CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-4-2

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 **35** questions. **All questions are compulsory.**

(ii) This question paper is divided into **five** Sections – **A, B, C, D** and **E**.

(iii) In **Section A** – Questions no. **1** to **18** are multiple choice (MCQ) type questions, carrying **1** mark each.

(iv) In **Section B** – Questions no. **19** to **25** very short answer (VSA) type questions, carrying **2** marks each.

(v) In **Section C** – Questions no. **26** to **30** are short answer (SA) type questions, carrying **3** marks each.

(vi) In **Section D** – Questions no. **31** and **32** are case-based questions carrying **4** marks each.

(vii) In **Section E** – Questions no. **33** to **35** are long answer (LA) type questions carrying **5** marks each.

(viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section B, 2 questions in Section C, 2 questions in Section D and 2 questions in Section E.

(ix) Use of calculators is not allowed.

Section A (18 marks)

*Questions no. **1** to **18** are Multiple Choice (MCQ) type Questions, carrying **1** mark each.*

1. A compound undergoes complete dimerization in a given organic solvent. The Van't Hoff factor '*i*' is: [1 mark]

(A) 2.0

(B) 0.5

(C) 0.25

(D) 1.0

Correct Answer: (B) 0.5

Solution:

Concept:

- The van't Hoff factor is $i = \dfrac{\text{actual solute particles}}{\text{particles before association}}$.
- In dimerization, two monomer molecules combine to form one dimer: $2\,\mathrm{M} \longrightarrow \mathrm{M}_2$.

Step 1: Count the particles after association Begin with n molecules of the compound. Complete dimerization means that no monomer remains; every pair becomes one dimer. Thus the number of independently moving solute particles in the solvent is $n/2$, although the total amount of solute material is unchanged.

Step 2: Calculate and compare the factor Using the particle ratio,

$$i = \frac{n/2}{n} = \frac{1}{2} = 0.5.$$

A value of 2.0 would indicate an increase in particle count, whereas association decreases it. The value 0.25 corresponds to complete tetramer formation, and 1.0 would mean no change in particle count.

Step 3: Conclusion The van't Hoff factor is $i = 0.5$. Hence, the correct option is (B).

Quick Tip to Solve: For complete association into an aggregate of m molecules, use $i = 1/m$; a dimer has $m = 2$.

2. For the reaction A + 2B $\rightarrow$ C + D, the rate law is given by r = k[A][B]^2, the concentration of A is kept constant while that of B is doubled. The rate of the reaction will: [1 mark]

(A) double

(B) become half

(C) not change

(D) quadruple

Correct Answer: (D) quadruple

Solution:

Concept:

- The experimentally given rate law is $r = k[A][B]^2$, where k is the rate constant and square brackets denote concentrations.
- At constant temperature and fixed $[A]$, the rate is proportional to the square of $[B]$.

Step 1: Substitute the changed concentration Let the initial concentrations be $[A] = a$ and $[B] = b$, so $r_1 = kab^2$. Doubling only the concentration of B gives $[B]_2 = 2b$; A remains at a. Therefore,

$$r_2 = ka(2b)^2 = 4kab^2.$$

Step 2: Compare the two rates The ratio is $r_2/r_1 = 4$. Doubling the rate would be appropriate for a first-order dependence on B, but the stated law is second order in B. Becoming half contradicts the positive concentration dependence, and an unchanged rate would require zero-order dependence on B.

Step 3: Conclusion The rate becomes four times its original value, that is, it quadruples. Hence, the correct option is (D).

Quick Tip to Solve: Raise the concentration multiplier to its exponent in the rate law: doubling B gives $2^2 = 4$.

3. Reaction of 1-phenyl-2-chloropropane with alcoholic KOH gives mainly: [1 mark]

(A) 1-phenylpropene

(B) 3-phenylpropene

(C) 1-phenylpropan-3-ol

(D) 1-phenylpropan-2-ol

Correct Answer: (A) 1-phenylpropene

Solution:

Concept:

- Alcoholic KOH promotes dehydrohalogenation: removal of a beta hydrogen and a halogen from adjacent carbon atoms forms an alkene.
- The more stable alkene is favoured; conjugation of a double bond with a benzene ring provides additional stability.

Quick Tip to Solve: Write the substrate as $\mathrm{PhCH_2CHClCH_3}$ and prefer elimination that puts the new double bond next to Ph.

Step 1: Identify the possible elimination products The substrate is $C_6H_5CH_2CHClCH_3$. Removal of a hydrogen from the carbon attached to the phenyl group gives $C_6H_5CH{=}CHCH_3$. Removal from the terminal methyl group instead gives $C_6H_5CH_2CH{=}CH_2$. Both eliminate HCl across adjacent carbons.

Step 2: Select the more stable alkene In $C_6H_5CH{=}CHCH_3$, the alkene double bond is conjugated with the aromatic ring and is also more substituted. In the other alkene, a saturated carbon separates the double bond from the ring. The two alcohol options correspond to substitution products; alcoholic alkali favours elimination here.

Step 3: Conclusion The major product is 1-phenylpropene, $C_6H_5CH{=}CHCH_3$. Hence, the correct option is (A).

Quick Tip to Solve: Write the substrate as $PhCH_2CHClCH_3$ and prefer elimination that puts the new double bond next to Ph.

4. The interstitial compounds of transition metals are _____ than the metal itself. [1 mark]

(A) softer

(B) more ductile

(C) harder

(D) more metallic

Correct Answer: (C) harder

Solution:

Concept:

- Interstitial compounds form when small atoms such as H, B, C or N occupy spaces in a transition-metal lattice.
- These compounds generally retain metallic conductivity but show high hardness and high melting points.

Step 1: Relate the occupied spaces to hardness The small atoms occupy interstitial sites rather than simply replacing all the metal atoms. Their presence strengthens the lattice and impedes the relative movement of metal layers. This makes deformation more difficult and increases hardness compared with the pure metal.

Step 2: Eliminate the other comparisons The description softer is opposite to this characteristic. More ductile would imply easier deformation, whereas the interstitial atoms hinder it. Retention of metallic conductivity does not mean that the compound is more metallic than the metal itself. The relevant mechanical property is hardness.

Step 3: Conclusion Interstitial compounds are harder than the metal itself. Hence, the correct option is (C).

Quick Tip to Solve: Associate small atoms in lattice gaps with restricted layer movement: interstitial compounds are hard, not more ductile.

5. What type of isomerism is shown by the following pair of complex compounds?
$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ [1 mark]

(A) Linkage isomerism

(B) Hydrate isomerism

(C) Coordination isomerism

(D) Ionization isomerism

Correct Answer: (C) Coordination isomerism

Solution:

Concept:

- Coordination isomerism occurs when both the cation and the anion are complex ions and ligands are interchanged between their metal centres.
- Linkage isomerism changes the donor atom of an ambidentate ligand; ionization isomerism exchanges a coordinated ligand with a counter-ion.

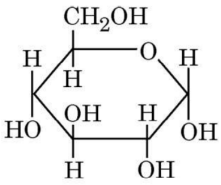
Step 1: Compare the coordination spheres In $[Co(NH_3)_6][Cr(CN)_6]$, the ammine ligands coordinate to cobalt and the cyanide ligands coordinate to chromium. In $[Cr(NH_3)_6][Co(CN)_6]$, the ammine ligands coordinate to chromium and the cyanide ligands coordinate to cobalt. Thus the ligand sets are exchanged between the complex cation and complex anion.

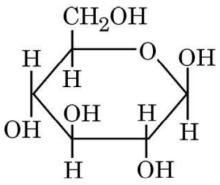
Step 2: Distinguish the other forms of isomerism No ligand is shown changing its donor atom, so this is not linkage isomerism. There is no redistribution of water between the lattice and the coordination sphere, excluding hydrate isomerism. Nor is a simple counter-ion exchanged with a coordinated ligand, as in ionization isomerism.

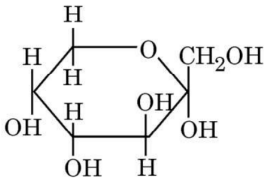
Step 3: Conclusion The pair exhibits coordination isomerism. Hence, the correct option is (C).

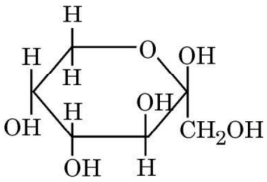
Quick Tip to Solve: When both ions are complexes, check whether their ligand sets have exchanged metal centres; that indicates coordination isomerism.

6. Which of the following structures represents α-D-glucose? [1 mark]

(a) 

(b) 

(c) 

(d) 

(A) Structure (a)

(B) Structure (b)

(C) Structure (c)

(D) Structure (d)

Correct Answer: (A) Structure (a)

Solution:

Concept:

- D-glucose has an aldehyde-derived anomeric carbon, C-1, adjacent to the ring oxygen in its pyranose form.
- In the usual Haworth projection of D-glucose, the C-5 CH_2OH group is above the ring; the alpha anomer has the C-1 hydroxyl group below the ring.

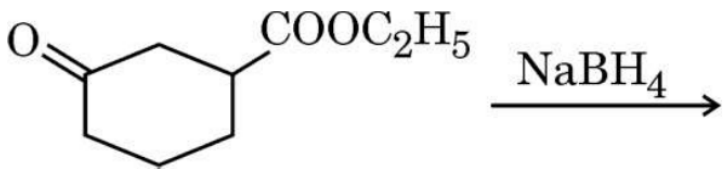
Step 1: Identify the D-glucose ring arrangement In structures (a) and (b), the CH_2OH group on C-5 points above the ring. The hydroxyl directions at C-2, C-3 and C-4 are respectively down, up and down, as required for D-glucose. The carbon immediately next to the ring oxygen on the right is C-1, the anomeric carbon.

Step 2: Read the anomeric hydroxyl direction In structure (a), the C-1 hydroxyl group points down, opposite to the upward C-5 CH_2OH group: this is the alpha configuration. In (b), it points up and is the beta anomer. Structures (c) and (d) put a CH_2OH group on the anomeric carbon and do not represent the required glucose arrangement.

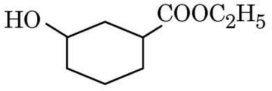
Step 3: Conclusion Structure (a) represents α-D-glucose. Hence, the correct option is (A).

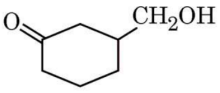
Quick Tip to Solve: For D-glucose in this Haworth orientation, locate C-1 first: its OH points down in alpha and up in beta.

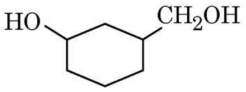
7. The product formed in the reaction: [1 mark]

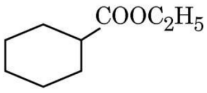


is

(a) 

(b) 

(c) 

(d) 

(A) Hydroxy ester (ketone reduced to OH, ester retained)

(B) Ketone retained, ester reduced to CH_2OH

(C) Both ketone and ester reduced to alcohols

(D) Ketone deoxygenated to a methylene group, ester retained

Correct Answer: (A) Hydroxy ester (ketone reduced to OH, ester retained)

Solution:

Concept:

- $NaBH_4$ is a mild reducing agent that reduces aldehydes and ketones to alcohols.
- Under the usual conditions, $NaBH_4$ does not reduce an ester group; a ketone gives a secondary alcohol.

Step 1: Identify the two functional groups The substrate contains a ketone carbonyl within the six-membered ring and an ethyl ester side group, $COOC_2H_5$. Hydride addition to the ketone carbonyl followed by protonation converts its $C{=}O$ group into $CH(OH)$. The ring skeleton and the ester substituent remain intact.

Step 2: Match the selective reduction product Structure (a) shows precisely a ring hydroxyl group with the ethyl ester retained. Structure (b) reduces the ester but leaves the ketone unchanged, contrary to the selectivity. Structure (c) reduces both groups, requiring a stronger reagent. Structure (d) removes the ketone oxygen completely; sodium borohydride gives an alcohol rather than such deoxygenation.

Step 3: Conclusion The product is the hydroxy ester shown in structure (a). Hence, the correct option is (A).

Quick Tip to Solve: With $NaBH_4$, change the ketone to a secondary alcohol and keep $COOC_2H_5$ unchanged.

8. The action of nitrous acid on ethylamine gives mainly: [1 mark]

(A) ethyl nitrite

(B) ethyl alcohol

(C) nitroethane

(D) ethane

Correct Answer: (B) ethyl alcohol

Solution:

Concept:

- Primary aliphatic amines react with nitrous acid, HNO_2, to replace the amino group by a hydroxyl group.
- The aliphatic diazonium intermediate is unstable and decomposes with evolution of N_2.

Step 1: Identify the amine Ethylamine, $CH_3CH_2NH_2$, is a primary aliphatic amine. Unlike an aromatic diazonium salt at low temperature, its diazonium intermediate does not persist.

Step 2: Follow the substitution The main reaction is

$$CH_3CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2OH + N_2 + H_2O.$$

Ethyl nitrite is an ester of nitrous acid, nitroethane contains a carbon–nitrogen nitro bond, and ethane has no hydroxyl group; these are not the main substitution product here.

Step 3: Conclusion The main product is ethyl alcohol (ethanol). Hence, the correct option is (B).

Quick Tip to Solve: For a primary aliphatic amine with nitrous acid, replace $-NH_2$ by $-OH$.

9. The number of faradays passed through a solution of $CuSO_4$ to produce 1 mol of Cu and O_2 will be: [1 mark]

(A) 1.0

(B) 4.0

(C) 8.0

(D) 2.0

Correct Answer: The printed demand for one mole of Cu and oxygen is ambiguous: simultaneous one-mole quantities are impossible. $2F$ produces one mole of Cu; $4F$ produces one mole of oxygen.

Solution:

Concept:

- One faraday, F, is the charge carried by one mole of electrons. The same charge passes through both electrodes.
- With inert electrodes, aqueous $CuSO_4$ deposits copper at the cathode and evolves oxygen at the anode.

Quick Tip to Solve: Write both half-reactions first: Cu requires two electrons per atom, while oxygen requires four per molecule.

Step 1: Count the electrons for copper The cathode reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu.$$

Thus, $1\,\text{mol}$ of copper requires $2F$. The options $1F$, $4F$ and $8F$ would deposit 0.5, 2 and $4\,\text{mol}$ of copper respectively.

Step 2: Count the electrons for oxygen The anode reaction is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-.$$

Thus, $1\,\text{mol}$ of oxygen requires $4F$. At $2F$, the oxygen produced is only $0.5\,\text{mol}$. Charge is not added between electrodes: the same electrons released at the anode are consumed at the cathode.

Step 3: Check the combined requirement The product ratio is always $n(Cu) : n(O_2) = 2 : 1$. Consequently, one charge cannot simultaneously produce one mole of each. If the one-mole requirement refers only to copper and oxygen is merely the accompanying gas, the charge is $2F$; if it refers to oxygen, the charge is $4F$.

Step 4: Conclusion No option satisfies production of $1\,\text{mol}$ each of Cu and O_2. Option (D), $2F$, gives $1\,\text{mol}$ Cu with $0.5\,\text{mol}$ O_2; option (B), $4F$, gives $1\,\text{mol}$ O_2 with $2\,\text{mol}$ Cu.

Quick Tip to Solve: Write both half-reactions first: Cu requires two electrons per atom, while oxygen requires four per molecule.

10. If the initial concentration is reduced to $\frac{1}{4}$ in a zero order reaction, then the time taken for half the reaction to complete: [1 mark]

(A) remains the same

(B) reduces to one-fourth

(C) increases four times

(D) doubles

Correct Answer: (B) reduces to one-fourth

Solution:

Concept:

- For a zero order reaction, $[A]_t = [A]_0 - kt$, where k is the constant reaction rate at the given temperature.
- The half-life is $t_{1/2} = [A]_0/(2k)$, so it is directly proportional to initial concentration.

Step 1: Obtain the half-life Half the reaction is complete when $[A]_t = [A]_0/2$. Substitution into the integrated rate law gives $[A]_0/2 = [A]_0 - kt_{1/2}$, and therefore $t_{1/2} = [A]_0/(2k)$.

Step 2: Compare the two concentrations For the new initial concentration $[A]_0/4$,

$$t'_{1/2} = \frac{[A]_0/4}{2k} = \frac{t_{1/2}}{4}.$$

Quick Tip to Solve: For zero order kinetics at fixed temperature, scale the half-life by exactly the same factor as the initial concentration.

The rate constant has not changed. An unchanged half-life is the characteristic concentration dependence of a first order reaction, whereas a fourfold increase or doubling contradicts the zero order formula.

Step 3: Conclusion The time reduces to one-fourth of its original value. Hence, the correct option is (B).

Quick Tip to Solve: For zero order kinetics at fixed temperature, scale the half-life by exactly the same factor as the initial concentration.

11. On hydrolysis, which of the following carbohydrates gives glucose and fructose? [1 mark]

(A) Sucrose

(B) Starch

(C) Lactose

(D) Maltose

Correct Answer: (A) Sucrose

Solution:

Concept:

- Hydrolysis breaks a carbohydrate glycosidic linkage using water and reveals its constituent monosaccharides.
- Sucrose is a disaccharide formed from glucose and fructose.

Step 1: Identify the hydrolysis products Sucrose undergoes hydrolysis according to

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

The monosaccharides have the same molecular formula but different structures.

Step 2: Compare the remaining choices Starch is a polymer of glucose and gives glucose on complete hydrolysis. Lactose gives glucose and galactose, while maltose gives two glucose molecules. Neither starch nor lactose nor maltose produces fructose on simple hydrolysis.

Step 3: Conclusion Sucrose gives glucose and fructose on hydrolysis. Hence, the correct option is (A).

Quick Tip to Solve: Remember the pairs: sucrose = glucose + fructose; lactose = glucose + galactose; maltose = glucose + glucose.

12. The deficiency of which of the following vitamins causes Scurvy? [1 mark]

(A) Vitamin A

(B) Vitamin B_6

(C) Vitamin C

(D) Vitamin B_{12}

Correct Answer: (C) Vitamin C

Solution:

Concept:

- Vitamins are essential micronutrients; their deficiencies produce characteristic disorders.
- Vitamin C, also called ascorbic acid, is needed for normal collagen formation and maintenance of connective tissue.

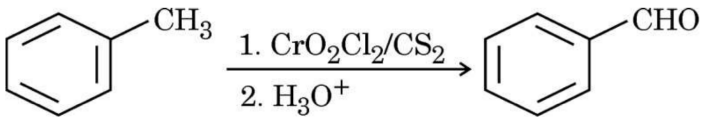
Step 1: Match the disorder with the vitamin Scurvy is associated with insufficient vitamin C. Defective collagen formation leads to symptoms such as bleeding gums, poor wound healing and fragile connective tissues.

Step 2: Eliminate the other vitamins Vitamin A deficiency is associated with night blindness. Vitamin B_6 deficiency may cause neurological problems and anaemia, while vitamin B_{12} deficiency causes megaloblastic anaemia and may affect nerves. These are distinct from the characteristic vitamin C deficiency disorder.

Step 3: Conclusion Scurvy is caused by deficiency of vitamin C. Hence, the correct option is (C).

Quick Tip to Solve: Link scurvy and bleeding gums to ascorbic acid (vitamin C); link night blindness to vitamin A.

13. This reaction is known as: [1 mark]



(A) Cannizzaro reaction

(B) Etard reaction

(C) Rosenmund reduction

(D) Aldol condensation

Correct Answer: (B) Etard reaction

Solution:

Concept:

- The Etard reaction selectively oxidises the benzylic methyl group of toluene to an aldehyde.
- Chromyl chloride, CrO_2Cl_2, in CS_2, followed by hydrolysis, gives benzaldehyde.

Step 1: Recognise the transformation The aromatic ring remains unchanged while its side chain

Quick Tip to Solve: The reagent pair chromyl chloride in CS_2, followed by hydrolysis, identifies the Etard reaction.

changes from $-CH_3$ to $-CHO$. The reagent sequence shown is chromyl chloride in carbon disulphide followed by H_3O^+, which hydrolyses the intermediate complex.

Step 2: Compare the named reactions Cannizzaro reaction is disproportionation of an aldehyde without an alpha hydrogen in concentrated alkali. Rosenmund reduction converts an acyl chloride to an aldehyde using hydrogen over poisoned palladium. Aldol condensation involves carbonyl compounds with alpha hydrogens forming a carbon–carbon bond. None matches the indicated side-chain oxidation.

Step 3: Conclusion The conversion of toluene to benzaldehyde shown is the Etard reaction. Hence, the correct option is (B).

Quick Tip to Solve: The reagent pair chromyl chloride in CS_2, followed by hydrolysis, identifies the Etard reaction.

14. In which of the following does the central atom exhibit an oxidation state of +4? [1 mark]

(A) $K_2[Ni(CN)_4]$

(B) $[Cu(NH_3)_4]^{2+}$

(C) $[Pt(NH_3)_2Cl_2]$

(D) $[Pt(en)_2Cl_2]^{2+}$

Correct Answer: (D) $[Pt(en)_2Cl_2]^{2+}$

Solution:

Concept:

- The oxidation state of the metal plus the sum of ligand charges equals the charge on the coordination entity.
- CN^- and Cl^- each have charge -1. Ammonia and ethane-1,2-diamine (en) are neutral ligands.

Step 1: Evaluate options A and B In $K_2[Ni(CN)_4]$, the two K^+ ions require a complex charge of -2. Thus $x - 4 = -2$, giving Ni oxidation state $+2$. In $[Cu(NH_3)_4]^{2+}$, ammonia contributes zero charge, so Cu is also $+2$.

Step 2: Evaluate options C and D For neutral $[Pt(NH_3)_2Cl_2]$, $x - 2 = 0$, hence Pt is $+2$. For $[Pt(en)_2Cl_2]^{2+}$, $x - 2 = +2$, giving $x = +4$. The two en ligands are neutral even though each coordinates through two donor atoms.

Step 3: Conclusion The central Pt atom has oxidation state $+4$ in $[Pt(en)_2Cl_2]^{2+}$. Hence, the correct option is (D).

Quick Tip to Solve: Ignore donor-atom count when calculating charge: en is neutral; add two units to the complex charge for two chloride ligands.

15. Assertion (A): When glucose is added to water, an elevation in boiling point is observed.
Reason (R): The lowering of vapour pressure causes elevation in the boiling point. [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 non-volatile solute lowers the vapour pressure of its solvent: $p = x_{\text{water}} p^\circ$, where x_{water} is the mole fraction of water and p° is its pure vapour pressure.
- A liquid boils when its vapour pressure equals the external pressure. For dilute solutions, $\Delta T_b = K_b m$, where K_b is the boiling-point elevation constant and m is molality.

Step 1: Judge the assertion Glucose is a non-volatile solute. Adding it to water decreases the mole fraction of water and lowers its vapour pressure at any given temperature. The solution consequently boils above the boiling point of pure water at the same external pressure. Assertion (A) is true.

Step 2: Judge the reason The vapour pressure of the solution at the boiling point of pure water is below the external pressure. Heating to a higher temperature is therefore necessary to reach the boiling condition. Thus lowering of vapour pressure causes elevation of boiling point, so Reason (R) is true.

Step 3: Check the explanatory link The reason supplies precisely the mechanism behind the effect stated in the assertion. Option (B) wrongly denies that link, while (C) and (D) incorrectly declare one of the true statements 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: For a non-volatile solute, connect lower vapour pressure directly to a higher temperature needed for boiling.

16. Assertion (A): Λ_m for weak electrolytes shows a sharp increase when the electrolytic solution is diluted.

Reason (R): For weak electrolytes, degree of dissociation decreases with dilution of solution. [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:

- Molar conductivity Λ_m is the conductivity contribution of the ions produced by one mole of electrolyte.
- For a weak electrolyte, $\alpha = \Lambda_m/\Lambda_m^\circ$, where α is the degree of dissociation and Λ_m° is the limiting molar conductivity.

Step 1: Judge the assertion A weak electrolyte is only partly dissociated in solution. On dilution, a much larger fraction of its molecules dissociates, increasing the number of conducting ions produced per mole. This produces the characteristic sharp increase in molar conductivity. Assertion (A) is true.

Step 2: Judge the reason Dilution favours dissociation of a weak electrolyte. Its degree of dissociation increases, rather than decreases, as the solution becomes more dilute. Consequently, the statement made in Reason (R) is false.

Step 3: Select the applicable code Since the assertion is true and the reason is false, the code for this combination is (C). Options (A) and (B) both require a true reason, while option (D) requires a false assertion. None of those conditions applies here.

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

Quick Tip to Solve: Keep molar conductivity distinct from conductivity: dilution increases dissociation of weak electrolytes.

17. Assertion (A): Monobromination of aniline can be conveniently done by protecting the amino group by acetylation.

Reason (R): Acetylation decreases the activating effect of the amino group. [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:

- The $-NH_2$ group strongly activates aniline toward electrophilic substitution and directs substitution to ortho and para positions.
- Acetylation converts $-NH_2$ into $-NHCOCH_3$; its nitrogen lone pair is partly delocalised toward the carbonyl group, reducing activation of the benzene ring.

Step 1: Judge the assertion Direct treatment of aniline with bromine water readily gives 2,4,6-tribromoaniline. Protecting the amino group as acetanilide first permits controlled monobromination, predominantly at the para position. Hydrolysis of the acetyl group then gives the corresponding bromoaniline. Assertion (A) is true.

Step 2: Judge the reason In acetanilide the nitrogen lone pair participates in resonance with the carbonyl group, so it is less available for donation into the benzene ring than in aniline. The acetylated amino group therefore has a weaker activating effect. Reason (R) is true.

Step 3: Check the explanatory link Reduced ring activation suppresses the ready multiple bromination of unprotected aniline and makes monobromination convenient under controlled conditions. R thus explains A. Option (B) denies this direct link, and (C) and (D) incorrectly treat a true statement as 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: To control bromination of aniline, acetylate first, brominate the protected ring, and then hydrolyse.

18. Assertion (A): Manganese shows the highest oxidation state of +7 in 3d series.

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

Solution:

Concept:

- Transition metals exhibit variable oxidation states because both $(n-1)d$ and ns electrons can participate in bonding.
- Manganese has configuration $[\mathrm{Ar}]\,3d^5 4s^2$, providing seven outer electrons; its maximum oxidation state in compounds such as $\mathrm{KMnO_4}$ is $+7$.

Step 1: Judge the assertion Manganese reaches oxidation state +7, for example in permanganate. For $\mathrm{MnO_4^-}$, if the Mn oxidation state is x, then $x + 4(-2) = -1$, giving $x = +7$. This is the highest oxidation state exhibited by an element of the 3d series. Assertion (A) is true.

Step 2: Judge the reason Transition metals commonly show more than one oxidation state because their s and d electrons can participate in bonding to different extents. Reason (R) is therefore true.

Step 3: Check whether the reason explains the maximum Variable oxidation states are a general feature of transition metals and do not identify why manganese specifically reaches +7. Its particular configuration, with five 3d and two 4s electrons, accounts for that maximum. Thus R does not correctly explain A. Option (A) incorrectly asserts an explanatory link; (C) and (D) incorrectly reject a true statement.

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

Quick Tip to Solve: A general property such as variable oxidation states cannot by itself explain a specific maximum of +7.

Section B (14 marks)

19(a). What type of deviation from Raoult's law is shown by a mixture of ethanol and acetone? Give reason. [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution gives $p_i = x_i p_i^\circ$, where p_i is a component's partial vapour pressure and x_i its mole fraction.
- Positive deviation occurs when unlike intermolecular attractions are weaker overall than the attractions in the pure components, allowing easier escape into the vapour phase.

Step 1: Compare the intermolecular attractions Pure ethanol contains an extensive network of hydrogen bonds between its molecules. Adding acetone places acetone molecules among ethanol molecules and disrupts this ethanol–ethanol hydrogen-bonded network. Although ethanol can interact with acetone, the unlike interactions are weaker overall than those responsible for the cohesion of the pure liquids.

Step 2: Relate weaker attractions to vapour pressure The molecules are held less strongly in the mixture and escape more readily into the vapour phase. At the same temperature and composition, the observed vapour pressure therefore exceeds the ideal value calculated using Raoult's law:

$$p_{\text{total}} > x_{\text{ethanol}} p^\circ_{\text{ethanol}} + x_{\text{acetone}} p^\circ_{\text{acetone}}.$$

The direction of this inequality identifies the deviation.

Step 3: Conclusion A mixture of ethanol and acetone shows positive deviation from Raoult's law because acetone disrupts the hydrogen-bonded ethanol network, weakening the overall intermolecular attractions and increasing vapour pressure.

Quick Tip to Solve: For ethanol mixed with acetone, use disruption of ethanol hydrogen bonding to infer higher vapour pressure.

OR

19(b). Define Azeotrope. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. [2 marks]

Solution:

Concept:

- An azeotrope is a liquid mixture that boils at a constant temperature and has the same composition in its liquid and vapour phases.
- Negative deviation from Raoult's law lowers vapour pressure because unlike intermolecular attractions are stronger than those in the pure components.

Step 1: Define an azeotrope and its distillation behaviour At the azeotropic composition, the vapour

Quick Tip to Solve: Lower vapour pressure requires more heating to boil: negative deviation is associated with maximum boiling.

leaving the boiling liquid has the same composition as that liquid. The mixture consequently boils at a constant temperature without changing composition during distillation at fixed pressure. Its components cannot be completely separated by fractional distillation because repeated vaporisation and condensation at this composition provides no enrichment of either component.

Step 2: Identify the type formed by negative deviation A sufficiently strong negative deviation gives a minimum in the total vapour-pressure curve. Since boiling requires vapour pressure to equal the external pressure, this lowered vapour pressure corresponds to a maximum in the boiling-temperature curve. The azeotrope is therefore a maximum-boiling azeotrope.

Step 3: Give a standard example A nitric acid–water mixture forms a maximum-boiling azeotrope. At atmospheric pressure, its composition is approximately 68 percent nitric acid by mass and 32 percent water; it boils near $393.5\,\mathrm{K}$. The example illustrates the higher boiling temperature associated with negative deviation.

Step 4: Conclusion An azeotrope has identical liquid and vapour compositions and boils at a constant temperature. Negative deviation forms a maximum-boiling azeotrope; nitric acid and water is an example.

Quick Tip to Solve: Lower vapour pressure requires more heating to boil: negative deviation is associated with maximum boiling.

20. An alkyl halide (A) of molecular formula $C_6H_{13}Cl$ on treatment with alcoholic KOH gives two isomeric alkenes (B) and (C) of molecular formula C_6H_{12}. Both alkenes on hydrogenation give 2,3-dimethylbutane. Write the structures of (A), (B) and (C). [2 marks]

Solution:

Concept:

- Alcoholic KOH causes beta-elimination: a hydrogen from a carbon adjacent to the carbon bearing chlorine is removed along with chlorine to form a double bond.
- Hydrogenation adds H_2 across a carbon-carbon double bond without changing the carbon skeleton. Both alkenes must therefore have the skeleton of 2,3-dimethylbutane.

Step 1: Identify the carbon skeleton and chlorine position The hydrogenation product has the structure

$$\mathrm{CH_3{-}CH(CH_3){-}CH(CH_3){-}CH_3}.$$

Placing chlorine on a central carbon gives 2-chloro-2,3-dimethylbutane:

$$\mathrm{CH_3{-}C(Cl)(CH_3){-}CH(CH_3){-}CH_3}.$$

Its molecular formula is $\mathrm{C_6H_{13}Cl}$. The chlorine-bearing carbon has two kinds of adjacent carbons: equivalent methyl carbons and the neighbouring methine carbon. Elimination can thus give two different alkene structures. Chlorine on a terminal carbon would give only one positional alkene on elimination.

Step 2: Eliminate hydrogen chloride in the two possible ways Removal of a beta-hydrogen from

Quick Tip to Solve: Retain the hydrogenation product's carbon skeleton; then place chlorine where two nonequivalent beta-carbon sites can produce two alkenes.

either equivalent methyl group produces the terminal alkene:

$$\mathrm{CH_2{=}C(CH_3){-}CH(CH_3){-}CH_3}.$$

This is 2,3-dimethylbut-1-ene. Removal of the beta-hydrogen from the neighbouring methine carbon produces the internal alkene:

$$\mathrm{(CH_3)_2C{=}C(CH_3)_2}.$$

This is 2,3-dimethylbut-2-ene. Both have formula $\mathrm{C_6H_{12}}$; adding hydrogen to either double bond restores 2,3-dimethylbutane. The more substituted internal alkene is the major product by Saytzeff's rule.

Step 3: Conclusion The required structures are:

$$\begin{aligned}
&\mathrm{(A):}\quad \mathrm{CH_3{-}C(Cl)(CH_3){-}CH(CH_3){-}CH_3}\\
&\mathrm{(B):}\quad \mathrm{CH_2{=}C(CH_3){-}CH(CH_3){-}CH_3}\\
&\mathrm{(C):}\quad \mathrm{(CH_3)_2C{=}C(CH_3)_2}.
\end{aligned}$$

The labels B and C may be interchanged.

Quick Tip to Solve: Retain the hydrogenation product's carbon skeleton; then place chlorine where two nonequivalent beta-carbon sites can produce two alkenes.

21. The rate constant for the first order decomposition of N_2O_5 is given by the following equation:

$$\log k = 23.6 - \frac{2 \times 10^4\ \mathrm{K}}{T}$$

Calculate E_a for this reaction.

[R = 8.314 J K^{-1} mol^{-1}] [2 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- In common logarithms it becomes $\log k = \log A - E_a/(2.303RT)$. Thus the coefficient of $1/T$ gives $E_a/(2.303R)$, not E_a/R.

Step 1: Compare the equation with the Arrhenius form The given expression is

$$\log k = 23.6 - \frac{2 \times 10^4\,\mathrm{K}}{T}.$$

Comparing coefficients of $1/T$ with the common-logarithm Arrhenius equation gives

$$\frac{E_a}{2.303R} = 2 \times 10^4\,\mathrm{K}.$$

The constant 23.6 represents $\log A$ and is not needed to calculate the activation energy. The negative

Quick Tip to Solve: When the equation uses log rather than ln, multiply the magnitude of the reciprocal-temperature coefficient by $2.303R$.

sign agrees with a positive activation energy.

Step 2: Substitute the gas constant and convert units Multiplying the coefficient by $2.303R$,

$$\begin{aligned} E_a &= 2.303(8.314\,\text{J K}^{-1}\text{mol}^{-1})(2 \times 10^4\,\text{K}) \\ &= 3.8294 \times 10^5\,\text{J mol}^{-1} \\ &= 382.94\,\text{kJ mol}^{-1}. \end{aligned}$$

Kelvin cancels, leaving energy per mole as required for activation energy.

Step 3: Conclusion The activation energy is $E_a \simeq 3.83 \times 10^5\,\text{J mol}^{-1} = 383\,\text{kJ mol}^{-1}$.

Quick Tip to Solve: When the equation uses log rather than ln, multiply the magnitude of the reciprocal-temperature coefficient by $2.303R$.

22. Name the cell which:

(a) was used in Apollo Space programme.

(b) is used in automobiles and inverters.

(c) is suitable for hearing aids and watches.

(d) does not give a steady potential and is used in transistors. [2 marks]

Solution:

Concept:

- Cells are selected according to their voltage, size, rechargeability and whether reactants can be supplied continuously. A fuel cell converts the energy of supplied fuel directly into electrical energy.
- Secondary batteries can be recharged. Primary cells are distinguished by their electrodes and electrolyte; the mercury cell maintains nearly constant potential, whereas a dry cell does not.

Step 1: Identify the cells for space missions and vehicles (a) The hydrogen-oxygen fuel cell was used in the Apollo Space programme. Hydrogen and oxygen are supplied to its electrodes, producing electricity and water; the water was also useful to astronauts.

(b) The lead storage battery, also called the lead-acid accumulator, is used in automobiles and inverters. Its electrodes involve lead and lead dioxide, with sulphuric acid as electrolyte. Its reversible discharge reaction allows recharging, which makes it suitable for repeated use.

Step 2: Identify the small primary cells (c) The mercury cell is suitable for hearing aids and watches. It is a small cell with zinc-mercury amalgam and mercury(II) oxide electrodes in alkaline electrolyte. Its potential remains nearly constant during its working life.

(d) The dry cell, or Leclanche cell, is used in transistors. It has a zinc container as anode and a carbon rod surrounded by manganese dioxide and carbon as the cathodic assembly. Unlike the mercury cell, it does not supply a steady potential throughout its use.

Step 3: Conclusion (a) Hydrogen-oxygen fuel cell; (b) lead storage battery; (c) mercury cell; (d) dry cell (Leclanche cell).

Quick Tip to Solve: Match Apollo with hydrogen-oxygen fuel, vehicles with rechargeable lead-acid, watches with steady mercury cells, and transistors with dry cells.

23. Write IUPAC names of the following coordination entities:

(a) $[Cr(NH_3)_3(H_2O)_3]Cl_3$

(b) $K_3[Al(C_2O_4)_3]$ [2 marks]

Solution:

Concept:

- In coordination nomenclature, ligand names precede the metal name and are arranged alphabetically, ignoring multiplicative prefixes. The metal's oxidation state is written in Roman numerals.
- Name the cation before the anion. A metal in an anionic complex takes the suffix -ate; neutral ligands ammonia and water are named ammine and aqua, respectively.

Step 1: Name the chromium complex salt (a) In $[Cr(NH_3)_3(H_2O)_3]Cl_3$, the three external chloride ions have total charge -3; hence the complex cation has charge $+3$. Both ammonia and water are neutral ligands, so chromium has oxidation state $+3$.

Three ammonia ligands give triammine, and three water ligands give triaqua. Ammine precedes aqua alphabetically. The metal remains chromium because the complex is cationic. Name the complex cation first, followed by the counterion chloride: triamminetriaquachromium(III) chloride.

Step 2: Name the aluminium complex salt (b) In $K_3[Al(C_2O_4)_3]$, three potassium ions require the complex anion to have charge -3. Each oxalato ligand, ${C_2O_4}^{2-}$, has charge -2. If aluminium's oxidation state is x, then

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

Three oxalato ligands are written as tris(oxalato). Since the complex is anionic, aluminium becomes aluminate. Name potassium first, then the complex anion: potassium tris(oxalato)aluminate(III).

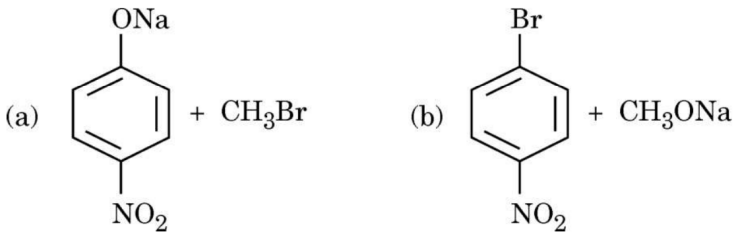
Step 3: Conclusion (a) Triamminetriaquachromium(III) chloride.

(b) Potassium tris(oxalato)aluminate(III).

Quick Tip to Solve: Use the ions outside the brackets to find complex charge, then subtract ligand charges; change the metal ending to -ate only for an anionic complex.

24. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

[2 marks]



Solution:

Concept:

- Williamson ether synthesis joins an alkoxide or phenoxide nucleophile to an alkyl halide by an S_N2 reaction.
- For an aryl methyl ether, put the aryl group in the phenoxide and use a methyl halide as the electrophile; methyl carbon is accessible to backside attack.

Step 1: Select the Williamson reactants Set (a), sodium 4-nitrophenoxide and methyl bromide, is appropriate. The negatively charged oxygen attacks the methyl carbon, displacing bromide and creating the oxygen–methyl bond:

$$4\text{-}NO_2{-}C_6H_4{-}ONa + CH_3Br \longrightarrow 4\text{-}NO_2{-}C_6H_4{-}OCH_3 + NaBr.$$

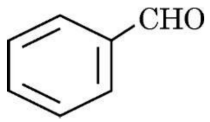
The nitro group stays in the para position, so the product has the required substitution pattern.

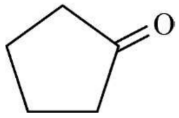
Step 2: Explain why the other set is unsuitable for Williamson synthesis In set (b), bromine is bonded directly to an sp^2-hybridised aromatic carbon. This aryl carbon does not undergo the normal S_N2 displacement used in Williamson synthesis. Resonance gives the aryl carbon–bromine bond partial double-bond character and strengthens it. Thus set (a) is the straightforward Williamson choice. The para nitro group can activate set (b) towards a different, nucleophilic aromatic substitution under suitable conditions; this is not the usual Williamson pathway.

Step 3: Conclusion Choose set (a): sodium 4-nitrophenoxide with CH_3Br gives 1-methoxy-4-nitrobenzene through substitution at the methyl carbon.

Quick Tip to Solve: For an aryl methyl ether, choose the phenoxide plus methyl halide: the carbon bearing the leaving group should be methyl, not aromatic.

25(a). Write the products of the following reactions: [2 marks]

(i)  $\xrightarrow[\Delta]{\text{Conc. NaOH}}$

(ii)  $+ \ H_2NNH - CO - NH_2 \xrightarrow{H^+}$

Solution:

Concept:

- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- Semicarbazide, $H_2NNHCONH_2$, condenses through its terminal $-NH_2$ group with a carbonyl compound to form a semicarbazone and water.

Step 1: Identify the products of reaction (i) The printed aromatic aldehyde is benzaldehyde, C_6H_5CHO. It has no alpha hydrogen and disproportionates on heating with concentrated $NaOH$:

$$2\,C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa.$$

The reduced product is benzyl alcohol, while the oxidised product is sodium benzoate. Benzoic acid would require a subsequent acidification, which is not included in the printed reaction.

Step 2: Identify the product of reaction (ii) The five-membered cyclic ketone shown is cyclopentanone. Its carbonyl oxygen is replaced by $=N-NH-CO-NH_2$ during acid-catalysed condensation with semicarbazide. The product is cyclopentanone semicarbazone, with the original five-membered carbon ring retained, and water is eliminated:

$$C_5H_8O + H_2NNHCONH_2 \xrightarrow{H^+} C_6H_{11}N_3O + H_2O.$$

Here $C_6H_{11}N_3O$ is the molecular formula of the semicarbazone: the former ring carbonyl carbon now bears the exocyclic $=N-NH-CO-NH_2$ group.

Step 3: Conclusion (i) Benzyl alcohol and sodium benzoate. (ii) Cyclopentanone semicarbazone, with water as the condensation by-product.

Quick Tip to Solve: With concentrated alkali, keep the Cannizzaro oxidation product as its sodium salt; for a semicarbazone, replace carbonyl oxygen by $=N-NH-CO-NH_2$.

OR

25(b). Do the following conversions in not more than two steps:

(i) Toluene to Benzoic acid

(ii) Benzaldehyde to 1-Phenylethanol [2 marks]

Solution:

Concept:

- A benzene side chain containing a benzylic hydrogen is oxidised by hot alkaline $KMnO_4$ to a carboxylate; acidification gives the carboxylic acid.
- A Grignard reagent adds its alkyl group to the carbonyl carbon of an aldehyde. Acidic hydrolysis then converts the magnesium alkoxide to an alcohol.

Step 1: Convert toluene to benzoic acid in two steps First heat toluene with alkaline potassium permanganate to obtain potassium benzoate. Then acidify the salt to give benzoic acid:

$$C_6H_5CH_3 \xrightarrow{KMnO_4/OH-,heat} C_6H_5COOK,$$
$$C_6H_5COOK + HCl \longrightarrow C_6H_5COOH + KCl.$$

The methyl carbon becomes the carboxyl carbon and the benzene ring remains intact. These are the required oxidation and acidification steps.

Step 2: Convert benzaldehyde to 1-phenylethanol in two steps Add methylmagnesium bromide to benzaldehyde in dry ether; then hydrolyse the magnesium alkoxide using dilute acid:

$$C_6H_5CHO + CH_3MgBr \xrightarrow{\text{dry ether}} C_6H_5CH(OMgBr)CH_3,$$
$$C_6H_5CH(OMgBr)CH_3 + H_2O \xrightarrow{H^+} C_6H_5CH(OH)CH_3 + Mg(OH)Br.$$

Addition introduces the extra methyl group required by the target. The former aldehyde carbon becomes the carbon carrying the hydroxyl group. Dry ether is essential because water would consume the Grignard reagent before it can add to the aldehyde.

Step 3: Conclusion (i) Hot alkaline $KMnO_4$, followed by acidification, converts toluene to benzoic acid. (ii) CH_3MgBr in dry ether, followed by acidic hydrolysis, converts benzaldehyde to $C_6H_5CH(OH)CH_3$, 1-phenylethanol.

Quick Tip to Solve: Compare carbon counts: converting benzaldehyde to 1-phenylethanol requires adding one methyl group, so choose CH_3MgBr before hydrolysis.

Section C (15 marks)

26. The following data were obtained during the first order thermal decomposition of C_2H_5Cl at a constant volume:

Calculate the rate constant.

(Given: $\log 2 = 0.3010,\ \log 3 = 0.4771,\ \log 4 = 0.6021$**)** [3 marks]

$$C_2H_5Cl\,(g) \longrightarrow C_2H_4\,(g) + HCl\,(g)$$

Experiment	Time (s^{-1})	Total pressure (atm)
1	0	0·4
2	100	0·6

Solution:

Concept:

- At constant volume and temperature, pressure is proportional to gas amount. For $A\,(g) \longrightarrow B\,(g) + C\,(g)$, each mole decomposed increases the total amount by one mole.
- The integrated first-order rate law is $k = \dfrac{2.303}{t}\log\dfrac{p_0}{p_A}$, where p_0 and p_A are the initial and remaining reactant partial pressures and t is elapsed time.

Step 1: Relate total pressure to decomposition Initially only ethyl chloride is present, so its initial partial pressure is $p_0 = 0.4\,\text{atm}$. Let x be the pressure equivalent of the amount that decomposes. Each product gains partial pressure x, whereas the reactant falls to $p_0 - x$. Therefore,

$$P_t = (p_0 - x) + x + x = p_0 + x,$$
$$x = P_t - p_0 = 0.6 - 0.4 = 0.2\,\text{atm}.$$

Step 2: Find the remaining reactant pressure Subtract the decomposed portion from the initial reactant pressure:

$$p_A = p_0 - x = 2p_0 - P_t,$$
$$= 2(0.4) - 0.6 = 0.2\,\text{atm}.$$

Thus half the initial ethyl chloride remains after $100\,\text{s}$.

Step 3: Apply the first-order rate equation Insert the reactant pressures and elapsed time into the integrated rate law:

$$k = \frac{2.303}{100}\log\frac{0.4}{0.2}$$
$$= \frac{2.303}{100}\log 2$$
$$= \frac{2.303 \times 0.3010}{100}$$
$$= 6.93203 \times 10^{-3}\,s^{-1}.$$

The pressure ratio is dimensionless, so the rate constant has units of inverse time.

Quick Tip to Solve: For one gas decomposing into two gases, calculate the reactant pressure as $2p_0 - P_t$; never put the measured total pressure directly into the first-order law.

Step 4: Conclusion The rate constant is $\boxed{k = 6.93 \times 10^{-3}\,\text{s}^{-1}}$.

Quick Tip to Solve: For one gas decomposing into two gases, calculate the reactant pressure as $2p_0 - P_t$; never put the measured total pressure directly into the first-order law.

27. If benzoic acid (M = 122 g mol^{-1}) is associated into a dimer when dissolved in benzene and the osmotic pressure of a solution of 6.1 g of benzoic acid in 100 mL benzene is 6.5 atm at 27°C, then what is the percentage association of benzoic acid?

(Given: R = 0.0821 L atm K^{-1} mol^{-1}) [3 marks]

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT = i\dfrac{wRT}{MV}$, where i is the van't Hoff factor, w the solute mass, M its molar mass and V the solution volume.
- Association reduces the number of solute particles. For dimerisation, $2A \rightleftharpoons A_2$; if α is the fraction of initial monomers associated, then $i = 1 - \alpha/2$.

Step 1: Calculate the pressure without association Use $T = 27 + 273 = 300\,\text{K}$ and $V = 100\,\text{mL} = 0.100\,\text{L}$. The initial amount of benzoic acid, counted as monomer units, is

$$n_0 = \frac{6.1}{122} = 0.050\,\text{mol}.$$

Thus the monomer concentration would be $C_0 = 0.050/0.100 = 0.500\,\text{mol L}^{-1}$, giving

$$\pi_0 = C_0RT = 0.500 \times 0.0821 \times 300 = 12.315\,\text{atm}.$$

The supplied solvent volume is used as the solution volume in this osmotic-pressure calculation.

Step 2: Obtain the particle-number factor The observed pressure is smaller than π_0 because two acid molecules associate to form each dimer. Therefore

$$i = \frac{\pi}{\pi_0} = \frac{6.5}{12.315} = 0.52781.$$

This lies between 0.5 (complete dimerisation) and 1 (no association), as required.

Step 3: Relate the factor to the associated fraction Starting with n_0 monomer units, $n_0(1-\alpha)$ remain unassociated and $n_0\alpha/2$ dimers are formed. The total number of solute particles is thus $n_0(1 - \alpha/2)$. Hence

$$i = 1 - \frac{\alpha}{2},$$

$$\alpha = 2(1 - i) = 2(1 - 0.52781) = 0.94438.$$

Multiplying this fraction by 100 expresses the association as a percentage.

Step 4: Conclusion The percentage association of benzoic acid is $\boxed{94.44\%}$ (approximately).

Quick Tip to Solve: For a dimer, first find $i = \pi/\pi_0$, then use percentage association $= 200(1 - i)$. Do not equate $1 - i$ directly with the associated fraction.

28. Answer any three of the following questions:

(a) Explain the type of hybridization in $[Fe(CN)_6]^{3-}$ on the basis of valence bond theory. (Given: Atomic number of Fe = 26)

(b) Draw the geometrical isomers of $[PtCl_2(en)_2]^{2+}$ ion.

(c) $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

(d) Name the type of isomerism when ambidentate ligands are attached to central metal ion. Give one example of ambidentate ligand. [3 marks]

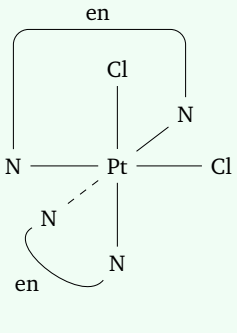
Solution:

Concept:

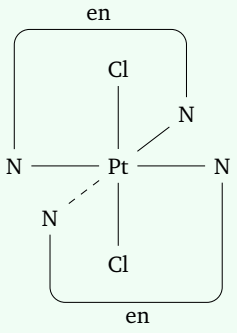
- Ligand strength controls electron pairing; unpaired electrons cause paramagnetism.
- Octahedral cis ligands are adjacent; trans ligands are opposite. Each en has two N donors.

Step 1: (a) Hybridisation of the iron complex In $[Fe(CN)_6]^{3-}$, $x - 6 = -3$ gives Fe^{3+}. Neutral Fe is $[Ar]3d^6 4s^2$, so Fe^{3+} is $3d^5$. Strong-field CN^- pairs the five electrons in three $3d$ orbitals (two pairs and one unpaired electron), leaving two $3d$ orbitals vacant. These combine with one $4s$ and three $4p$ orbitals to give d^2sp^3 hybridisation: an inner-orbital octahedral complex.

Step 2: (b) Geometrical isomers of the platinum complex Two bidentate en ligands and two Cl ligands give octahedral coordination. The Cl ligands are adjacent in cis and opposite in trans. Each en connection below represents its chelate backbone, joining two N donors.



cis: Cl–Pt–Cl angle 90°



trans: Cl–Pt–Cl angle 180°

Cis and trans forms of the 2+ ion; en joins its two N donors.

Step 3: (c) Different magnetic behaviour of the nickel complexes In $[NiCl_4]^{2-}$, Ni^{2+} has $3d^8$ configuration. Weak-field chloride leaves two unpaired electrons, giving a paramagnetic, tetrahedral sp^3 complex. In $[Ni(CO)_4]$, neutral CO gives Ni oxidation state zero. Strong-field CO pairs the metal valence electrons into $3d^{10}$, leaving $4s$ and $4p$ orbitals for sp^3 hybridisation. All electrons are paired, so this tetrahedral complex is diamagnetic.

Step 4: (d) Isomerism involving an ambidentate ligand This is linkage isomerism. An example is nitrite, NO_2^-: it binds through N as nitro or through O as nitrito. The ligand composition is unchanged, but its donor atom changes.

Step 5: Conclusion (a) d^2sp^3; (b) cis and trans as drawn; (c) two versus zero unpaired electrons; (d) linkage isomerism, e.g. NO_2^-.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons; in $[PtCl_2(en)_2]^{2+}$, compare the two Cl positions to identify cis or trans.

29. Account for the following:

(a) Benzyl chloride is highly reactive towards S_N1 reaction.

(b) $(\pm)$-Butan-2-ol is optically inactive, though it contains a chiral carbon atom.

(c) Chloroform is stored in closed dark coloured bottles. [3 marks]

Solution:

Concept:

- The rate-determining step of an S_N1 reaction is ionisation to form a carbocation. Greater carbocation stability favours this step.
- A racemic mixture contains equal amounts of two enantiomers whose optical rotations cancel. Chloroform can undergo oxidative decomposition in air and light.

Step 1: (a) Resonance stabilisation of the benzyl carbocation Benzyl chloride ionises by cleavage of its carbon–chlorine bond:

$$C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2^+ + Cl^-.$$

The resulting benzyl carbocation is resonance stabilised because its vacant p orbital conjugates with the aromatic ring. The positive charge is delocalised from the benzylic carbon to the ortho and para positions of the ring. Formation of this stabilised carbocation is easier than formation of an ordinary primary alkyl carbocation, so benzyl chloride is highly reactive towards the S_N1 mechanism.

Step 2: (b) External compensation in racemic butan-2-ol The carbon bearing the hydroxyl group in $CH_3CH(OH)CH_2CH_3$ is bonded to four different groups: H, OH, CH_3 and C_2H_5. Each pure enantiomer is therefore optically active. However, the symbol $(\pm)$ means that the sample is a racemic mixture containing equal amounts of the two enantiomers. They rotate plane-polarised light through equal angles in opposite directions. Their rotations cancel by external compensation, making the mixture optically inactive despite the chiral carbon in each molecule.

Step 3: (c) Prevent formation of poisonous phosgene In the presence of oxygen and light, chloroform slowly oxidises to carbonyl chloride (phosgene), a highly poisonous gas:

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl.$$

The dark colour of the bottle reduces exposure to light, while keeping it closed limits contact with atmospheric oxygen. Both measures suppress the oxidative decomposition and the formation of phosgene.

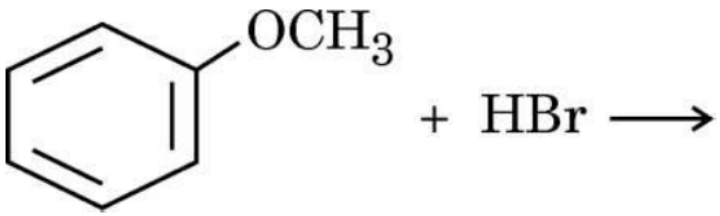
Step 4: Conclusion (a) Benzyl chloride forms a resonance-stabilised benzyl carbocation. (b) $(\pm)$-Butan-2-ol is a racemic mixture with cancelling optical rotations. (c) Closed dark bottles suppress air- and light-induced formation of poisonous phosgene.

Quick Tip to Solve: For benzyl S_N1 reactivity, focus on carbocation resonance; for $(\pm)$, identify a racemate; for chloroform storage, name phosgene and both air and light.

30(a). (i) Write hydroboration-oxidation reaction with an example.

(ii) Write the products of the following reaction:

(iii) Why is p-nitrophenol more acidic than phenol? [3 marks]



Solution:

Concept:

- Hydroboration followed by oxidation adds water across an alkene in the anti-Markovnikov orientation: the hydroxyl group goes to the less substituted carbon.
- In an aryl alkyl ether, hydrogen halides cleave the alkyl–oxygen bond; the aryl–oxygen bond has partial double-bond character.
- Acidity increases when an electron-withdrawing substituent stabilises the conjugate base formed by loss of H^+.

Step 1: (i) Hydroboration and oxidation An alkene reacts with diborane (or borane in tetrahydrofuran, THF) to form a trialkylborane. Oxidation with alkaline hydrogen peroxide replaces the carbon–boron bond by a carbon–oxygen bond. For example, propene gives propan-1-ol:

$$3CH_3CH{=}CH_2 + BH_3 \longrightarrow (CH_3CH_2CH_2)_3B,$$

$$(CH_3CH_2CH_2)_3B + 3H_2O_2 \xrightarrow{OH^-} 3CH_3CH_2CH_2OH + B(OH)_3.$$

Here borane is used in THF. Addition places boron on the terminal carbon, and oxidation retains this position, giving the primary alcohol without rearrangement.

Step 2: (ii) Cleavage of anisole The ether oxygen is protonated by HBr. Bromide attacks the methyl group by an S_N2 process, cleaving the methyl–oxygen bond:

$$C_6H_5OCH_3 + HBr \longrightarrow C_6H_5OH + CH_3Br.$$

The products are phenol and bromomethane. Bromobenzene is not formed because nucleophilic substitution does not occur at the aromatic sp^2 carbon under these conditions.

Step 3: (iii) Compare the conjugate bases The para nitro group exerts both an electron-withdrawing inductive effect and a resonance-withdrawing effect. It disperses and stabilises the negative charge of the p-nitrophenoxide ion more effectively than in unsubstituted phenoxide. The more stable conjugate base makes loss of the phenolic proton easier, so p-nitrophenol is more acidic than phenol.

Step 4: Conclusion (i) Propene gives propan-1-ol by hydroboration–oxidation. (ii) Anisole gives phenol and bromomethane with HBr. (iii) The nitro group stabilises the conjugate base, increasing acidity.

Quick Tip to Solve: For anisole cleavage, break the O–methyl bond; for acidity, compare the stability of the phenoxide ions.

OR

30(b). (i) What happens when phenol reacts with

(1) Conc. HNO_3, and

(2) $CHCl_3$ in presence of aqueous NaOH followed by acidification?

Write equations only.

(ii) Why does the reaction of CH_3ONa with $(CH_3)_3C$-Br give 2-methylpropene and not $(CH_3)_3C$-OCH_3?

[3 marks]

Solution:

Concept:

- Phenol directs electrophilic substitution to the ortho and para positions. Concentrated nitric acid introduces three nitro groups.
- The Reimer–Tiemann reaction introduces a formyl group mainly ortho to the phenolic hydroxyl group.
- Williamson ether synthesis requires S_N2 attack; tertiary alkyl halides instead undergo elimination with a strong alkoxide base.

Step 1: (i)(1) Reaction with concentrated nitric acid

$$C_6H_5OH + 3HNO_3 \xrightarrow{\text{conc.}} 2,4,6-(NO_2)_3C_6H_2OH + 3H_2O.$$

Step 2: (i)(2) Reaction with chloroform and aqueous alkali

$$C_6H_5OH + CHCl_3 + 4NaOH \longrightarrow o\text{-}CHO\text{-}C_6H_4ONa + 3NaCl + 3H_2O,$$

$$o\text{-}CHO\text{-}C_6H_4ONa + HCl \longrightarrow o\text{-}CHO\text{-}C_6H_4OH + NaCl.$$

Step 3: (ii) Why elimination gives 2-methylpropene The carbon bearing bromine in $(CH_3)_3CBr$ is tertiary. Three methyl groups hinder the backside attack required for S_N2 substitution, preventing formation of tert-butyl methyl ether.

Methoxide is a strong base. It abstracts a beta hydrogen from a neighbouring methyl group as bromide leaves simultaneously in E2 elimination. Formation of the double bond gives 2-methylpropene:

$$(CH_3)_3CBr + NaOCH_3 \longrightarrow CH_2{=}C(CH_3)_2 + CH_3OH + NaBr.$$

All three methyl groups are equivalent, so removal of a beta hydrogen from any of them gives the same alkene.

Step 4: Conclusion (i) The products are 2,4,6-trinitrophenol and, after acidification, 2-hydroxybenzaldehyde (salicylaldehyde), respectively. (ii) Steric hindrance prevents substitution at the tertiary carbon, while methoxide promotes elimination to 2-methylpropene.

Quick Tip to Solve: In Williamson synthesis, place the less hindered group on the halide; a tertiary halide with methoxide gives an alkene.

Section D (8 marks)

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

31(i). Amines are usually formed from nitro compounds, halides, amides, imides, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and hydrogen bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Presence of amino group in aromatic ring enhances reactivity of the aromatic amines. Aryl diazonium salts provide advantageous methods for producing aryl halides, cyanides, phenols and arenes by reductive removal of the diazo group.

Answer the following questions:

Arrange the following in the increasing order of their pK_b values in aqueous solution: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ [1 mark]

Solution:

Concept:

- $pK_b = -\log_{10} K_b$; a stronger base has a larger K_b and hence a smaller pK_b.
- In aqueous ethylamines, inductive electron donation, steric effects and hydration of the conjugate ammonium ion act together.

Step 1: Compare the basic strengths in water The aqueous basicity order for these ethyl-substituted amines is

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2.$$

The secondary amine has a favourable combination of electron donation and hydration. Although the tertiary ammonium ion is less effectively hydrated, the electron donation of its three ethyl groups makes triethylamine more basic than ethylamine.

Step 2: Convert basicity to the requested order Increasing pK_b means decreasing basic strength. Reverse the basicity order when listing pK_b values; do not confuse a large pK_b with a strong base.

Step 3: Conclusion The increasing order of pK_b is

$$\boxed{(C_2H_5)_2NH < (C_2H_5)_3N < C_2H_5NH_2}.$$

Quick Tip to Solve: For ethylamines in water, first recall secondary > tertiary > primary basicity, then reverse it for increasing pKb.

31(ii). Aniline on nitration gives a substantial amount of m-nitroaniline, though amino group is o/p directing. Why? [1 mark]

Solution:

Concept:

- The free $-NH_2$ group donates its lone pair to the ring and directs substitution ortho and para.
- Protonation converts $-NH_2$ into the electron-withdrawing, meta-directing $-NH_3^+$ group.

Step 1: Identify the species in the nitrating mixture Nitration uses a strongly acidic mixture of nitric acid and sulphuric acid. Under these conditions, aniline is protonated:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

Nitrogen in the anilinium ion has no free lone pair available for donation into the aromatic ring.

Step 2: Explain the meta product The positively charged $-NH_3^+$ group withdraws electron density and is meta directing. Nitration of the protonated fraction therefore gives the meta-substituted product. This accounts for a substantial amount of m-nitroaniline even though unprotonated aniline is ortho/para directing.

Step 3: Conclusion Aniline is protonated to the meta-directing anilinium ion in the strongly acidic nitrating mixture, so a substantial amount of m-nitroaniline is obtained.

Quick Tip to Solve: Before applying an amino groups directing effect, check whether the acidic medium has converted it to anilinium.

31(iii). An aromatic compound 'A' of molecular formula $C_7H_6O_2$ on treatment with aqueous ammonia and heating forms compound 'B'. Compound 'B' on heating with Br_2 and aqueous KOH gives a compound 'C' of molecular formula C_6H_7N. Write the structures of A, B and C. [2 marks]

Solution:

Concept:

- A carboxylic acid reacts with aqueous ammonia to form an ammonium carboxylate, which loses water on heating to give a primary amide.
- Hofmann bromamide degradation converts $RCONH_2$ into RNH_2 using Br_2 and aqueous KOH; the product contains one fewer carbon atom.

Step 1: Identify the aromatic acid and its amide The aromatic acid with formula $C_7H_6O_2$ is benzoic acid, C_6H_5COOH. Its carboxyl group first forms ammonium benzoate with aqueous ammonia. Heating this salt eliminates water and gives benzamide:

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COO^-NH_4^+$$

$$C_6H_5COO^-NH_4^+ \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

Thus A has a benzene ring bonded to $-COOH$, while B has that ring bonded to $-CONH_2$.

Quick Tip to Solve: Work backwards from the amine: Hofmann degradation removes the carbonyl carbon of a primary amide.

Step 2: Apply Hofmann bromamide degradation Benzamide has the primary amide group required for this reaction. On treatment with bromine and aqueous alkali, its carbonyl carbon is lost and the phenyl group becomes attached directly to the amino group:

$$C_6H_5CONH_2 + Br_2 + 4KOH$$

$$\xrightarrow{\Delta} C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

The resulting aniline has six ring carbons, five ring hydrogens and two hydrogens on nitrogen, agreeing with the given formula C_6H_7N.

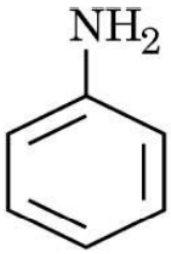
Step 3: Conclusion The required structures are:

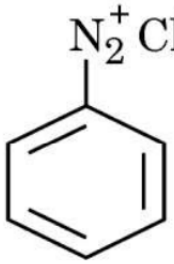
$$\begin{aligned} A &= C_6H_5{-}COOH \quad \text{(benzoic acid)}, \\ B &= C_6H_5{-}CO{-}NH_2 \quad \text{(benzamide)}, \\ C &= C_6H_5{-}NH_2 \quad \text{(aniline)}. \end{aligned}$$

Quick Tip to Solve: Work backwards from the amine: Hofmann degradation removes the carbonyl carbon of a primary amide.

OR

31(iii). Complete the following reactions giving main products: [2 marks]

(1)  $+ Br_2\ (aq) \longrightarrow$

(2)  $\xrightarrow[(ii)\ NaNO_2/Cu,\ \Delta]{(i)\ HBF_4}$

Solution:

Concept:

- The $-NH_2$ group strongly activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- An aryl diazonium group can be replaced by $-NO_2$ after forming its tetrafluoroborate and heating

Quick Tip to Solve: For reaction (2), read both reagent steps: nitrite and copper replace the diazonium group by a nitro group.

with sodium nitrite and copper.

Step 1: Complete the bromination of aniline In bromine water, the strong activating effect of $-NH_2$ permits substitution at both ortho positions and at the para position without a Lewis acid catalyst. The main product is 2,4,6-tribromoaniline, a white precipitate:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow 2,4,6{-}C_6H_2Br_3NH_2 + 3HBr.$$

Numbering the amino-bearing carbon as 1 places bromine at positions 2, 4 and 6.

Step 2: Complete the diazonium substitution The starting compound is benzenediazonium chloride, $C_6H_5N_2^+Cl^-$. Treatment with HBF_4 replaces chloride by tetrafluoroborate, forming $C_6H_5N_2^+BF_4^-$. Heating this salt with sodium nitrite in the presence of copper replaces the diazonium group by $-NO_2$, releasing nitrogen:

$$C_6H_5N_2^+BF_4^- + NaNO_2 \xrightarrow{Cu,\,\Delta}$$

$$C_6H_5NO_2 + N_2 + NaBF_4.$$

Thus the final product after both reagent steps is nitrobenzene; the nitrite/copper step determines which group replaces the diazonium group.

Step 3: Conclusion The main products are (1) $\boxed{\text{2,4,6-tribromoaniline}}$, $2,4,6{-}C_6H_2Br_3NH_2$, and (2) $\boxed{\text{nitrobenzene}}$, $C_6H_5NO_2$.

Quick Tip to Solve: For reaction (2), read both reagent steps: nitrite and copper replace the diazonium group by a nitro group.

32(i). Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Carbohydrates are optically active polyhydroxy aldehydes or ketones or molecules which provide such units on hydrolysis. They are broadly classified into three groups - monosaccharides, oligosaccharides and polysaccharides. Monosaccharides are held together by glycosidic linkages to form disaccharides like sucrose, maltose or polysaccharides like starch and cellulose.

Another biomolecule: proteins are polymers of α-amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. Structure and shape of proteins can be studied at four different levels i.e. primary, secondary, tertiary and quaternary, each level being more complex than the previous one.

Answer the following questions:

What is the difference between a glycosidic linkage and peptide linkage? [1 mark]

Solution:

Concept:

- A linkage is the covalent bond joining monomer units in a biomolecule.
- Carbohydrates contain glycosidic linkages, whereas proteins contain peptide linkages between amino acid residues.

Quick Tip to Solve: Associate sugar units with an oxygen bridge and amino acid residues with the amide group.

Step 1: Describe the carbohydrate linkage A glycosidic linkage is a $C-O-C$ linkage joining monosaccharide units through an oxygen atom. It forms by condensation of hydroxyl groups, including the anomeric hydroxyl of a sugar, with elimination of water. Such linkages join sugar units in disaccharides and polysaccharides.

Step 2: Describe the protein linkage A peptide linkage is the amide group $-CO-NH-$. It forms when the carboxyl group of one amino acid condenses with the amino group of another amino acid, eliminating water. Thus it joins amino acid residues in a protein rather than joining monosaccharide units.

Step 3: Conclusion A glycosidic linkage is the oxygen bridge $\boxed{C-O-C}$ between sugar units; a peptide linkage is $\boxed{-CO-NH-}$ between amino acid residues.

Quick Tip to Solve: Associate sugar units with an oxygen bridge and amino acid residues with the amide group.

32(ii). Which amino acids are called essential amino acids? [1 mark]

Solution:

Concept:

- Amino acids supply the building units for proteins in the human body.
- Essential amino acids are identified by the body's inability to synthesise them in adequate amounts, rather than by a special peptide bond.

Step 1: State the defining limitation Essential amino acids are those that the human body cannot synthesise in sufficient amounts to meet its requirements. They are needed for protein synthesis and normal physiological functions, so absence of a sufficient supply limits the formation of the proteins that require them.

Step 2: State how they are supplied These amino acids must therefore be obtained through the diet. For example, valine and leucine are essential amino acids. In contrast, non-essential amino acids can be synthesised by the body; the word essential refers to dietary necessity, not to whether an amino acid participates in proteins.

Step 3: Conclusion $\boxed{\text{Essential amino acids must be supplied in the diet}}$ because the human body cannot synthesise them in adequate amounts.

Quick Tip to Solve: Define essential by dietary requirement, then give valine or leucine as a suitable example.

32(iii). What are the common types of secondary structures of proteins? Write any two forces which stabilise the secondary and tertiary structures of protein. [2 marks]

Solution:

Concept:

- Secondary structure is the regular local folding of a polypeptide backbone, chiefly into an α-helix or a β-pleated sheet.
- Tertiary structure is the overall three-dimensional folding of the polypeptide, stabilised by interactions involving its side chains as well as its backbone.

Step 1: Name the common secondary structures The two common types are the α-helix and the β-pleated sheet. In the α-helix, the polypeptide chain coils into a regular helix. In the β-pleated sheet, extended polypeptide segments lie alongside one another in a sheet-like arrangement. These describe folding patterns of the chain, while the amino acid sequence constitutes the primary structure.

Step 2: Identify two stabilising interactions **Hydrogen bonding:** attractions between backbone $C = O$ groups and $N - H$ groups stabilise both the helix and the pleated sheet. Hydrogen bonds between suitable polar groups also support tertiary folding.

Van der Waals attractions: weak attractions between closely packed atoms, especially those of non-polar side chains, contribute to the stability of the compact tertiary structure. Together these interactions help maintain the folded protein. Hydrogen bonding is the characteristic stabilising interaction for the regular secondary structures.

Step 3: Conclusion The common secondary structures are $\boxed{\alpha\text{-helix and } \beta\text{-pleated sheet}}$. Two stabilising interactions are $\boxed{\text{hydrogen bonds and van der Waals attractions}}$.

Quick Tip to Solve: Name the helix and sheet first; then identify hydrogen bonding for the backbone and van der Waals attractions for close packing.

OR

32(iii). Define denaturation of protein with an example. During denaturation which structures of protein lose their biological activity? [2 marks]

Solution:

Concept:

- A native protein has a specific three-dimensional shape, maintained by interactions such as hydrogen bonds. Its biological activity depends on this shape.
- The primary structure is the sequence of amino acids joined by covalent peptide bonds; secondary and tertiary structures describe the folding of this chain.

Step 1: Define denaturation and give an example Denaturation is the loss of the native conformation and biological activity of a protein when it is subjected to a physical change, such as heating, or a chemical change, such as a change in pH. For example, on boiling an egg, the albumin of the egg white denatures and coagulates into an insoluble solid.

Quick Tip to Solve: Distinguish unfolding from hydrolysis: denaturation changes protein folding without breaking the peptide-bond sequence.

Step 2: Identify the structures affected During denaturation, the interactions maintaining the folded shape are disrupted. The secondary structure and tertiary structure are destroyed or altered, so the protein loses its characteristic biological activity. The peptide bonds are not hydrolysed in ordinary denaturation; consequently, the primary structure, that is, the amino-acid sequence, remains intact.

Step 3: Conclusion Denaturation is the loss of a protein's native shape and biological activity, as in coagulation of egg albumin on boiling. Secondary and tertiary structures are disrupted, while the primary structure remains unchanged.

Quick Tip to Solve: Distinguish unfolding from hydrolysis: denaturation changes protein folding without breaking the peptide-bond sequence.

Section E (15 marks)

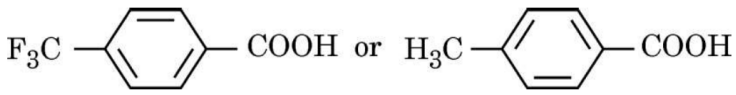
33. (a) Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(b) Which acid of the following pair is a stronger acid?

(c) Write the chemical equation involved in Rosenmund's reduction.

(d) Why are α-hydrogen atoms of aldehydes and ketones acidic in nature?

(e) Write a chemical test to distinguish between Benzaldehyde and Benzoic acid. [5 marks]



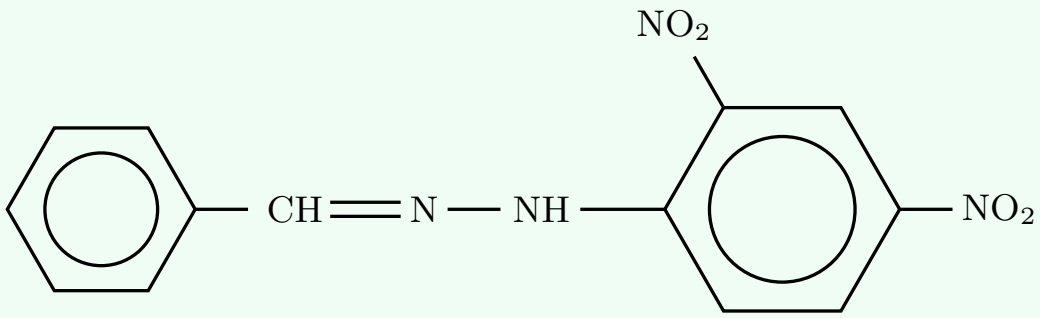
Solution:

Concept:

- An aldehyde reacts with 2,4-dinitrophenylhydrazine by condensation to give a hydrazone, with the carbonyl group replaced by $C = N - NH - Ar$.
- Electron-withdrawing groups stabilise a carboxylate ion and increase acidity; electron-donating groups have the opposite effect.
- Resonance stabilises the enolate ion obtained by removing an α-hydrogen from a carbonyl compound. Carboxylic acids also release carbon dioxide from aqueous sodium hydrogen carbonate.

Step 1: (a) Structure of the benzaldehyde hydrazone The terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine condenses with the carbonyl group of benzaldehyde, eliminating water. The product is $C_6H_5 - CH = N - NH - C_6H_3(NO_2)_2$. In the second benzene ring the nitro groups occupy positions 2 and 4 relative to the carbon attached to $-NH - N = CH - C_6H_5$. The hydrogen originally attached to the aldehyde carbon is retained in the $-CH = N-$ group. Its structure is shown below.

Quick Tip to Solve: For the hydrazone retain the aldehydic hydrogen; for the acid comparison compare conjugate-base stability, and use bicarbonate effervescence to identify COOH.



Benzaldehyde 2,4-dinitrophenylhydrazone; the nitro groups are ortho and para to the hydrazone attachment.

Step 2: (b) Compare the two acids The stronger acid is the first acid shown, $\mathrm{p}-\mathrm{CF_3}-\mathrm{C_6H_4}-\mathrm{COOH}$, called p-trifluoromethylbenzoic acid. The $-\mathrm{CF_3}$ group exerts a strong electron-withdrawing inductive effect, stabilising the negative charge of the conjugate carboxylate ion. The $-\mathrm{CH_3}$ group in p-methylbenzoic acid is electron donating and makes its conjugate base less stable. Greater conjugate-base stability favours acid dissociation.

Step 3: (c) Rosenmund reduction An acyl chloride is hydrogenated using palladium supported on barium sulphate to obtain an aldehyde:

$$\mathrm{RCOCl}+\mathrm{H_2}\xrightarrow{\mathrm{Pd/BaSO_4}}\mathrm{RCHO}+\mathrm{HCl}.$$

The catalyst is poisoned to reduce its activity, preventing further reduction of the aldehyde to the primary alcohol. For example, benzoyl chloride gives benzaldehyde under these conditions.

Step 4: (d) Acidity of alpha-hydrogen atoms An α-hydrogen is attached to a carbon adjacent to the carbonyl carbon. Its removal as a proton produces an enolate ion whose negative charge is delocalised between the α-carbon and the electronegative oxygen atom. For an aldehyde:

$$\mathrm{R}-\mathrm{CH_2}-\mathrm{CHO}\rightleftharpoons\mathrm{R}-\mathrm{CH^-}-\mathrm{CHO}+\mathrm{H^+},$$

with resonance contributors

$$\mathrm{R}-\mathrm{CH^-}-\mathrm{CH}=\mathrm{O}\ \leftrightarrow\ \mathrm{R}-\mathrm{CH}=\mathrm{CH}-\mathrm{O^-}.$$

This resonance stabilisation, together with the electron-withdrawing effect of the carbonyl group, accounts for the acidity of the α-hydrogens in aldehydes and ketones.

Step 5: (e) Sodium hydrogen carbonate test Add aqueous $\mathrm{NaHCO_3}$ separately to the two samples. Benzoic acid produces brisk effervescence of carbon dioxide, whereas benzaldehyde does not produce effervescence:

$$\mathrm{C_6H_5COOH}+\mathrm{NaHCO_3}\longrightarrow\mathrm{C_6H_5COONa}+\mathrm{H_2O}+\mathrm{CO_2}\uparrow.$$

The evolved gas turns limewater milky. Benzaldehyde has no carboxylic acid group and does not liberate carbon dioxide from the reagent.

Step 6: Conclusion (a) The hydrazone is $\mathrm{C_6H_5CH}=\mathrm{N}-\mathrm{NHC_6H_3(NO_2)_2}$, with nitro groups at posi-

Quick Tip to Solve: For the hydrazone retain the aldehydic hydrogen; for the acid comparison compare conjugate-base stability, and use bicarbonate effervescence to identify COOH.

tions 2 and 4. (b) The p-CF_3-substituted acid is stronger. (c) $RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$. (d) The conjugate enolate is resonance stabilised. (e) Only benzoic acid gives CO_2 effervescence with aqueous $NaHCO_3$.

Quick Tip to Solve: For the hydrazone retain the aldehydic hydrogen; for the acid comparison compare conjugate-base stability, and use bicarbonate effervescence to identify COOH.

34(a). (i) Calculate the emf of the following cell at 298 K:

Al(s) | Al^{3+} (0.001 M) || Ni^{2+} (0.1 M) | Ni(s)

[Given: $E^\circ_{Al^{3+}/Al}$ = -1.66 V, $E^\circ_{Ni^{2+}/Ni}$ = -0.25 V, log 10 = 1]

(ii) With the help of a graph explain why it is not possible to determine Λ°_m for a weak electrolyte by extrapolating the molar conductivity (Λ_m) versus $C^{1/2}$ curve as for strong electrolyte. [5 marks]

Solution:

Concept:

- For a galvanic cell, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$. Electrode potentials are intensive quantities and are not multiplied when balancing the reaction.
- At 298 K, the Nernst equation is $E_{cell} = E^\circ_{cell} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient; pure solids have unit activity.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$. A weak electrolyte's degree of ionisation increases substantially on dilution, giving a curved plot of molar conductivity Λ_m against $\sqrt{C}$.

Step 1: (i) Balance the cell reaction and find the standard emf Aluminium is oxidised at the left electrode and nickel ions are reduced at the right electrode:

$$\begin{aligned} Al(s) &\longrightarrow Al^{3+}(aq) + 3e^- \\ Ni^{2+}(aq) + 2e^- &\longrightarrow Ni(s). \end{aligned}$$

Multiplying the oxidation by 2 and the reduction by 3 gives

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Ni(s), \qquad n = 6.$$

Thus $E^\circ_{cell} = (-0.25) - (-1.66) = 1.41\,V$.

Step 2: (i) Substitute the concentrations in the Nernst equation Using the stoichiometric powers from the balanced reaction,

$$Q = \frac{[Al^{3+}]^2}{[Ni^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = 10^{-3}, \qquad \log Q = -3.$$

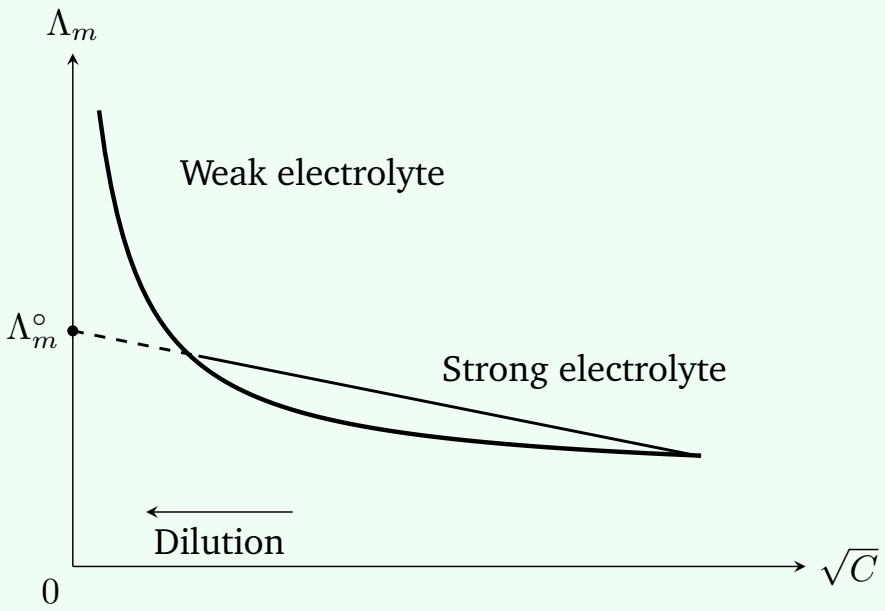
Therefore,

$$\begin{aligned} E_{cell} &= 1.41 - \frac{0.0591}{6}(-3) \\ &= 1.41 + 0.02955 = 1.43955\,V. \end{aligned}$$

Quick Tip to Solve: Balance the Al/Ni reaction first: six electrons determine the Nernst denominator, and the coefficients 2 and 3 determine the concentration powers.

The small reaction quotient makes the emf greater than the standard emf. Using $n = 3$ or omitting the stoichiometric powers would give an incorrect concentration correction.

Step 3: (ii) Compare the strong and weak electrolyte graphs The schematic below plots Λ_m against $\sqrt{C}$. For the strong electrolyte, the low-concentration points lie approximately on a straight line. Extending that line to $\sqrt{C} = 0$ gives a well-defined intercept, Λ_m°. For the weak electrolyte, dilution both reduces interionic effects and greatly increases ionisation. Hence Λ_m rises steeply and nonlinearly as $\sqrt{C}$ approaches zero. The measured curved portion cannot be extended linearly to obtain a reliable limiting intercept. The graph is qualitative; it compares the shapes, rather than numerical conductivities of particular substances.



Qualitative molar conductivity curves: the strong-electrolyte line can be extrapolated to zero concentration; the weak-electrolyte curve rises sharply on dilution.

Step 4: (ii) State how the limiting conductivity is obtained instead Kohlrausch's law of independent migration of ions is used to calculate the weak electrolyte's limiting molar conductivity from ionic contributions or known strong-electrolyte limiting conductivities. For example,

$$\Lambda_m^\circ(\mathrm{CH_3COOH}) = \Lambda_m^\circ(\mathrm{HCl}) + \Lambda_m^\circ(\mathrm{CH_3COONa}) - \Lambda_m^\circ(\mathrm{NaCl}).$$

The sodium and chloride contributions cancel, leaving those of hydrogen and acetate ions.

Step 5: Conclusion (i) The cell emf at 298 K is $\boxed{1.440\,\mathrm{V\ (approximately)}}$. (ii) A weak electrolyte gives a strongly curved Λ_m versus $\sqrt{C}$ plot because its ionisation increases on dilution, so straight-line extrapolation cannot determine Λ_m°; use Kohlrausch's law instead.

Quick Tip to Solve: Balance the Al/Ni reaction first: six electrons determine the Nernst denominator, and the coefficients 2 and 3 determine the concentration powers.

OR

34(b). (i) The molar conductivities of NH_4^+ and Cl^- ion are 73.8 S cm^2 mol^{-1} and 76.2 S cm^2 mol^{-1} respectively. The conductivity of 0.1 M NH_4Cl is 1.29 $\times$ 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation.

(ii) Calculate the half-cell potential at 298 K for the reaction Zn^{2+} + 2e$^-$ $\rightarrow$ Zn if [Zn^{2+}] = 0.1 M and $E^\circ_{Zn^{2+}/Zn}$ = -0.76 V. [5 marks]

Solution:

Concept:

- Conductivity κ measures conduction per unit length and cross-sectional area. The molar conductivity is $\Lambda_m = 1000\kappa/C$ when κ is in S cm^{-1} and concentration C is in mol L^{-1}; its unit is S cm^2 mol^{-1}.
- Kohlrausch's law of independent migration of ions gives $\Lambda_m^\circ = \lambda^\circ_{NH_4^+} + \lambda^\circ_{Cl^-}$ for the 1:1 electrolyte NH_4Cl. The conductivity-ratio estimate requested for the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- For a reduction half-reaction, the Nernst equation at 298 K is $E = E^\circ - (0.0591/n)\log Q$, with n the number of electrons and Q the reaction quotient. A pure solid has unit activity; dilute ion activity is approximated by its molar concentration relative to the standard concentration.

Step 1: (i) Calculate the molar conductivity The given conductivity is $\kappa = 1.29 \times 10^{-2}$ S cm^{-1} and the concentration is $C = 0.1$ mol L^{-1}. The factor 1000 converts the volume from litres to cubic centimetres, so that the concentration and conductivity use compatible length units. Substituting gives

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{C}\\ &= \frac{1000(1.29\times10^{-2})}{0.1}\\ &= 129\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

Step 2: (i) Obtain the limiting conductivity and the requested degree of dissociation Each formula unit supplies one ammonium ion and one chloride ion, so their limiting ionic conductivities are added without additional stoichiometric factors:

$$\Lambda_m^\circ = 73.8 + 76.2 = 150.0\,\text{S cm}^2\,\text{mol}^{-1}.$$

Using the conductivity-ratio method specified by the numerical data,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{129}{150} = 0.86, \qquad 100\alpha = 86\%.$$

The ratio is dimensionless because both conductivities have identical units. Strictly, ammonium chloride is a strong electrolyte: the lower molar conductivity at finite concentration also reflects interionic effects on mobility. Thus 0.86 is the apparent degree obtained from the prescribed ratio, rather than proof that exactly 14% of its formula units remain undissociated.

Quick Tip to Solve: Add the two ionic conductivities before finding the ratio; for zinc reduction use $Q = 1/[Zn^{2+}]$, so a tenfold dilution lowers E by $0.0591/2$ V.

Step 3: (ii) Set up the reaction quotient for zinc reduction The printed half-reaction is

$$\mathrm{Zn}^{2+} + 2e^- \longrightarrow \mathrm{Zn}(s).$$

Hence $n = 2$. Electrons are not included in the reaction quotient, and the activity of solid zinc is unity. Therefore

$$Q = \frac{1}{[\mathrm{Zn}^{2+}]} = \frac{1}{0.1} = 10.$$

Here the concentration in the quotient is understood relative to $1\,\mathrm{mol\,L^{-1}}$, making Q dimensionless. Use the supplied standard reduction potential directly, since the reaction is written as a reduction.

Step 4: (ii) Substitute in the Nernst equation With $E^\circ = -0.76\,\mathrm{V}$, the half-cell potential becomes

$$\begin{aligned} E &= -0.76 - \frac{0.0591}{2}\log 10 \\ &= -0.76 - 0.02955 \\ &= -0.78955\,\mathrm{V} \simeq -0.790\,\mathrm{V}. \end{aligned}$$

Equivalently, $E = E^\circ + (0.0591/2)\log[\mathrm{Zn}^{2+}]$, and $\log 0.1 = -1$ gives the same sign. Lowering the concentration of the reactant zinc ions below its standard value makes their reduction less favourable, consistent with the potential becoming more negative.

Step 5: Conclusion (i) The molar conductivity is $\boxed{129\,\mathrm{S\,cm^2\,mol^{-1}}}$, and the requested conductivity-ratio degree of dissociation is $\boxed{\alpha = 0.86 = 86\%}$. (ii) The zinc reduction half-cell potential at 298 K is $\boxed{E = -0.78955\,\mathrm{V} \simeq -0.790\,\mathrm{V}}$.

Quick Tip to Solve: Add the two ionic conductivities before finding the ratio; for zinc reduction use $Q = 1/[\mathrm{Zn}^{2+}]$, so a tenfold dilution lowers E by $0.0591/2\,\mathrm{V}$.

35(a). (i) Account for the following:

(1) Zn^{2+} salts are colourless while Ni^{2+} salts are coloured.

(2) Cr^{2+} is a strong reducing agent.

(3) Transition metals and their compounds show catalytic activities.

(ii) Write the ionic equations for the oxidizing action of MnO_4^- in acidic medium with

(1) I^- ion, and

(2) Fe^{2+} ion. [5 marks]

Solution:

Concept:

- The colour of many transition-metal ions arises from absorption of visible light for electronic transitions between split d orbitals. A completely filled d^{10} subshell cannot undergo such d-d transitions.
- A reducing agent loses electrons and is oxidised. Formation of a more stable oxidation state favours this electron loss.

Quick Tip to Solve: Start both permanganate equations with its five-electron acidic half-reaction; use 10 iodide ions for two permanganate ions, or 5 iron(II) ions for one.

- Transition-metal catalysts can provide an alternative reaction pathway through intermediate compounds and variable oxidation states; metal surfaces can also adsorb reactants.
- In acidic medium, permanganate is reduced from Mn(VII) to Mn(II):

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

Balance both atoms and total charge when combining half-reactions.

Step 1: (i)(1) Explain the different colours of zinc(II) and nickel(II) salts Zinc has the electronic configuration $[\mathrm{Ar}]3d^{10}4s^2$, so $\mathrm{Zn^{2+}}$ has $[\mathrm{Ar}]3d^{10}$. Its d subshell is completely filled, leaving no vacant d orbital for a d-d transition. Hence its salts are colourless. Nickel has $[\mathrm{Ar}]3d^8 4s^2$, and $\mathrm{Ni^{2+}}$ has $[\mathrm{Ar}]3d^8$. In a ligand field, its partially filled d orbitals split into levels of different energy. Absorption of visible light promotes electrons between these levels, so the transmitted light is coloured.

Step 2: (i)(2) Explain the reducing power of chromium(II) The configuration of $\mathrm{Cr^{2+}}$ is $[\mathrm{Ar}]3d^4$. It readily loses an electron to form $\mathrm{Cr^{3+}}$, with configuration $[\mathrm{Ar}]3d^3$:

$$\mathrm{Cr^{2+} \rightarrow Cr^{3+} + e^-}.$$

The d^3 configuration is especially stable in the usual octahedral environment, because the three lower-energy t_{2g} orbitals are singly occupied. Thus oxidation to Cr(III) is favoured, and Cr(II) supplies electrons to other substances, acting as a strong reducing agent.

Step 3: (i)(3) Explain catalytic activity Transition metals and their compounds show variable oxidation states. They can form intermediate compounds with reactants, transfer electrons during the reaction and regenerate the catalyst at the end. This provides a pathway with lower activation energy. Finely divided transition metals also offer a large surface on which reactants are adsorbed; adsorption brings reacting species together and can weaken their bonds, facilitating reaction.

Step 4: (ii)(1) Balance oxidation of iodide in acidic medium Iodide loses electrons to form iodine, while permanganate gains electrons to form manganese(II):

$$\mathrm{2I^- \rightarrow I_2 + 2e^-},$$
$$\mathrm{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O}.$$

Multiply the iodide half-reaction by 5 and the permanganate half-reaction by 2, then cancel the ten electrons. This yields the balanced ionic equation:

$$\boxed{\mathrm{2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2}}.$$

Both sides have a total charge of $+4$, and all Mn, O, H and I atoms are conserved.

Step 5: (ii)(2) Balance oxidation of iron(II) in acidic medium Each iron(II) ion loses one electron: $\mathrm{Fe^{2+} \rightarrow Fe^{3+} + e^-}$. One permanganate ion accepts five electrons, so five iron(II) ions are required. Adding five times this iron half-reaction to the permanganate reduction half-reaction gives:

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

The total charge is $+17$ on each side. Oxygen is balanced with four water molecules and hydrogen

Quick Tip to Solve: Start both permanganate equations with its five-electron acidic half-reaction; use 10 iodide ions for two permanganate ions, or 5 iron(II) ions for one.

with eight hydrogen ions, as required for acidic medium.

Step 6: Conclusion Zn^{2+} is colourless because it is d^{10}, whereas Ni^{2+} is coloured because it is d^8 and permits d-d transitions. Cr^{2+} readily forms stable Cr^{3+}; transition metals catalyse reactions through variable oxidation states, intermediates and adsorption. Acidic permanganate oxidises I^- to I_2 and Fe^{2+} to Fe^{3+}, according to the balanced equations above.

Quick Tip to Solve: Start both permanganate equations with its five-electron acidic half-reaction; use 10 iodide ions for two permanganate ions, or 5 iron(II) ions for one.

OR

35(b). (i) Name two oxometal anions of the 3d series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

(ii) What is the effect of increasing pH on a solution of $K_2Cr_2O_7$?

(iii) Why is Cu^+ not stable in aqueous solution?

(iv) Name a member of Lanthanoid series which is well-known to exhibit +4 oxidation state.

(v) Name two elements of 3d series which show anomalous electronic configuration. [5 marks]

Solution:

Concept:

- In an oxometal anion, oxygen has oxidation state -2; the sum of all oxidation states equals the ionic charge. The highest oxidation states of chromium and manganese equal their group numbers, 6 and 7 respectively.
- Chromate and dichromate ions are linked by an acid-base equilibrium. Increasing pH reduces H^+ concentration and favours the chromate form.
- Stability of aqueous metal ions depends on hydration as well as electronic configuration. A half-filled d^5 or fully filled d^{10} subshell gives additional stability to the atomic ground state.

Step 1: (i) Identify the two oxometal anions Chromate, CrO_4^{2-}, and permanganate, MnO_4^-, are suitable examples. If x is the oxidation state of the metal, then

$$\begin{aligned} CrO_4^{2-}: &\quad x + 4(-2) = -2 \Rightarrow x = +6, \\ MnO_4^-: &\quad x + 4(-2) = -1 \Rightarrow x = +7. \end{aligned}$$

Chromium belongs to group 6 and manganese to group 7. Thus, each metal has the required oxidation state equal to its group number.

Step 2: (ii) Explain the effect of increasing pH A potassium dichromate solution is orange because it contains $Cr_2O_7^{2-}$ ions. The relevant equilibrium is

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

Increasing pH removes H^+ from solution, so the equilibrium shifts to the right. Orange dichromate is converted into yellow chromate; the solution becomes yellow. In alkaline medium this can also be

Quick Tip to Solve: For these five facts, pair Cr with group 6 and Mn with group 7, remember that alkali makes chromate yellow, and write the actual Cr and Cu configurations before naming the exceptions.

written as

$$\mathrm{Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O}.$$

Step 3: (iii) Explain why aqueous copper(I) is unstable Although $\mathrm{Cu^+}$ has a filled $3d^{10}$ subshell, $\mathrm{Cu^{2+}}$ has a much more negative hydration enthalpy. This greater stabilisation by water compensates for the energy required to form $\mathrm{Cu^{2+}}$. Hence aqueous $\mathrm{Cu^+}$ disproportionates:

$$\mathrm{2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)}.$$

One copper(I) ion is oxidised to copper(II), while the other is reduced to copper metal.

Step 4: (iv) Name the lanthanoid exhibiting the +4 state Cerium, Ce, is well known to exhibit the $+4$ oxidation state. Formation of $\mathrm{Ce^{4+}}$ gives the stable noble-gas configuration $[\mathrm{Xe}]$, with an empty $4f$ subshell.

Step 5: (v) Name the elements with anomalous configurations Chromium and copper have anomalous ground-state electronic configurations:

$$\begin{aligned} \mathrm{Cr}: &\quad [\mathrm{Ar}]\,3d^5\,4s^1, \\ \mathrm{Cu}: &\quad [\mathrm{Ar}]\,3d^{10}\,4s^1. \end{aligned}$$

These differ from the simple filling-order predictions $[\mathrm{Ar}]\,3d^4\,4s^2$ and $[\mathrm{Ar}]\,3d^9\,4s^2$, respectively. The closely spaced $3d$ and $4s$ levels allow a half-filled or fully filled $3d$ subshell to be favoured.

Step 6: Conclusion (i) Chromate and permanganate; (ii) orange dichromate changes to yellow chromate on increasing pH; (iii) $\mathrm{Cu^+}$ disproportionates because hydration stabilises $\mathrm{Cu^{2+}}$; (iv) cerium; (v) chromium and copper.

Quick Tip to Solve: For these five facts, pair Cr with group 6 and Mn with group 7, remember that alkali makes chromate yellow, and write the actual Cr and Cu configurations before naming the exceptions.