxyl groups on different carbons; (c) glucose gives its cyanohydrin, $\mathrm{NC - CH(OH) - (CHOH)_4 - CH_2OH}$.

Quick Tip to Solve: For glucose reactions, write its open-chain aldehyde formula first; acetylation counts hydroxyl groups, while HCN reacts at the aldehyde carbon.

Section D (8 marks)

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

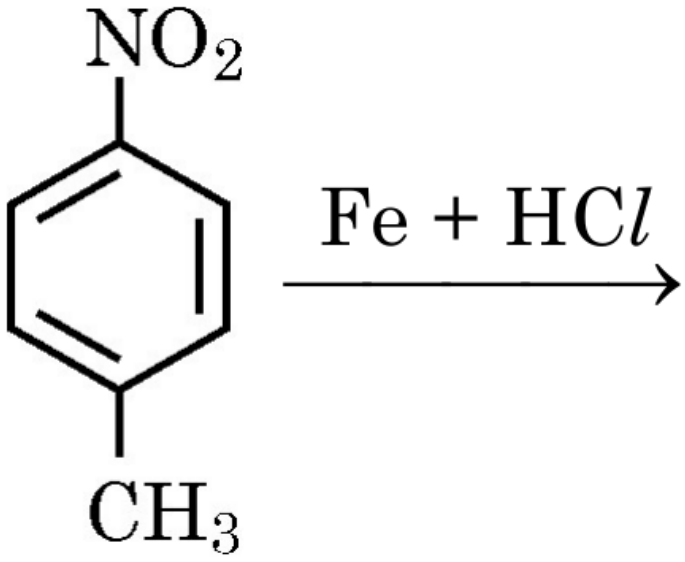
29(a). Read the passage carefully and answer the questions that follow:

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

(a) Complete the following equations:

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

(ii) $\xrightarrow{Fe + HCl}$ **?** [2 marks]



Solution:

Concept:

- Lithium aluminium hydride reduces an amide, $RCONH_2$, to RCH_2NH_2: the carbonyl oxygen is removed and the carbon skeleton is retained.
- Iron and hydrochloric acid reduce an aromatic nitro group, $-NO_2$, to an amino group, $-NH_2$, without changing the methyl substituent.

Step 1: (i) Reduce ethanamide In CH_3CONH_2, the carbonyl carbon becomes the methylene carbon

Quick Tip to Solve: An amide reduction retains its carbonyl carbon; a nitro reduction changes only $-NO_2$ to $-NH_2$.

next to nitrogen. The product therefore contains both original carbon atoms and is ethanamine (ethylamine), not methylamine. The requested transformation is

$$\mathrm{CH_3CONH_2} \xrightarrow[\text{(ii) } \mathrm{H_2O}]{\text{(i) } \mathrm{LiAlH_4}} \mathrm{CH_3CH_2NH_2}.$$

Water in the second step completes the work-up of the reduction.

Step 2: (ii) Reduce the aromatic nitro group The printed ring has a nitro group and a methyl group at para positions; it is 4-nitrotoluene. Reduction with Fe/HCl converts only the nitro group to an amino group:

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

Thus the organic product is 4-methylaniline, also called p-toluidine. In the acidic reaction mixture the amine can be protonated; the usual organic reduction product is written as the free amine.

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

Quick Tip to Solve: An amide reduction retains its carbonyl carbon; a nitro reduction changes only $-NO_2$ to $-NH_2$.

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

Solution:

Concept:

- Boiling requires separation of molecules against intermolecular attractions. Stronger attractions generally give a higher boiling point for comparable compounds.
- Primary amines have N-H bonds and a nitrogen lone pair; tertiary amines have a lone pair but no N-H bond.

Step 1: Identify hydrogen-bond formation A primary amine, RNH_2, can form intermolecular $N-H\cdots N$ hydrogen bonds with other primary amine molecules. Its N-H bonds provide hydrogen-bond donors and its nitrogen lone pair acts as an acceptor.

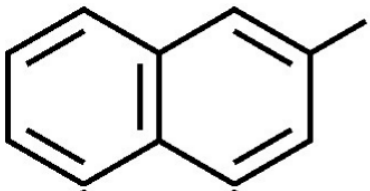
Step 2: Compare the energy needed for boiling A tertiary amine, R_3N, has no hydrogen directly bonded to nitrogen, so it cannot form such hydrogen bonds between its own molecules. Consequently, for comparable isomeric amines, primary amines have stronger intermolecular association and need more energy to separate their 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 lack N-H bonds and cannot self-associate in this way.

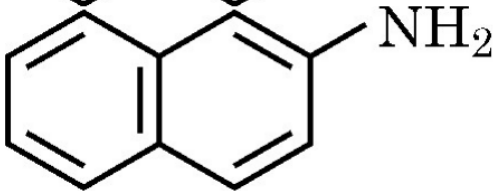
Quick Tip to Solve: Count hydrogen atoms bonded directly to nitrogen before comparing hydrogen bonding in pure amines.

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

(i)



(ii)



Solution:

Concept:

- An amine is primary, secondary or tertiary according as nitrogen is directly attached to one, two or three carbon-containing groups.
- Count groups attached to nitrogen itself; the number of rings or carbon atoms elsewhere in the molecule does not determine the class.

Step 1: (i) Count the groups bonded to nitrogen In structure (i), nitrogen is attached to the naphthyl group and to two methyl groups, as indicated by $N(CH_3)_2$. There are three carbon-containing groups directly bonded to nitrogen, with no N-H bond. This is a tertiary amine.

Step 2: (ii) Inspect the amino group In structure (ii), the substituent is $-NH_2$. Its nitrogen is bonded to one naphthyl group and two hydrogen atoms. Hence only one carbon-containing group is directly bonded to nitrogen, making this a primary amine. The fused aromatic rings count together as one substituent on nitrogen.

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

Quick Tip to Solve: Ignore the size of the aromatic group: count only the carbon-containing groups directly attached to nitrogen.

OR

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

Solution:

Concept:

- Water solubility depends on hydrogen bonding with water and on the opposing effect of the nonpolar hydrocarbon chain.
- Oxygen is more electronegative than nitrogen, so the hydroxyl group of an alcohol interacts more strongly with water than the amino group of a comparable amine.

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 four-carbon chain. Their hydrophobic portions are therefore

Quick Tip to Solve: For equal-length alkyl chains, compare the polar groups: an alcohol forms stronger hydrogen bonds with water than an amine.

comparable, so the difference in solubility is explained by their polar functional groups.

Step 2: Compare hydrogen bonding with water Both compounds can form hydrogen bonds with water. However, oxygen is more electronegative than nitrogen, making the alcohol group more effective in forming strong hydrogen bonds with water. The interaction of butan-1-ol with water is consequently stronger than that of butan-1-amine in the stated comparison.

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

Quick Tip to Solve: For equal-length alkyl chains, compare the polar groups: an alcohol forms stronger hydrogen bonds with water than an amine.

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

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

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

Solution:

Concept:

- Osmotic pressure of a dilute electrolyte solution is $\pi = iCRT = i\frac{n}{V}RT$, where i is the van't Hoff factor, C the molarity, T the absolute temperature and R the gas constant.
- If the solute mass is m and its molar mass is M, then $n = m/M$; hence $m = \pi VM/(iRT)$. The given i already accounts for the effective number of dissolved particles.

Step 1: Convert temperature and identify the data The temperature must be expressed in kelvin:

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

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

Step 2: Calculate the required solute mass Rearrange the osmotic-pressure expression before substi-

Quick Tip to Solve: Use the given $i = 2.59$, not the ideal dissociation value 3, and convert Celsius to kelvin before substituting.

tuting:

$$\pi = i\frac{m}{MV}RT,$$
$$m = \frac{\pi V M}{iRT}$$
$$= \frac{0.70 \times 2.46 \times 111}{2.59 \times 0.082 \times 300}\,\text{g}$$
$$= 3.00\,\text{g}.$$

The atmosphere and litre units cancel consistently with those in R; multiplying the calculated amount in moles by the molar mass gives grams.

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

Quick Tip to Solve: Use the given $i = 2.59$, not the ideal dissociation value 3, and convert Celsius to kelvin before substituting.

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

Solution:

Concept:

- Osmosis is the passage of solvent through a semipermeable membrane from lower solute concentration to higher solute concentration.
- When water enters a cell or enclosed tissue by osmosis, this inward movement is called endosmosis.

Step 1: Compare the concentrations The liquid within a raisin contains dissolved sugars and other solutes. The surrounding water has a lower solute concentration than the liquid inside the raisin.

Step 2: Trace the movement of water The raisin's skin acts as a semipermeable barrier. Water passes from the surroundings into the raisin by osmosis; the inward movement increases its volume and causes swelling. Exosmosis would mean water leaving the raisin and would cause shrinkage.

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

Quick Tip to Solve: Associate swelling with water entering (endosmosis) and shrinking with water leaving (exosmosis).

OR

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

Solution:

Concept:

- Osmotic pressure is a colligative property: for a dilute solution, $\pi = CRT$, where C is solute molarity, R the gas constant and T absolute temperature.

Quick Tip to Solve: For this comparison, recall both practical advantages: a measurable effect in dilute solutions and room-temperature measurement.

- Colligative properties can determine molar masses, but their practical usefulness depends on whether the measured change is appreciable.

Step 1: Compare the ease of measurement Even very dilute solutions can have an appreciable, measurable osmotic pressure. Their elevation of boiling point or depression of freezing point may be too small to measure accurately, especially for solutes of high molar mass.

Step 2: Identify the temperature advantage Osmotic pressure can be measured at room temperature. This avoids heating or cooling the sample substantially, which is particularly useful for biomolecules such as proteins that may decompose or change on heating. It therefore enables convenient molar-mass determination in dilute solutions.

Step 3: Conclusion Osmotic pressure is advantageous because it is appreciable in very dilute solutions and can be measured at room temperature, making it suitable for determining the molar masses of large, heat-sensitive molecules.

Quick Tip to Solve: For this comparison, recall both practical advantages: a measurable effect in dilute solutions and room-temperature measurement.

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

Solution:

Concept:

- In ordinary osmosis, solvent passes through a semipermeable membrane toward the solution with higher solute concentration.
- Reverse osmosis occurs when pressure greater than the osmotic pressure is applied on the solution side, reversing the solvent flow.

Step 1: Apply pressure to sea water Sea water contains dissolved salts. It is placed on one side of a semipermeable membrane and subjected to an external pressure greater than its osmotic pressure.

Step 2: Separate water from the dissolved salts The applied pressure forces water through the membrane toward the fresh-water side. The membrane retains the dissolved salts, so the collected permeate has a much lower salt concentration. Ordinary osmosis would draw water toward the salt solution and would not perform this separation.

Step 3: Conclusion The phenomenon responsible for desalination of sea water is $\boxed{\text{reverse osmosis}}$.

Quick Tip to Solve: Look for pressure greater than osmotic pressure: it forces water out of the salt solution through the membrane.

Section E (15 marks)

31(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 react with sodium through their hydroxyl hydrogen to form alkoxides and hydrogen gas. Ethers have no hydroxyl hydrogen.
- Ethanol gives the iodoform test. At $413\,K$, concentrated sulphuric acid causes intermolecular dehydration to an ether.
- Excess HI cleaves an ether and also converts the alcohol initially formed into an alkyl iodide.

Step 1: Identify A and B using the sodium reaction The functional isomers of C_2H_6O are ethanol and methoxymethane. Liberation of hydrogen with sodium requires an $O-H$ bond, so A is ethanol, CH_3CH_2OH. Its sodium derivative B is sodium ethoxide:

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

Methoxymethane is excluded since it does not contain the hydroxyl hydrogen needed for this reaction.

Step 2: Identify C from the iodoform reaction Iodine and aqueous sodium hydroxide oxidise ethanol to ethanal, which then undergoes iodination and cleavage to give yellow iodoform. Thus C is triiodomethane, CHI_3. The balanced overall reaction is

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

Sodium methanoate is the other carbon-containing product. The characteristic product designated C in this test is the yellow iodoform precipitate.

Step 3: Identify D at the specified temperature At $413\,K$, two ethanol molecules lose one water molecule in the presence of concentrated sulphuric acid. The product D is ethoxyethane, also called diethyl ether:

$$2C_2H_5OH \xrightarrow[413\,K]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$

This product has the stated molecular formula $C_4H_{10}O$. The specified temperature favours intermolecular dehydration to ether, rather than elimination to ethene.

Step 4: Identify E using excess hydrogen iodide Protonation of the ether oxygen by HI permits iodide to cleave an ethyl-oxygen bond, initially giving iodoethane and ethanol:

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

Quick Tip to Solve: Select the alcohol isomer using the sodium test, and use the 413 K condition to recognise ether formation; excess HI converts both ethyl groups to iodides.

Excess HI also converts the ethanol into iodoethane:

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

Therefore the complete reaction is

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

Both equivalent ethyl groups of the symmetrical ether give the same product, E.

Step 5: Conclusion A is ethanol, C_2H_5OH; B is sodium ethoxide, C_2H_5ONa; C is iodoform, CHI_3; D is ethoxyethane, $C_2H_5OC_2H_5$; E is iodoethane, C_2H_5I.

Quick Tip to Solve: Select the alcohol isomer using the sodium test, and use the 413 K condition to recognise ether formation; excess HI converts both ethyl groups to iodides.

OR

31(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 phenol towards electrophilic substitution at the ortho and para positions; bromine water gives tribromination.
- Hydroboration followed by oxidation gives an anti-Markovnikov alcohol from an alkene. Reduction of a ketone gives a secondary alcohol.
- Acid-catalysed hydration proceeds by protonation of the double bond, attack of water on the carbocation, and deprotonation to regenerate the catalyst.

Step 1: (a)(i) Phenol to 2,4,6-tribromophenol Use bromine water, $Br_2(aq)$, at room temperature. The strongly activating hydroxyl group permits substitution at both ortho positions and the para position without a Lewis acid catalyst:

$$C_6H_5OH + 3Br_2(aq) \longrightarrow 2,4,6\text{–}C_6H_2Br_3OH + 3HBr.$$

A white precipitate of 2,4,6-tribromophenol forms. Bromine in a nonpolar solvent under controlled conditions would favour monobromination, so bromine water is the appropriate reagent here.

Step 2: (a)(ii) Propene to propan-1-ol Use (1) diborane, B_2H_6, in ether (or BH_3/THF), followed by (2) $H_2O_2/NaOH$. Hydroboration-oxidation places the hydroxyl group on the less substituted terminal

Quick Tip to Solve: For propan-1-ol choose hydroboration-oxidation; acid hydration follows Markovnikov orientation and would give propan-2-ol instead.

carbon:

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

Direct acid-catalysed hydration would instead predominantly yield propan-2-ol, so it cannot give the required terminal alcohol selectively.

Step 3: (a)(iii) Butan-2-one to butan-2-ol Use sodium borohydride, $NaBH_4$, followed by aqueous work-up. Alternatively, $LiAlH_4$ in dry ether followed by hydrolysis is suitable. Reduction changes the carbonyl group to a secondary alcohol without altering the carbon skeleton:

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

The carbonyl carbon remains carbon 2, giving the required butan-2-ol.

Step 4: (b) Protonation of the alkene In dilute aqueous acid, hydronium provides the proton. Taking propene as an example, its electron-rich pi bond accepts a proton to generate the more stable secondary carbocation rather than a primary carbocation:

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

The pi electrons form the new carbon-hydrogen bond; hydrogen adds to the terminal carbon. This is the basis of Markovnikov orientation for this unsymmetrical alkene.

Step 5: (b) Water attack and regeneration of the acid A lone pair on the oxygen of water attacks the positively charged carbon, producing a protonated alcohol:

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

Another water molecule removes a proton from this oxonium ion:

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

The acid catalyst is regenerated, and the net addition of hydrogen and hydroxyl across the double bond gives the alcohol. For propene this is propan-2-ol.

Step 6: Conclusion (a) The reagents are (i) bromine water, (ii) diborane in ether followed by alkaline hydrogen peroxide, and (iii) sodium borohydride followed by aqueous work-up. (b) Acid-catalysed hydration follows protonation, nucleophilic attack by water, and deprotonation, regenerating the acid catalyst.

Quick Tip to Solve: For propan-1-ol choose hydroboration-oxidation; acid hydration follows Markovnikov orientation and would give propan-2-ol instead.

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

(i) Propanone to Propene

(ii) Benzoic acid to Benzaldehyde

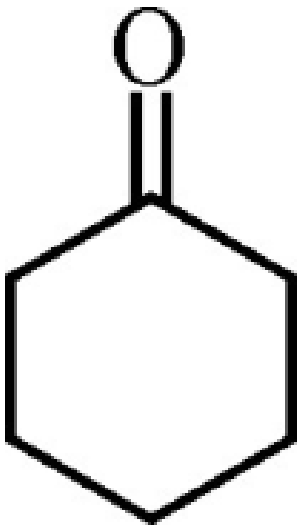
(iii) Benzene to *m*-Nitroacetophenone

(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; dehydration of that alcohol gives an alkene. Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over poisoned palladium.
- In electrophilic aromatic substitution, the acetyl group $-COCH_3$ is deactivating and meta-directing. The sequence of introducing substituents therefore matters.
- HCN adds across a carbonyl group by nucleophilic attack of CN^-. Less steric hindrance and less electron donation favour addition. Aldol condensation requires at least one hydrogen on the carbon next to the carbonyl group, called an α-hydrogen.

Step 1: (a)(i) Convert propanone to propene First reduce propanone to propan-2-ol using $NaBH_4$, followed by aqueous work-up. Then heat the alcohol with concentrated sulphuric acid to eliminate water:

$$CH_3COCH_3 \xrightarrow[\text{then water}]{NaBH_4} CH_3CH(OH)CH_3$$

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

Reduction supplies the hydroxyl group needed for the subsequent dehydration.

Step 2: (a)(ii) Convert benzoic acid to benzaldehyde Convert benzoic acid to benzoyl chloride with

Quick Tip to Solve: Acylate benzene before nitration; for aldol condensation, check the carbon beside C=O for a hydrogen.

thionyl chloride, then carry out Rosenmund reduction:

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

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

The poisoned catalyst limits the reduction to the aldehyde stage instead of reducing the product further to benzyl alcohol.

Step 3: (a)(iii) Convert benzene to m-nitroacetophenone Carry out Friedel–Crafts acylation first, followed by nitration:

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

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

The acetyl group directs nitration predominantly to the meta position. Nitrating benzene first would give strongly deactivated nitrobenzene, which does not undergo the required Friedel–Crafts acylation.

Step 4: (b)(i) Compare reactivity towards HCN The increasing order is

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

The two bulky tert-butyl groups strongly hinder approach of the nucleophile to the first carbonyl carbon. Propanone has two methyl groups, whereas ethanal has only one methyl group and a small hydrogen atom. Ethanal therefore has less hindrance and less electron donation to the carbonyl carbon, making it the most reactive of the three.

Step 5: (b)(ii) Identify compounds undergoing aldol condensation CH_3CHO and the cyclic ketone shown, cyclohexanone, undergo aldol condensation because both contain α-hydrogens. Ethanal has these hydrogens on its methyl group; cyclohexanone has them on the two ring carbons adjacent to $C{=}O$. In contrast, $HCHO$ has no α-carbon, and C_6H_5CHO has no α-hydrogen. Hence 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 bulky ketone to propanone to ethanal. The aldol-positive compounds are ethanal and cyclohexanone.

Quick Tip to Solve: Acylate benzene before nitration; for aldol condensation, check the carbon beside C=O for a hydrogen.

OR

32(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, containing CH_3CO-, give a yellow precipitate of iodoform with iodine and aqueous alkali. Aldehydes reduce Tollens' reagent to metallic silver, whereas ordinary ketones do not.
- Electron-withdrawing substituents stabilise carboxylate ions and increase acid strength through the inductive effect. Boiling points rise as intermolecular attractions become stronger, especially when hydrogen bonding is possible.

Step 1: (a)(i) Distinguish acetophenone and benzophenone Warm each compound with iodine and aqueous sodium hydroxide (iodoform test). Acetophenone, $C_6H_5COCH_3$, gives a yellow precipitate of CHI_3, because it contains the methyl-ketone group. Benzophenone, $C_6H_5COC_6H_5$, gives no yellow precipitate because it has no CH_3CO- group. The positive reaction is

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

Step 2: (a)(ii) Distinguish propanal and propanone Warm the compounds separately with freshly prepared Tollens' reagent in a water bath. Propanal, an aldehyde, produces a silver mirror on the test-tube wall; propanone, a ketone, does not. Propanal is oxidised to propanoate while silver(I) is reduced:

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

Thus the silver mirror identifies propanal, while absence of that mirror identifies propanone.

Step 3: (a)(iii) Distinguish pentan-2-one and pentan-3-one Use the iodoform test with iodine and aqueous sodium hydroxide. Pentan-2-one, $CH_3COCH_2CH_2CH_3$, gives a yellow precipitate of iodoform. Pentan-3-one, $CH_3CH_2COCH_2CH_3$, gives no yellow precipitate, since neither group directly bonded to its carbonyl carbon is methyl. For pentan-2-one,

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

Step 4: (b)(i) Compare the two acids CH_2FCOOH is stronger than CH_3COOH. Fluorine exerts a strong electron-withdrawing $-I$ effect, which stabilises the negative charge of the conjugate base

Quick Tip to Solve: Check for CH3 directly beside C=O for iodoform; use Tollens' reagent for aldehyde versus ketone.

CH_2FCOO^-. This favours dissociation of the acid. The methyl group in ethanoic acid instead has an electron-donating $+I$ effect, which makes its carboxylate ion relatively less stable. Therefore fluoroethanoic acid releases a proton more readily.

Step 5: (b)(ii) Arrange the boiling points The increasing order is

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

Propane is non-polar and has only London dispersion forces. Dimethyl ether is polar and also has dipole–dipole attractions. Ethanal has a more strongly polar carbonyl group, giving stronger intermolecular attraction than the ether. Ethanol forms intermolecular hydrogen bonds through its $O-H$ group and therefore has the highest boiling point. The ether and aldehyde lack an $O-H$ bond and cannot form such hydrogen-bonded networks in their pure liquids.

Step 6: Conclusion Iodoform distinguishes acetophenone from benzophenone and pentan-2-one from pentan-3-one; Tollens' reagent distinguishes propanal from propanone. Fluoroethanoic acid is stronger. Boiling points increase in the order propane, dimethyl ether, ethanal, ethanol.

Quick Tip to Solve: Check for CH3 directly beside C=O for iodoform; use Tollens' reagent for aldehyde versus ketone.

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

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

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

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

Predict the direction of flow of current.

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

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$, 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 estimate of dissociation is $\alpha = \Lambda_m/\Lambda^\circ_m$.
- In a galvanic cell, oxidation supplies electrons at the anode and reduction consumes them at the cathode. Conventional current in the external circuit flows opposite to electrons.
- Primary batteries have practically irreversible discharge reactions; secondary batteries have reactions that can be reversed by an external electrical supply.

Step 1: (a) Calculate molar conductivity Given $c = 0.1$ mol L^{-1} and $\kappa = 1.06 \times 10^{-2}$ S cm^{-1}, the factor 1000 converts the concentration to the cubic-centimetre basis of conductivity:

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

Quick Tip to Solve: Convert conductivity to molar conductivity with 1000/c, and reverse the electron-flow arrow to obtain conventional current.

Molar conductivity measures the conducting ability associated with one mole of dissolved electrolyte, so its units differ from those of conductivity.

Step 2: (a) Find limiting conductivity and the dissociation estimate At infinite dilution the ionic contributions add independently:

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

Therefore, using the requested conductivity-ratio method,

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

For a strong electrolyte such as NaCl, this ratio is an apparent degree of dissociation: NaCl is essentially dissociated, while interionic interactions reduce ion mobility at finite concentration. The ratio should not be interpreted as showing that the remaining NaCl consists of undissociated molecules.

Step 3: (b)(i) Determine the direction of current The reaction separates into the oxidation and reduction half-reactions:

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

Zinc is the negative anode and silver is the positive cathode. Electrons travel through the external wire from zinc to silver. Conventional current travels in the opposite direction, from the silver electrode to the zinc electrode through the external circuit. The positive standard cell potential is consistent with this spontaneous galvanic reaction.

Step 4: (b)(ii) Distinguish the battery types In a primary battery, the discharge reaction is practically irreversible; after the reactants are consumed it cannot normally be recharged for repeated use. A dry cell is an example. In a secondary battery, the discharge reaction is reversible: applying an external voltage reverses the chemical changes and restores the active materials. It can therefore undergo repeated charging and discharging; a lead storage battery is an example.

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

Quick Tip to Solve: Convert conductivity to molar conductivity with 1000/c, and reverse the electron-flow arrow to obtain conventional current.

OR

33(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:

- Conductance is $G = 1/R$, where R is resistance in ohms. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant in cm^{-1}.
- For the same conductivity cell, electrode separation l and electrode area A remain fixed. Hence $\kappa R = l/A$ is constant for both solutions.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$, with c in mol L^{-1} and κ in S cm^{-1}.
- Fuel cells convert the chemical energy of continuously supplied fuel and oxidant directly into electrical energy. A mercury cell has an overall reaction that does not change the electrolyte concentration.

Step 1: (a) Determine the cell constant from the reference solution For the $0.1\,\text{M}$ KCl solution, $R_1 = 100\,\Omega$ and $\kappa_1 = 1.29 \times 10^{-2}\,\text{S cm}^{-1}$. Thus,

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

This calibration determines the geometrical factor of the cell. Since the same cell is used for the dilute solution, its cell constant remains $1.29\,\text{cm}^{-1}$.

Step 2: (a) Calculate the conductivity of the dilute solution The resistance of the 0.01 mol L^{-1} solution is $R_2 = 300\,\Omega$, so its conductance is $G_2 = 1/300\,\text{S}$. Therefore,

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

The resistance increases by a factor of three, so the conductivity decreases by the same factor for this fixed cell geometry. This also checks the numerical result against the reference conductivity.

Step 3: (a) Convert conductivity to molar conductivity Use the concentration of the dilute solution, $c_2 = 0.01$ mol L^{-1}, in the molar-conductivity formula:

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

The concentration converts the measured conductivity into a per-mole quantity. The calculation uses the values specified in the question.

Step 4: (b)(i) State two advantages of the hydrogen-oxygen fuel cell First, it has high energy-conversion efficiency because chemical energy is converted directly into electrical energy. Second, its

Quick Tip to Solve: Calibrate the cell with kappa times R first; then divide that constant by the new resistance before using 1000 kappa/c.

reaction product is water, so operation of the cell does not produce polluting combustion gases. The overall reaction is

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

These advantages concern the working fuel cell itself: efficient conversion and a clean reaction product.

Step 5: (b)(ii) Explain the constant potential of the mercury cell In an alkaline mercury cell, zinc amalgam is oxidised and mercury(II) oxide is reduced. The discharge half-reactions can be written as

$$Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-,$$
$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-.$$

Adding them gives $Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l)$. Hydroxide ions and water cancel; the net reaction does not involve a change in the electrolyte's ionic concentration. The activities of the solid and liquid phases remain effectively constant, so the cell potential stays nearly constant throughout its useful life.

Step 6: Conclusion (a) The cell constant is $1.29\,cm^{-1}$, conductivity is $4.30 \times 10^{-3}\,S\ cm^{-1}$, and molar conductivity is $430\,S\ cm^2\ mol^{-1}$. (b)(i) The fuel cell offers high efficiency and water as its clean product. (ii) Mercury-cell potential remains constant because its net reaction leaves electrolyte concentration unchanged.

Quick Tip to Solve: Calibrate the cell with kappa times R first; then divide that constant by the new resistance before using 1000 kappa/c.