

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-4-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **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 tetramerization in a given organic solvent. The Van't Hoff factor 'i' is: [1 mark]

- (A) 4.0
- (B) 0.25
- (C) 0.125
- (D) 2.0

Correct Answer: (B) 0.25

Solution:

Concept:

- Complete association combines four solute molecules into one tetramer. The van't Hoff factor is the ratio of the actual number of solute particles to the number before association.
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Count the particles If initially there are N molecules, complete tetramerization gives $N/4$ tetramers. No unassociated molecules remain; each tetramer behaves as one dissolved particle.

Step 2: Calculate the factor Therefore $i = (N/4)/N = 1/4 = 0.25$. The value 4.0 would describe an increase to four particles per formula unit; association instead decreases the particle count. Values 0.125 and 2.0 correspond to different particle ratios and cannot describe tetramerization.

Step 3: Conclusion $i = 0.25$. Hence, the correct option is (B).

Quick Tip to Solve: For complete association into an n-mer, divide the initial particle count by n: $i = 1/n$.

2. The half-life for a zero order reaction equals (where R is the initial concentration): [1 mark]

- (A) $\frac{2k}{R}$
- (B) $\frac{1k}{2R^2}$
- (C) $\frac{R^2}{2k}$
- (D) $\frac{R}{2k}$

Correct Answer: (D) $\frac{R}{2k}$

Solution:

Concept:

- For a zero-order reaction, $[R]_t = R - kt$, where R is the initial reactant concentration and k is the rate constant. Half-life is the time for concentration to become $R/2$.
- Determine the answer from the stated conditions and compare it with all four printed options.

Quick Tip to Solve: Set the remaining concentration equal to half its initial value in the zero-order integrated law.

Step 1: Apply the half-life condition Substitute $[R]_t = R/2$ and $t = t_{1/2}$ in the integrated rate law:

$$R/2 = R - kt_{1/2}.$$

Thus the amount consumed by the half-life is half the initial concentration.

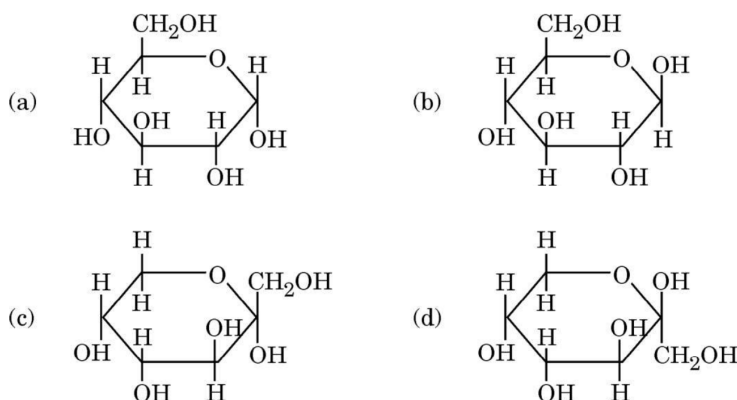
Step 2: Rearrange and check the alternatives Rearranging gives $kt_{1/2} = R/2$, so $t_{1/2} = R/(2k)$. Since a zero-order rate constant has units of concentration per time, R/k has units of time. Option (A) has inverse-time units, and (B) has units of inverse concentration times inverse time; neither is a time. Option (C) has concentration-times-time units and incorrectly squares the initial concentration.

Step 3: Conclusion $t_{1/2} = \frac{R}{2k}$. Hence, the correct option is (D).

Quick Tip to Solve: Set the remaining concentration equal to half its initial value in the zero-order integrated law.

3. Which of the following structures represents α -D-glucose?

[1 mark]



(A) Structure (a)

(B) Structure (b)

(C) Structure (c)

(D) Structure (d)

Correct Answer: (A) Structure (a)

Solution:

Concept:

- In the usual Haworth representation of D-glucopyranose, the CH₂OH group at C5 lies above the ring. The alpha anomer has the anomeric hydroxyl at C1 on the opposite side from this group.
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Identify the glucose skeleton In structures (a) and (b), the ring carbon next to oxygen on the right is C1, with a hydrogen and a hydroxyl group attached. The CH₂OH substituent is attached at C5 above the ring. The C2, C3 and C4 hydroxyl arrangement matches D-glucose. Structures (c) and (d) have a different substituent arrangement and are not the required glucopyranose structure.

Quick Tip to Solve: For a D-glucose Haworth ring, locate the C1 hydroxyl: down is alpha when the C5 CH₂OH group is up.

Step 2: Distinguish alpha from beta In structure (a), the C1 hydroxyl points down while the C5 CH₂OH group points up: they are trans, so this is alpha-D-glucose. In (b), both groups point up, making it the beta anomer. Merely seeing a six-membered ring is insufficient; the anomeric hydroxyl orientation decides between (a) and (b).

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

Quick Tip to Solve: For a D-glucose Haworth ring, locate the C1 hydroxyl: down is alpha when the C5 CH₂OH group is up.

4. The ions of metals of Group 12 (Zn, Cd and Hg) have completely filled d orbitals and so they:

[1 mark]

- (A) behave like semiconductors
- (B) are very high melting solids
- (C) do not behave like transition metals
- (D) behave like superconductors

Correct Answer: (C) do not behave like transition metals

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its characteristic ions. A completely filled d subshell has configuration d^{10} .
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Apply the electronic criterion Zn, Cd and Hg have filled d subshells, and their usual divalent ions retain d^{10} configurations. For example, zinc loses its two 4s electrons to form Zn^{2+} , leaving $3d^{10}$. There is no partially occupied d subshell in this ion.

Step 2: Assess the stated consequences They therefore do not show the characteristic transition-metal behaviour associated with partially filled d orbitals. Filled d orbitals do not imply semiconductor or superconductor behaviour, so (A) and (D) do not follow. Nor do they imply very high melting points: mercury is liquid at ordinary room temperature, excluding (B).

Step 3: Conclusion They do not behave like transition metals. Hence, the correct option is (C).

Quick Tip to Solve: Check whether the atom or characteristic ion has an incomplete d subshell before calling it a transition element.

5. $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$ exhibit:

[1 mark]

- (A) linkage isomerism
- (B) ionization isomerism
- (C) optical isomerism
- (D) coordination isomerism

Correct Answer: (B) ionization isomerism

Solution:

Concept:

- Ionization isomerism occurs when a ligand inside the coordination sphere exchanges places with a counter-ion outside it. The resulting compounds release different ions on dissolution.
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Compare the coordination spheres In $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$, nitrate is coordinated to cobalt and sulfate is the counter-ion. In $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$, sulfate is coordinated and nitrate is the counter-ion. Thus these two anions exchange their positions across the square brackets.

Step 2: Identify the isomerism and exclude alternatives The first compound releases sulfate ions, whereas the second releases nitrate ions. This difference identifies ionization isomerism. Linkage isomerism changes the donor atom of the same ligand; optical isomerism concerns non-superimposable mirror images; coordination isomerism exchanges ligands between complex cations and complex anions. None describes this ligand-counter-ion exchange.

Step 3: Conclusion The compounds exhibit ionization isomerism. Hence, the correct option is (B).

Quick Tip to Solve: Compare what lies inside and outside the square brackets: swapping a ligand with a counter-ion gives ionization isomers.

6. 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 favours beta-elimination (dehydrohalogenation) of a haloalkane. A beta hydrogen and the halogen are removed from adjacent carbon atoms, creating a carbon-carbon double bond.
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Identify the possible eliminations The substrate is $\text{C}_6\text{H}_5\text{CH}_2\text{CHClCH}_3$. Removing a beta hydrogen from the benzylic CH_2 group gives $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$, while removal from the terminal methyl group gives $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2$. These correspond to 1-phenylpropene and 3-phenylpropene

Quick Tip to Solve: List both beta-elimination products, then favour the alkene conjugated with the phenyl ring.

respectively.

Step 2: Choose the major product The double bond in $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3$ is conjugated with the benzene ring and is more substituted, making this alkene more stable. It is therefore the major elimination product. The terminal alkene is less favoured. The alcohol options would require substitution rather than the elimination favoured by alcoholic KOH.

Step 3: Conclusion The major product is 1-phenylpropene. Hence, the correct option is (A).

Quick Tip to Solve: List both beta-elimination products, then favour the alkene conjugated with the phenyl ring.

7. When diethyl ether is heated with excess of HI, it produces:

[1 mark]

- (A) ethanol
- (B) iodoform
- (C) methyl iodide
- (D) ethyl iodide

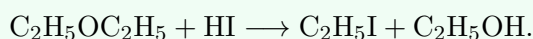
Correct Answer: (D) ethyl iodide

Solution:

Concept:

- HI cleaves ethers after protonation of the ether oxygen. For a primary alkyl ether, iodide attacks an alkyl carbon to form an alkyl iodide and an alcohol. Excess hot HI further converts the alcohol into an alkyl iodide.
- Determine the answer from the stated conditions and compare it with all four printed options.

Step 1: Write the initial cleavage Diethyl ether has two identical ethyl groups, so the first cleavage yields ethyl iodide and ethanol:



Thus ethanol is an intermediate product when only the initial cleavage is considered.

Step 2: Use the excess HI condition The ethanol then reacts with additional HI:



Overall, one mole of ether consumes two moles of HI to form two moles of ethyl iodide and water. Ethanol does not remain as the principal organic product under excess hot HI. Methyl iodide would require a methyl group, and iodoform is not formed by this acid cleavage.

Step 3: Conclusion The organic product is ethyl iodide. Hence, the correct option is (D).

Quick Tip to Solve: With excess hot HI, continue past ether cleavage: convert the alcohol intermediate to the corresponding alkyl iodide.

8. The reduction of ethanenitrile with sodium and alcohol gives:

[1 mark]

- (A) 1-aminopropane
- (B) 1-aminoethane
- (C) Ethanoic acid
- (D) Ethanamide

Correct Answer: (B) 1-aminoethane

Solution:

Concept:

- Reduction of a nitrile converts its $-C \equiv N$ group into $-CH_2NH_2$.
- The carbon atom of the nitrile group remains in the product; sodium and alcohol provide reducing conditions.

Step 1: Identify the starting carbon skeleton Ethanenitrile is CH_3CN , which contains two carbon atoms, including the nitrile carbon. Reduction does not add another carbon atom, so the resulting amine must also have two carbon atoms.

Step 2: Apply nitrile reduction The conversion is



The product is a primary amine. 1-Aminopropane has three carbons and cannot arise here. Ethanoic acid and ethanamide are hydrolysis products under suitable conditions, rather than the product of this reduction.

Step 3: Conclusion The product is 1-aminoethane (ethylamine). Hence, the correct option is (B).

Quick Tip to Solve: Count the nitrile carbon as part of the chain before naming the reduced amine.

9. How many Faradays are required to reduce 1 mol of MnO_4^- to Mn^{2+} ?

[1 mark]

- (A) 4
- (B) 3
- (C) 6
- (D) 5

Correct Answer: (D) 5

Solution:

Concept:

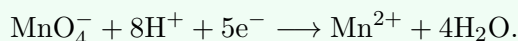
- One Faraday is the charge carried by one mole of electrons.
- The electron requirement for reduction equals the decrease in oxidation number per atom.

Step 1: Determine the oxidation numbers In MnO_4^- , oxygen has oxidation number -2 . Thus $x + 4(-2) = -1$, giving manganese oxidation number $+7$. In Mn^{2+} , its oxidation number is $+2$.

Step 2: Count the required electrons Each manganese atom gains $7 - 2 = 5$ electrons. In acidic

Quick Tip to Solve: For one mole of ions, subtract final oxidation number from initial oxidation number.

medium the balanced half-reaction is



Hence one mole of permanganate accepts five moles of electrons. The values 4, 3 and 6 do not equal the oxidation-number change and are excluded.

Step 3: Conclusion The charge required is $5F$, or five Faradays. Hence, the correct option is (D).

Quick Tip to Solve: For one mole of ions, subtract final oxidation number from initial oxidation number.

10. In a reaction, the initial concentration of the reactants increases four fold and the rate becomes sixteen times its initial value. The order of the reaction is: [1 mark]

- (A) 2.0
- (B) 3.5
- (C) 1.5
- (D) 2.5

Correct Answer: (A) 2.0

Solution:

Concept:

- For overall order n , multiplying all reactant concentrations by a factor a multiplies the rate by a^n .
- The rate constant remains unchanged when the reaction conditions, including temperature, remain fixed.

Step 1: Form the rate ratio Let the initial rate be r_1 and the new rate be r_2 . The concentrations increase by a factor of four, while the rate becomes sixteen times the original value. Therefore

$$\frac{r_2}{r_1} = 4^n = 16.$$

Step 2: Determine and check the exponent Since $16 = 4^2$, comparison of exponents gives $n = 2$. The alternatives give $4^{3.5} = 128$, $4^{1.5} = 8$, and $4^{2.5} = 32$. None matches the stated sixteen-fold rate increase.

Step 3: Conclusion The order of the reaction is 2.0. Hence, the correct option is (A).

Quick Tip to Solve: Express the rate multiplier as a power of the concentration multiplier to read off order.

11. On hydrolysis, which of the following carbohydrates gives only glucose?

[1 mark]

- (A) Maltose
- (B) Sucrose
- (C) Lactose
- (D) Galactose

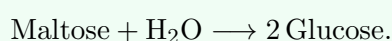
Correct Answer: (A) Maltose

Solution:

Concept:

- Hydrolysis breaks a disaccharide glycosidic bond and releases its constituent monosaccharides.
- Maltose contains two glucose units; sucrose and lactose contain two different monosaccharides.

Step 1: Identify the glucose-only disaccharide Maltose consists of two glucose units linked by a glycosidic bond. Hydrolysis yields



Both released monosaccharide units are therefore glucose.

Step 2: Compare the other options Sucrose gives glucose and fructose, so its products are not exclusively glucose. Lactose gives glucose and galactose, again a mixed pair. Galactose is itself a monosaccharide and cannot be hydrolysed into simpler carbohydrate units to yield glucose. Thus only maltose meets the condition.

Step 3: Conclusion Maltose gives only glucose on hydrolysis. Hence, the correct option is (A).

Quick Tip to Solve: Remember the pairs: maltose glucose-glucose, sucrose glucose-fructose, lactose glucose-galactose.

12. Deficiency of which of the following vitamins causes Pernicious anaemia?

[1 mark]

- (A) Vitamin B₁
- (B) Vitamin B₂
- (C) Vitamin B₆
- (D) Vitamin B₁₂

Correct Answer: (D) Vitamin B₁₂

Solution:

Concept:

- Vitamin B₁₂ is associated with normal red blood cell formation.
- The standard vitamin-deficiency association for pernicious anaemia is vitamin B₁₂.

Step 1: Use the stated deficiency association Pernicious anaemia is associated with deficiency of vitamin B₁₂, also called cobalamin. In this condition inadequate availability of the vitamin disrupts normal development of red blood cells.

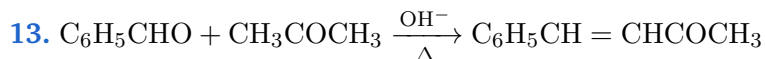
Step 2: Eliminate the other vitamin choices Vitamin B₁ deficiency is associated with beriberi. Vitamin

Quick Tip to Solve: Link the name pernicious anaemia specifically with cobalamin, vitamin B₁₂.

B_2 deficiency is associated with cheilosis and digestive disorders. Vitamin B_6 deficiency is associated with convulsions and other deficiency effects. These are different textbook associations and do not identify the vitamin asked for here.

Step 3: Conclusion The vitamin is B_{12} . Hence, the correct option is (D).

Quick Tip to Solve: Link the name pernicious anaemia specifically with cobalamin, vitamin B12.



This reaction is known as:

[1 mark]

- (A) Aldol condensation
- (B) Cross-Aldol condensation
- (C) Cannizzaro's reaction
- (D) Friedel-Crafts reaction

Correct Answer: (B) Cross-Aldol condensation

Solution:

Concept:

- A cross-aldol condensation involves two different aldehydes or ketones, with at least one possessing an α -hydrogen.
- An aldol addition product loses water on heating to form an α, β -unsaturated carbonyl compound.

Step 1: Identify the reacting carbonyl compounds The reactants are benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, and acetone, CH_3COCH_3 . Acetone has α -hydrogens and forms an enolate under basic conditions; benzaldehyde has no α -hydrogen.

Step 2: Classify the condensation The acetone enolate adds to benzaldehyde. The resulting hydroxy ketone loses water on heating to form $\text{C}_6\text{H}_5\text{CH} = \text{CHCOCH}_3$. Since two different carbonyl compounds participate, cross-aldol condensation is the specific name. Option (A) names the general family but omits the distinguishing cross reaction. Cannizzaro involves disproportionation, and Friedel-Crafts involves electrophilic aromatic substitution; neither gives the transformation shown.

Step 3: Conclusion This is cross-aldol condensation. Hence, the correct option is (B).

Quick Tip to Solve: Two different carbonyl reactants plus an unsaturated carbonyl product indicate cross-aldol condensation.

14. In which of the following does the central atom exhibit an oxidation state of +3?

[1 mark]

- (A) $\text{K}_2[\text{Ni}(\text{CN})_4]$
- (B) $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (C) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (D) $[\text{Cu}(\text{NH}_3)_4]^{2+}$

Correct Answer: (C) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

Solution:

Concept:

- The sum of metal oxidation number and ligand charges equals the charge on the complex ion.
- CN^- has charge -1 , oxalate $\text{C}_2\text{O}_4^{2-}$ has charge -2 , and ammonia is neutral.

Step 1: Check the cyanide complexes For $\text{K}_2[\text{Ni}(\text{CN})_4]$, the complex has charge -2 : $x - 4 = -2$, so nickel is $+2$. For $\text{K}_4[\text{Fe}(\text{CN})_6]$, the complex has charge -4 : $x - 6 = -4$, so iron is $+2$. Neither satisfies the required $+3$ state.

Step 2: Check oxalate and ammonia complexes For $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, three oxalate ligands contribute -6 , so $x - 6 = -3$, giving iron $+3$. For $[\text{Cu}(\text{NH}_3)_4]^{2+}$, all ligands are neutral, so copper is $+2$. The oxalate complex alone has its central atom in the specified oxidation state.

Step 3: Conclusion Iron is $+3$ in $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$. Hence, the correct option is (C).

Quick Tip to Solve: Use the charge of the complex ion, excluding counterions, when summing ligand charges.

15. Assertion (A): When NaCl is added to water, a depression in freezing point is observed.

Reason (R): The lowering of vapour pressure of a solution causes depression in the freezing 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:

- Depression in freezing point is a colligative property: $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality.
- A solution freezes when the chemical potential of its solvent equals that of the solid solvent. Dissolved non-volatile solute lowers the solvent vapour pressure.

Quick Tip to Solve: For freezing-point A-R questions, link lower solvent vapour pressure to a lower ice-solution equilibrium temperature.

Step 1: Judge the assertion NaCl dissolves in water to give Na^+ and Cl^- ions. These dissolved particles lower the freezing temperature below that of pure water. Thus Assertion (A) is true.

Step 2: Judge the reason Adding a non-volatile solute lowers the vapour pressure of liquid water at a given temperature. The solution reaches equilibrium with ice at a lower temperature than pure water does. Therefore Reason (R) is true.

Step 3: Check the explanatory link The lowered vapour pressure reflects the lowered chemical potential of water in the solution. Cooling further is necessary to establish solid-liquid equilibrium, which explains the observed depression. Option (B) wrongly denies this link, while (C) and (D) wrongly reject a true statement.

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 freezing-point A-R questions, link lower solvent vapour pressure to a lower ice-solution equilibrium temperature.

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

Reason (R): For weak electrolytes, degree of dissociation increases 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Molar conductivity Λ_m measures conductivity per mole of electrolyte; $\Lambda_m = \kappa \times 1000/c$ for c in mol L^{-1} and κ in S cm^{-1} .
- For a weak electrolyte, the degree of dissociation α increases on dilution, and approximately $\Lambda_m = \alpha \Lambda_m^\circ$, where Λ_m° is the limiting molar conductivity.

Step 1: Judge the assertion Weak electrolytes show a sharp increase, not a decrease, in molar conductivity when diluted. The number of ions produced per mole of electrolyte increases markedly. Hence Assertion (A) is false.

Step 2: Judge the reason Dilution favours the dissociation of a weak electrolyte into ions. Its degree of dissociation therefore increases as concentration decreases. Reason (R) is true.

Step 3: Select the matching code The reason explains why the direction of change stated in A is wrong: increasing α increases Λ_m . Options (A) and (B) require a true assertion; option (C) requires a false reason. None matches the actual truth values.

Quick Tip to Solve: Distinguish molar conductivity from conductivity: dilution lowers conductivity but raises the molar conductivity of a weak electrolyte.

Step 4: Conclusion A is false and R is true. Hence, the correct option is (D).

Quick Tip to Solve: Distinguish molar conductivity from conductivity: dilution lowers conductivity but raises the molar conductivity of a weak electrolyte.

17. Assertion (A): Zr and Hf have almost identical radii.

Reason (R): Both Zr and Hf exhibit similar properties.

[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:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids, caused by the poor shielding of increasing nuclear charge by $4f$ electrons.
- Elements of the same group often have similar chemistry because of their similar valence electronic configurations.

Step 1: Judge the assertion Zr and Hf have almost identical radii. Although Hf lies below Zr, the lanthanoid contraction preceding Hf largely offsets the increase in radius expected from an additional shell. Assertion (A) is true.

Step 2: Judge the reason Zr and Hf are both group 4 elements and commonly show the +4 oxidation state. Their nearly equal sizes and similar valence configurations give them closely similar properties. Reason (R) is true.

Step 3: Check the direction of explanation Similar properties do not cause the equality of their radii. The cause is lanthanoid contraction; similarity of properties is a consequence of their related size and electronic structure. Thus (A) incorrectly claims an explanatory link, while (C) and (D) incorrectly call one statement false.

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

Quick Tip to Solve: For the Zr-Hf size comparison, identify lanthanoid contraction as the cause; similar chemistry is a consequence.

18. 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 $-\text{NH}_2$ group strongly activates the benzene ring through resonance donation of its nitrogen lone pair.
- Acetylation converts $-\text{NH}_2$ into $-\text{NHCOCH}_3$; delocalisation of the lone pair towards the carbonyl reduces its donation to the ring.

Step 1: Judge the assertion Aniline reacts with bromine water readily to form 2,4,6-tribromoaniline. Protecting its amino group as acetanilide permits controlled monobromination, chiefly at the para position, followed by hydrolysis to obtain p-bromoaniline. Thus A is true.

Step 2: Judge the reason In acetanilide the nitrogen lone pair is shared with the carbonyl group as well as the ring. The acetamido group consequently activates the ring less strongly than the free amino group. Therefore R is true.

Step 3: Check the explanatory link This reduced activation prevents the easy multiple bromination characteristic of unprotected aniline. Acetylation is therefore the reason monobromination can be achieved conveniently. (B) wrongly denies the explanation, and (C) and (D) wrongly reject a true statement.

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 selective bromination of aniline, use acetylation, bromination and then hydrolysis in that order.

Section B (14 marks)

19. 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:

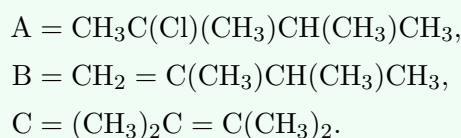
- Alcoholic KOH promotes β -elimination: a hydrogen on a carbon adjacent to the carbon bearing chlorine is removed along with chlorine, forming a double bond.
- Catalytic hydrogenation adds H_2 across a double bond without changing the carbon skeleton.

Step 1: Recover the common carbon skeleton The hydrogenation product is 2,3-dimethylbutane, $CH_3CH(CH_3)CH(CH_3)CH_3$. Both alkenes must retain this branched six-carbon skeleton. The double bond can occupy a terminal position or the position between the two central carbons.

Step 2: Locate chlorine in the alkyl halide To produce both positions by elimination, chlorine must be on a central carbon, so $A = CH_3C(Cl)(CH_3)CH(CH_3)CH_3$, named 2-chloro-2,3-dimethylbutane. Its formula is $C_6H_{13}Cl$. A terminal chloride would provide only the terminal alkene.

Step 3: Form and verify the two alkenes Removal of a hydrogen from either equivalent methyl group adjacent to the chlorine-bearing carbon gives $B = CH_2 = C(CH_3)CH(CH_3)CH_3$, 2,3-dimethylbut-1-ene. Removal from the adjacent central carbon gives $C = (CH_3)_2C = C(CH_3)_2$, 2,3-dimethylbut-2-ene. Both have formula C_6H_{12} ; adding one molecule of hydrogen to either restores 2,3-dimethylbutane.

Step 4: Conclusion The required structures are



The labels B and C may be interchanged.

Quick Tip to Solve: Work backwards from the hydrogenation product: retain its carbon skeleton and place chlorine where two distinct beta-eliminations are possible.

20(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 solution gives $p_i = x_i p_i^\circ$, where p_i is the partial vapour pressure, x_i its liquid mole fraction and p_i° the pure-component vapour pressure.
- Positive deviation occurs when unlike-component attractions are weaker overall than the attractions in the pure liquids, so molecules escape into the vapour more easily.

Quick Tip to Solve: When acetone is mixed with ethanol, track the disrupted ethanol hydrogen bonds: weaker overall attraction means higher vapour pressure.

Step 1: Compare the molecular interactions Pure ethanol molecules form an extensive network of intermolecular hydrogen bonds through their hydroxyl groups. When acetone is added, its molecules enter between ethanol molecules and disrupt some ethanol-ethanol hydrogen bonds. The resulting ethanol-acetone interactions do not compensate fully for the original attractions.

Step 2: Relate the interaction change to vapour pressure Because the overall intermolecular attractions become weaker, the molecules have a greater tendency to leave the liquid. Their escaping tendency and the vapour pressure exceed those predicted by ideal-solution behaviour. Consequently, the mixture has positive deviation from Raoult's law, with $p_{\text{total}} > x_{\text{ethanol}}p_{\text{ethanol}}^{\circ} + x_{\text{acetone}}p_{\text{acetone}}^{\circ}$. This is consistent with an endothermic enthalpy of mixing.

Step 3: Conclusion The ethanol-acetone mixture shows positive deviation from Raoult's law because adding acetone disrupts ethanol hydrogen bonding and weakens the overall intermolecular attractions.

Quick Tip to Solve: When acetone is mixed with ethanol, track the disrupted ethanol hydrogen bonds: weaker overall attraction means higher vapour pressure.

OR

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

Solution:

Concept:

- Azeotropes are liquid mixtures that boil at a constant temperature and have the same composition in the liquid and vapour phases at their azeotropic composition.
- Negative deviation from Raoult's law means that the total vapour pressure is lower than the ideal value because unlike molecular attractions are stronger than those in the pure liquids.

Step 1: Define an azeotrope An azeotrope is a constant-boiling mixture of two or more liquids whose vapour composition is identical to its liquid composition. As boiling does not change the composition at this point, the components cannot be separated by fractional distillation.

Step 2: Identify the type and give an example A mixture showing sufficiently large negative deviation from Raoult's law forms a maximum-boiling azeotrope. Stronger attractions between unlike molecules reduce their escaping tendency and lower the total vapour pressure. A higher temperature is therefore needed for the vapour pressure to equal atmospheric pressure. A standard example is a mixture of nitric acid and water, HNO_3 and H_2O .

Step 3: Conclusion Negative deviation forms a **maximum-boiling azeotrope**; nitric acid and water provide an example. Its liquid and vapour compositions are identical at the constant boiling point.

Quick Tip to Solve: Remember: negative deviation lowers vapour pressure and raises the azeotropic boiling temperature.

21. 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:

- A cell is selected according to its reactants, ability to be recharged, size and the constancy of its operating potential.
- Fuel cells receive reactants continuously; lead storage batteries are rechargeable, whereas mercury cells and dry cells are primary cells.

Step 1: Identify cells for the space programme and rechargeable use (a) The **hydrogen–oxygen fuel cell** was used in the Apollo Space programme. It converts the chemical energy of continuously supplied hydrogen and oxygen into electrical energy, producing water. (b) The **lead storage battery**, also called the lead–acid battery, is used in automobiles and inverters because it can supply substantial current and can be recharged.

Step 2: Identify small primary cells (c) The **mercury cell** is suitable for hearing aids and watches. It is compact and gives a nearly constant potential during its working life because the overall reaction does not appreciably change electrolyte concentration. (d) The **dry cell**, or Leclanche cell, is used in transistors. Its potential decreases during use as the conditions and concentrations associated with the cell reaction change.

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

Quick Tip to Solve: Use the clues: Apollo means fuel cell; rechargeable vehicle battery means lead–acid; steady miniature cell means mercury.

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

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

Calculate E_a for this reaction.

[$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$]

[2 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the pre-exponential factor, E_a is activation energy, R is the gas constant and T is absolute temperature.
- For common logarithms, $\log k = \log A - E_a/(2.303RT)$; the coefficient of $1/T$ equals $-E_a/(2.303R)$.

Quick Tip to Solve: For a base-10 logarithm include the factor 2.303; multiply the magnitude of the reciprocal-temperature coefficient by 2.303R.

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

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

Comparing it term by term with $\log k = \log A - \frac{E_a}{2.303RT}$, we obtain

$$\log A = 23.6, \quad \frac{E_a}{2.303R} = 2 \times 10^4 \text{ K}.$$

The intercept determines the pre-exponential factor; activation energy follows from the coefficient of the reciprocal temperature.

Step 2: Calculate activation energy with units Using $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$,

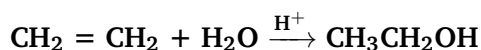
$$\begin{aligned} E_a &= 2.303R(2 \times 10^4 \text{ K}) \\ &= 2.303 \times 8.314 \times 2 \times 10^4 \text{ J mol}^{-1} \\ &= 3.8294284 \times 10^5 \text{ J mol}^{-1} \\ &\approx 382.9 \text{ kJ mol}^{-1}. \end{aligned}$$

Kelvin cancels with the inverse-kelvin factor in R , leaving energy per mole. The negative coefficient in the logarithmic equation corresponds to a positive activation energy.

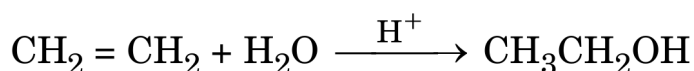
Step 3: Conclusion $E_a \approx 3.83 \times 10^5 \text{ J mol}^{-1} = 383 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: For a base-10 logarithm include the factor 2.303; multiply the magnitude of the reciprocal-temperature coefficient by 2.303R.

23. Write the mechanism of the following reaction:



[2 marks]

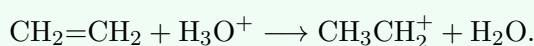


Solution:

Concept:

- Acid-catalysed hydration adds the elements of water across an alkene double bond through protonation, nucleophilic attack by water and deprotonation.
- The electron-rich pi bond accepts a proton; water supplies an oxygen lone pair to the carbocation. The acid catalyst is regenerated in the final step.

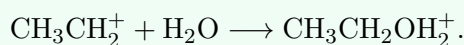
Step 1: Protonate the double bond The pi electrons of ethene attack a proton supplied by hydronium. One carbon gains hydrogen, while the other becomes positively charged:



Quick Tip to Solve: Write the three stages in order: protonation of the pi bond, water attack, and loss of a proton from the oxonium ion.

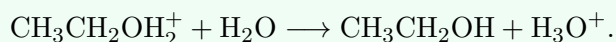
Ethene is symmetrical, so protonation at either carbon gives the same ethyl carbocation. This step converts the double bond into a single bond.

Step 2: Attack the carbocation with water A lone pair on the oxygen atom of water attacks the electron-deficient carbon of the ethyl carbocation, forming a carbon–oxygen bond and protonated ethanol:



The positive charge is now on oxygen because it has three bonds.

Step 3: Remove a proton and regenerate the catalyst Another water molecule removes a proton from the oxonium ion. The electrons of that oxygen–hydrogen bond remain on oxygen, producing neutral ethanol:



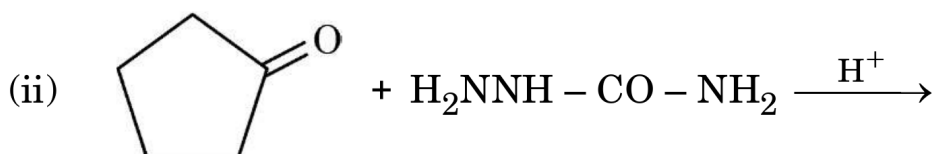
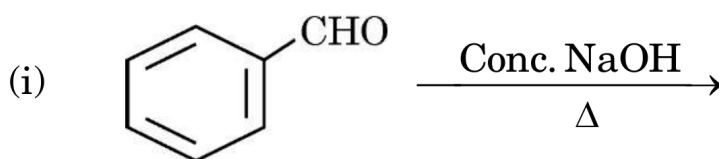
Hydronium is regenerated, so acid is a catalyst rather than a reactant consumed in the overall hydration.

Step 4: Conclusion The mechanism proceeds through CH_3CH_2^+ , then $\text{CH}_3\text{CH}_2\text{OH}_2^+$, and finally gives ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, with regeneration of the acid catalyst.

Quick Tip to Solve: Write the three stages in order: protonation of the pi bond, water attack, and loss of a proton from the oxonium ion.

24(a). Write the products of the following reactions:

[2 marks]



Solution:

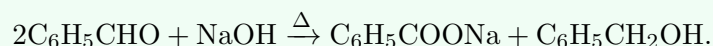
Concept:

- An aldehyde without an α -hydrogen undergoes the Cannizzaro reaction in concentrated alkali: two aldehyde molecules give one alcohol and one carboxylate salt.
- A ketone condenses with semicarbazide, $\text{H}_2\text{NNHCONH}_2$, to form a semicarbazone with elimination of water. The terminal amino group forms the new carbon-nitrogen double bond.

Step 1: (i) Disproportionation of benzaldehyde The printed aromatic ring is benzene, so the reactant is benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$. Its carbon adjacent to the aldehyde group belongs to the ring and carries

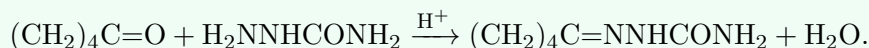
Quick Tip to Solve: Count the ring vertices first; in Cannizzaro reactions with NaOH, write the carboxylate salt unless acidification is specified.

no α -hydrogen. In concentrated sodium hydroxide, one molecule is oxidised while another is reduced:



The carboxylic product remains a sodium salt in this alkaline medium; free benzoic acid would require subsequent acidification.

Step 2: (ii) Condensation of cyclopentanone The printed ketone contains a five-membered ring. Its carbonyl oxygen is replaced by = NNHCONH₂ on condensation with semicarbazide:



Here (CH₂)₄C denotes the closed cyclopentane ring, whose carbonyl carbon remains part of the ring. Mild acid catalyses the condensation without changing the ring size.

Step 3: Conclusion (i) Benzyl alcohol and sodium benzoate; (ii) cyclopentanone semicarbazone and water.

Quick Tip to Solve: Count the ring vertices first; in Cannizzaro reactions with NaOH, write the carboxylate salt unless acidification is specified.

OR

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

(i) Toluene to Benzoic acid

(ii) Benzaldehyde to 1-Phenylethanol

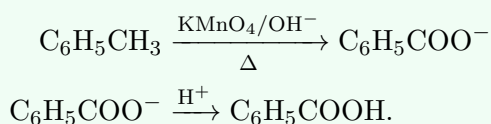
[2 marks]

Solution:

Concept:

- Hot alkaline potassium permanganate oxidises a benzylic side chain containing a benzylic hydrogen to a carboxylate; acidification gives the carboxylic acid.
- A Grignard reagent adds its alkyl group to an aldehyde carbonyl. Hydrolysis of the resulting magnesium alkoxide yields an alcohol.

Step 1: (i) Convert toluene into benzoic acid Oxidise toluene with hot alkaline potassium permanganate, then acidify the benzoate salt:

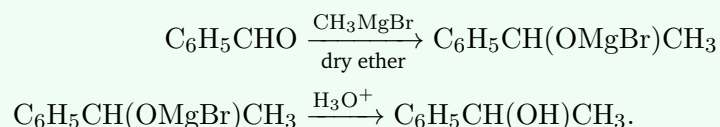


The methyl carbon becomes the carboxyl carbon, while the benzene ring is retained. The second step is necessary because oxidation in alkaline medium leaves the acid in its deprotonated form.

Step 2: (ii) Convert benzaldehyde into 1-phenylethanol Add methylmagnesium bromide to benzalde-

Quick Tip to Solve: Compare carbon counts: benzaldehyde needs one extra carbon, so use methylmagnesium bromide rather than a reducing agent.

hyde in dry ether, followed by acidic hydrolysis:

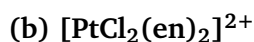
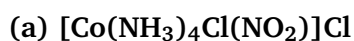


The methyl group creates the additional carbon-carbon bond needed for the target secondary alcohol. Simple reduction of benzaldehyde instead produces benzyl alcohol and does not supply this extra carbon. Water must be excluded during addition because it destroys the Grignard reagent.

Step 3: Conclusion Toluene: alkaline KMnO_4 , heat, then acidification. Benzaldehyde: CH_3MgBr in dry ether, then acidic hydrolysis. Each conversion uses two steps.

Quick Tip to Solve: Compare carbon counts: benzaldehyde needs one extra carbon, so use methylmagnesium bromide rather than a reducing agent.

25. Write IUPAC names of the following coordination entities:



[2 marks]

Solution:

Concept:

- Name ligands alphabetically before the metal. Neutral NH_3 is ammine, Cl^- is chlorido, and N-bonded NO_2^- is nitrito-N.
- Find the metal oxidation state from the total entity charge. Ethane-1,2-diamine, abbreviated en, is neutral and bidentate; use bis for two such ligands.

Step 1: (a) Name the cobalt salt The chloride outside the brackets has charge -1 , so the complex ion has charge $+1$. If cobalt has oxidation state x , the four neutral ammine ligands, one chlorido ligand and one nitrito ligand give

$$x + 4(0) - 1 - 1 = +1 \Rightarrow x = +3.$$

List ammine, chlorido and nitrito alphabetically, ignoring multiplicative prefixes. The formula NO_2 denotes nitrogen attachment in this school-level notation, so identify it as nitrito-N. Since the coordination entity is cationic, retain the metal name cobalt. Finally name the counter-ion chloride.

Step 2: (b) Name the platinum entity Each en ligand is neutral, while each chlorido ligand has charge -1 . The entity carries a $+2$ charge, so

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

Chlorido precedes ethane-1,2-diamine alphabetically. Use dichlorido for the two simple anionic ligands and bis(ethane-1,2-diamine) for the two named bidentate ligands. The positive complex retains the name platinum; no counter-ion is given and none should be appended.

Quick Tip to Solve: First separate bracket charge from counter-ion charge; neutral en contributes zero even though each ligand occupies two sites.

Step 3: Conclusion (a) Tetraamminechloridonitrito-N-cobalt(III) chloride.
(b) Dichloridobis(ethane-1,2-diamine)platinum(IV) ion.

Quick Tip to Solve: First separate bracket charge from counter-ion charge; neutral en contributes zero even though each ligand occupies two sites.

Section C (15 marks)

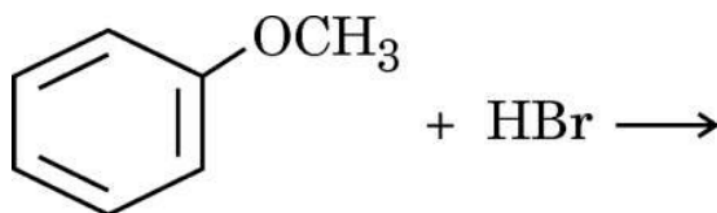
26(a). (i) Write hydroboration-oxidation reaction with an example.

(ii) Write the products of the following reaction:



(iii) Why is p-nitrophenol more acidic than phenol?

[3 marks]

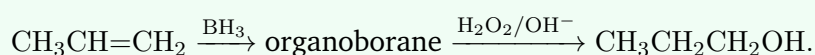


Solution:

Concept:

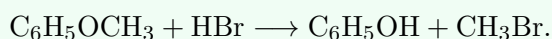
- Hydroboration followed by alkaline peroxide oxidation converts an alkene to an alcohol with anti-Markovnikov orientation: the hydroxyl group enters the less substituted carbon.
- Hydrogen halides cleave aryl-alkyl ethers at the alkyl-oxygen bond. Electron-withdrawing groups stabilise phenoxide ions and increase phenol acidity.

Step 1: (i) Hydroboration-oxidation with an example An alkene first reacts with diborane (or borane), producing an organoborane. Oxidation with hydrogen peroxide in aqueous alkali replaces the carbon-boron bond by a carbon-oxygen bond. For propene:



Boron adds preferentially to the less substituted terminal carbon, so oxidation gives propan-1-ol. This gives the anti-Markovnikov alcohol without a carbocation rearrangement.

Step 2: (ii) Cleavage of anisole by HBr After protonation of the ether oxygen, bromide attacks the methyl carbon by an $\text{S}_{\text{N}}2$ process:



The products are phenol and bromomethane. The aryl-oxygen bond has partial double-bond character through resonance and its aryl carbon does not undergo the usual $\text{S}_{\text{N}}2$ attack. Thus cleavage produces methyl bromide, not bromobenzene.

Step 3: (iii) Compare the acidity of p-nitrophenol and phenol Acidity depends on the stability of the

Quick Tip to Solve: For anisole plus HBr, break the methyl-oxygen bond; for acidity, compare stabilisation of the conjugate bases.

conjugate base formed after loss of H^+ . The para nitro group withdraws electrons by both inductive and resonance effects. In p-nitrophenoxide, the negative charge can be delocalised through the aromatic ring towards the nitro group and onto its oxygen atoms. This provides greater stabilisation than is available to the ordinary phenoxide ion. Consequently, loss of the phenolic proton is more favourable for p-nitrophenol.

Step 4: Conclusion (i) Propene gives propan-1-ol by hydroboration-oxidation. (ii) Anisole gives phenol and bromomethane. (iii) The nitro group stabilises p-nitrophenoxide by electron withdrawal, increasing acidity.

Quick Tip to Solve: For anisole plus HBr , break the methyl-oxygen bond; for acidity, compare stabilisation of the conjugate bases.

OR

26(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 $(\text{CH}_3)_3\text{C-Br}$ give 2-methylpropene and not $(\text{CH}_3)_3\text{C-OCH}_3$?

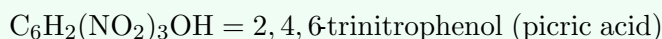
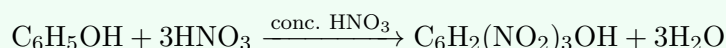
[3 marks]

Solution:

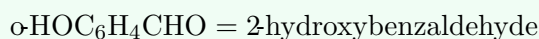
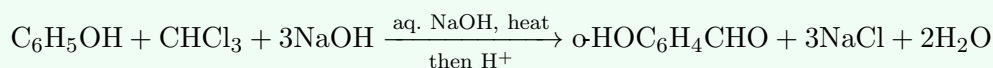
Concept:

- Phenol undergoes electrophilic substitution readily because the hydroxyl group activates the benzene ring and directs substitution to the ortho and para positions.
- The Reimer-Tiemann reaction introduces a formyl group mainly at the ortho position of phenol. Methoxide, CH_3O^- , is both a nucleophile and a strong base; the structure of the halide determines whether substitution or elimination predominates.

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



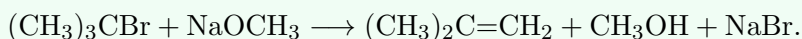
Step 2: (i)(2) Reaction with chloroform and aqueous sodium hydroxide



Step 3: (ii) Elimination with a tertiary alkyl halide The carbon bearing bromine in $(\text{CH}_3)_3\text{C-Br}$ is tertiary and is crowded by three methyl groups. Backside attack by methoxide, required for the $\text{S}_{\text{N}}2$ step of Williamson ether synthesis, is strongly hindered. Instead, the strong base removes a hydrogen

Quick Tip to Solve: For Williamson synthesis, inspect the carbon bonded to the halogen: a tertiary carbon favours elimination with a strong alkoxide base.

from a neighbouring methyl group while bromide leaves, giving a double bond by β -elimination (E2):



Thus a tertiary halide is unsuitable for preparing this ether by Williamson synthesis; a primary methyl halide with tert-butoxide would be the appropriate substitution combination.

Step 4: Conclusion The products in (i) are picric acid and mainly salicylaldehyde; in (ii), steric hindrance suppresses S_N2 substitution and methoxide gives 2-methylpropene by elimination.

Quick Tip to Solve: For Williamson synthesis, inspect the carbon bonded to the halogen: a tertiary carbon favours elimination with a strong alkoxide base.

27. 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.

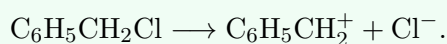
[3 marks]

Solution:

Concept:

- The rate-determining step of an S_N1 reaction is ionisation to a carbocation; greater carbocation stability makes this step easier.
- Optical rotation depends on the net contribution of the enantiomers present. Light and oxygen together can oxidise chloroform to poisonous phosgene.

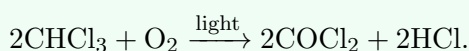
Step 1: (a) Resonance stabilisation of the benzyl carbocation Benzyl chloride ionises as follows:



The positive charge of the benzyl carbocation is delocalised through conjugation with the benzene ring; resonance contributors place it at the ortho and para positions. This stabilisation facilitates C–Cl bond ionisation, the slow step of the S_N1 mechanism. Consequently benzyl chloride is highly reactive towards this reaction.

Step 2: (b) External compensation in racemic butan-2-ol Butan-2-ol contains a chiral carbon bonded to four different groups: H, OH, CH_3 and C_2H_5 . However, $(\pm)$ -butan-2-ol denotes an equimolar mixture of its two enantiomers. They rotate plane-polarised light by equal amounts in opposite directions under identical conditions. Their rotations cancel, so the mixture is optically inactive by external compensation, although each enantiomer individually is optically active.

Step 3: (c) Prevention of phosgene formation Chloroform is slowly oxidised by atmospheric oxygen in the presence of light to carbonyl chloride (phosgene), a highly poisonous gas:



A tightly closed bottle restricts contact with atmospheric oxygen, and dark-coloured glass reduces

Quick Tip to Solve: Distinguish molecular chirality from the optical activity of a mixture: equal amounts of opposite enantiomers give zero net rotation.

exposure to light. Both precautions suppress the oxidation and therefore the formation of phosgene.

Step 4: Conclusion Benzyl chloride reacts readily through a resonance-stabilised carbocation; racemic butan-2-ol has cancelling optical rotations; closed dark bottles suppress oxidation of chloroform to phosgene.

Quick Tip to Solve: Distinguish molecular chirality from the optical activity of a mixture: equal amounts of opposite enantiomers give zero net rotation.

28. Answer any three of the following questions:

- (a) Explain the type of hybridization in $[\text{Fe}(\text{CN})_6]^{3-}$ on the basis of valence bond theory. (Given: Atomic number of Fe = 26)
- (b) Draw the geometrical isomers of $[\text{PtCl}_2(\text{en})_2]^{2+}$ ion.
- (c) $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ 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:

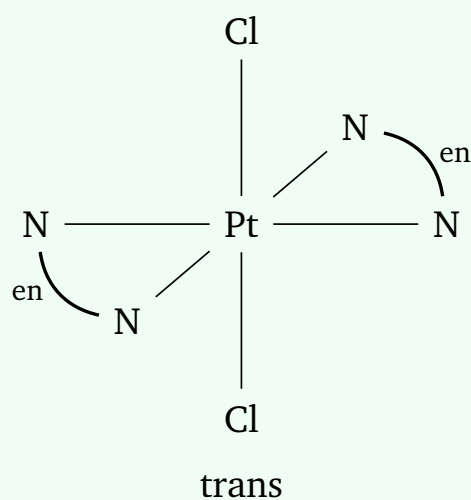
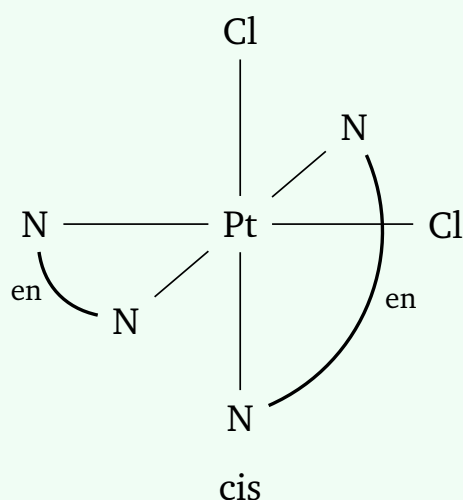
Concept:

- In valence bond theory, ligand strength determines electron pairing and whether inner d orbitals become available for hybridisation.
- The ligand en (ethane-1,2-diamine) is bidentate and occupies two adjacent coordination positions. In an octahedral complex, cis ligands are adjacent and trans ligands are opposite.
- A species with unpaired electrons is paramagnetic. An ambidentate ligand has two alternative donor atoms but bonds through one at a time.

Step 1: (a) Hybridisation of ferricyanide In $[\text{Fe}(\text{CN})_6]^{3-}$, six cyanide ligands contribute a total charge of -6 , so iron is in oxidation state $+3$. Fe has configuration $[\text{Ar}]3d^64s^2$, hence Fe^{3+} is $3d^5$. The strong-field CN^- ligands cause pairing: the five electrons occupy three $3d$ orbitals as two pairs and one unpaired electron. Two vacant inner $3d$ orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrid orbitals. The complex is an inner-orbital octahedral complex with one unpaired electron.

Step 2: (b) Geometrical isomers of the platinum complex The coordination number of $[\text{PtCl}_2(\text{en})_2]^{2+}$ is six, since each en provides two nitrogen donor atoms. Its octahedral geometrical isomers are cis, with the two chloride ligands at 90° , and trans, with the chlorides at 180° . In the sketches each curved connection pairs the two N donors of one en ligand; each en therefore binds adjacent positions.

Quick Tip to Solve: First determine the metal oxidation state and d-electron count; then use ligand strength to predict pairing and magnetic behaviour.



Octahedral cis and trans isomers; connected N donor pairs belong to one en ligand.

Step 3: (c) Different magnetic behaviour of the nickel complexes For $[\text{NiCl}_4]^{2-}$, nickel is Ni^{2+} , with $3d^8$ configuration. Weak-field chloride does not pair the two unpaired electrons; sp^3 hybridisation gives a tetrahedral, paramagnetic complex. In $\text{Ni}(\text{CO})_4$, CO is neutral, so nickel has oxidation state zero. Strong-field CO leads to pairing and a filled $3d^{10}$ arrangement, leaving the $4s$ and $4p$ orbitals for sp^3 hybridisation. No unpaired electron remains, so this tetrahedral complex is diamagnetic. Tetrahedral shape alone does not determine magnetism.

Step 4: (d) Isomerism due to ambidentate ligands Attachment of an ambidentate ligand through different donor atoms produces linkage isomerism. For example, NO_2^- can coordinate through nitrogen as nitro or through oxygen as nitrito. These are alternative linkages of the same ligand, rather than simultaneous binding through both atoms.

Step 5: Conclusion Any three parts may be selected: (a) d^2sp^3 , inner-orbital octahedral; (b) cis and trans; (c) two versus zero unpaired electrons; (d) linkage isomerism, exemplified by NO_2^- .

Quick Tip to Solve: First determine the metal oxidation state and d-electron count; then use ligand strength to predict pairing and magnetic behaviour.

29. If benzoic acid ($M = 122 \text{ g mol}^{-1}$) 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: $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$)

[3 marks]

Solution:

Concept:

- Osmotic pressure is $\pi = iCRT = i \frac{wRT}{MV}$, where i is the van't Hoff factor, w is solute mass, M its molar mass, V the solution volume and T absolute temperature.
- For dimerisation, two monomer molecules form one dimer. If the fraction of monomers associated

Quick Tip to Solve: For a dimer, first divide the observed osmotic pressure by the monomer pressure, then use $\alpha = 2(1 - i)$.

is α , then $i = 1 - \frac{\alpha}{2}$.

Step 1: Calculate the pressure without association Use the given volume $V = 100 \text{ mL} = 0.100 \text{ L}$ and $T = 27 + 273 = 300 \text{ K}$. The amount of benzoic acid before association is $n = 6.1/122 = 0.050 \text{ mol}$, giving $C = 0.050/0.100 = 0.500 \text{ mol L}^{-1}$. Thus the ideal monomer pressure would be

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

Association reduces the number of independent solute particles, so the observed pressure is less than this value.

Step 2: Obtain the fraction associated The observed pressure gives

$$i = \frac{\pi}{\pi_0} = \frac{6.5}{12.315} = 0.5278.$$

Starting with one mole of monomers, association leaves $1 - \alpha$ mole of monomer and produces $\alpha/2$ mole of dimer. The total particle amount is therefore $1 - \alpha/2$, giving

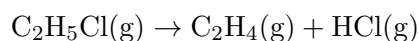
$$\alpha = 2(1 - i) = 2(1 - 0.5278) = 0.9444.$$

This value lies between zero and one, as required for a physically possible degree of association.

Step 3: Conclusion The percentage association of benzoic acid is $\alpha \times 100 = 94.44\%$, approximately 94.4%.

Quick Tip to Solve: For a dimer, first divide the observed osmotic pressure by the monomer pressure, then use $\alpha = 2(1 - i)$.

30. The following data were obtained during the first order thermal decomposition of $\text{C}_2\text{H}_5\text{Cl}$ at a constant volume:

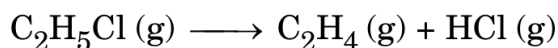


Experiment	Time (s^{-1})	Total pressure (atm)
1	0	0.4
2	100	0.6

Calculate the rate constant.

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

[3 marks]



Experiment	Time (s^{-1})	Total pressure (atm)
1	0	0.4
2	100	0.6

Solution:

Concept:

- For a first order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial reactant amount and x is the amount decomposed in time t .
- At constant volume and temperature, gas partial pressure is proportional to its amount. Total pressure must first be converted to the partial pressure of the remaining reactant.

Step 1: Relate total pressure to reactant pressure The printed heading gives s^{-1} ; since the entries are elapsed times, use $t = 100\text{ s}$ in the rate law. Let $p_0 = 0.4\text{ atm}$ be the initial pressure of $\text{C}_2\text{H}_5\text{Cl}$ and let x be the pressure corresponding to the amount decomposed. The reaction $\text{C}_2\text{H}_5\text{Cl(g)} \rightarrow \text{C}_2\text{H}_4\text{(g)} + \text{HCl(g)}$ produces one mole of each product per mole of reactant. Hence the partial pressures are $p_0 - x$, x and x , respectively, and the total pressure at time t is $p_t = p_0 + x$. At 100 s , $x = 0.6 - 0.4 = 0.2\text{ atm}$.

Step 2: Substitute the remaining reactant pressure The partial pressure of undecomposed ethyl chloride is

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

The first order rate constant is therefore

$$k = \frac{2.303}{100} \log \frac{0.4}{0.2} = \frac{2.303 \times 0.3010}{100} = 6.932 \times 10^{-3}\text{ s}^{-1}.$$

The reactant has fallen to half its initial amount in 100 s , consistent with $k = \ln 2/t_{1/2}$.

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

Quick Tip to Solve: For a gas decomposition giving two product molecules, use the remaining reactant pressure $2p_0 - p_t$, not the total pressure.

Section D (8 marks)

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

31(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 the repeating units of a biomolecule.
- Glycosidic bonds join sugar units, whereas peptide bonds join amino acid residues.

Step 1: Identify a glycosidic linkage A glycosidic linkage is an oxygen bridge, $C - O - C$, joining two monosaccharide units. It forms by elimination of water between suitable hydroxyl groups of the sugar molecules, including the anomeric hydroxyl group of one sugar. It occurs in disaccharides and polysaccharides.

Step 2: Identify a peptide linkage A peptide linkage is the amide group $-CO - NH-$. It forms by elimination of water between the carboxyl group of one amino acid and the amino group of another. Thus its joining atoms and the monomer units differ from those in a glycosidic linkage.

Step 3: Conclusion Glycosidic linkage: $C - O - C$ between monosaccharides; peptide linkage: $-CO - NH-$ between amino acids.

Quick Tip to Solve: Remember the joining groups: sugars use an oxygen bridge, amino acids use the amide group.

31(ii). Which amino acids are called essential amino acids?

[1 mark]

Solution:

Concept:

- Amino acids are the building units of proteins; dietary supply depends on whether the body can synthesise them.
- Essential amino acids must be supplied through food because the human body cannot synthesise them in sufficient amounts.

Quick Tip to Solve: Define essential amino acids by the need for dietary supply; a list of examples alone is insufficient.

Step 1: State the defining property Essential amino acids are those amino acids which cannot be synthesised by the human body in the amounts required for normal growth and maintenance. Their essentiality refers to the need for a dietary source, rather than to their being more important in proteins than other amino acids.

Step 2: Explain the dietary requirement They must therefore be obtained from food containing suitable proteins. For example, valine and lysine are essential amino acids. In contrast, amino acids that the body can synthesise adequately are termed non-essential.

Step 3: Conclusion Amino acids that the human body cannot synthesise adequately and must obtain through the diet are called essential amino acids.

Quick Tip to Solve: Define essential amino acids by the need for dietary supply; a list of examples alone is insufficient.

31(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 describes regular local folding of the polypeptide backbone; tertiary structure is its overall three-dimensional folding.
- Hydrogen bonds involve backbone or side-chain donors and acceptors; disulphide bonds are covalent links between cysteine side chains.

Step 1: Name the common secondary structures The two common forms are the α -helix and the β -pleated sheet. In an α -helix, the polypeptide backbone coils into a helix. In a β -pleated sheet, extended chain segments lie alongside one another and form a folded sheet.

Step 2: State two stabilising interactions Hydrogen bonding between peptide C = O and N – H groups stabilises the helix and pleated sheet; hydrogen bonding also contributes to tertiary folding. Disulphide bridges, –S – S–, between cysteine residues stabilise tertiary structure. Thus hydrogen bonds and disulphide bonds are two suitable stabilising forces, with disulphide bonds particularly relevant to tertiary structure.

Step 3: Conclusion The common secondary structures are the α -helix and β -pleated sheet. Two stabilising forces are hydrogen bonding and disulphide bonding.

Quick Tip to Solve: Name both secondary forms first, then distinguish backbone hydrogen bonds from tertiary disulphide bridges.

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

Solution:

Concept:

- A protein functions through its specific three-dimensional conformation, which is maintained by interactions within the folded chain.
- Denaturation disrupts secondary and tertiary structures without hydrolysing the peptide bonds of the primary structure.

Step 1: Define denaturation and give an example Denaturation is the loss of the native conformation and biological activity of a protein due to a physical change, such as heating, or a chemical change, such as a change in pH. For example, heating an egg coagulates the proteins of egg white: the native soluble protein becomes an insoluble coagulated mass.

Step 2: Identify the affected structures During denaturation, the regular secondary arrangement and the overall tertiary folding are disrupted. The protein therefore loses its biological activity because its functional shape is destroyed. The primary structure, namely the amino-acid sequence joined by peptide bonds, remains intact; denaturation is not the same process as complete hydrolysis of a protein.

Step 3: Conclusion Denaturation destroys the native secondary and tertiary structures and hence biological activity; coagulation of egg white on heating is an example. Primary structure remains intact.

Quick Tip to Solve: Use heated egg white as the example and explicitly preserve the peptide-bonded primary sequence.

32(i). 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:

- $pK_b = -\log K_b$: a stronger base has a larger K_b and a smaller pK_b .
- In aqueous ethylamines, the electron-releasing effect of ethyl groups and hydration of the conjugate ammonium ions together determine basicity.

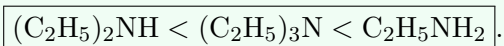
Step 1: Compare the aqueous basic strengths For the printed ethylamines, the aqueous basicity order is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$. The secondary amine has a favourable combination of electron donation and hydration. The tertiary ethylamine is more basic than the primary ethylamine in this particular aqueous series.

Step 2: Translate basicity into pK_b order Since pK_b decreases as basicity increases, the strongest base must be placed first when arranging increasing pK_b . Apply this inverse relation to the basicity order,

Quick Tip to Solve: Check whether the groups are methyl or ethyl, and remember that stronger basicity means lower pK_b .

retaining secondary, tertiary, primary in that sequence for increasing pK_b .

Step 3: Conclusion Increasing pK_b :



Quick Tip to Solve: Check whether the groups are methyl or ethyl, and remember that stronger basicity means lower pK_b .

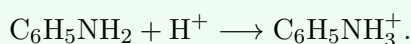
32(ii). Aniline on nitration gives a substantial amount of m-nitroaniline, though amino group is o/p directing. Why? [1 mark]

Solution:

Concept:

- The neutral amino group, $-NH_2$, activates a benzene ring and directs electrophilic substitution to the ortho and para positions.
- In strongly acidic nitrating medium, aniline is protonated to the anilinium ion, $C_6H_5NH_3^+$.

Step 1: Recognise the species in the nitrating mixture The concentrated acid mixture used in nitration protonates the nitrogen lone pair of aniline:



The reacting mixture consequently contains the anilinium ion as well as unprotonated aniline.

Step 2: Explain meta substitution The $-NH_3^+$ group is electron withdrawing and meta directing. Nitrogen no longer has an available lone pair to donate into the ring. Nitration of this protonated species therefore produces meta-nitroaniline after work-up, accounting for the substantial meta product despite the ortho/para directing behaviour of neutral aniline.

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

Quick Tip to Solve: Determine the protonation state before applying the directing effect of an amino substituent.

32(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 ammonia to form an ammonium carboxylate, which loses water on heating to form the corresponding amide.

Quick Tip to Solve: Work backward from aniline: add a carbonyl group to its nitrogen precursor to obtain benzamide.

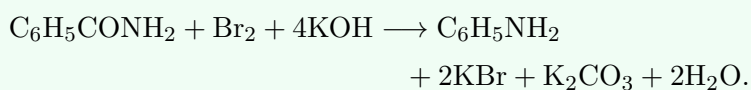
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon from the organic product.

Step 1: Identify C and work back to B The aromatic amine of formula $\text{C}_6\text{H}_7\text{N}$ is aniline, $\text{C}_6\text{H}_5 - \text{NH}_2$. Because Br_2 and aqueous KOH convert an amide into an amine with one fewer carbon atom, its precursor B must be benzamide, $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH}_2$.

Step 2: Identify A from amide formation The compound A has formula $\text{C}_7\text{H}_6\text{O}_2$ and yields benzamide with ammonia on heating, so A is benzoic acid, $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{OH}$. The reaction proceeds through ammonium benzoate:



Step 3: Confirm the degradation The second reaction is



The organic product has six carbon atoms, as required by the stated formula of C.

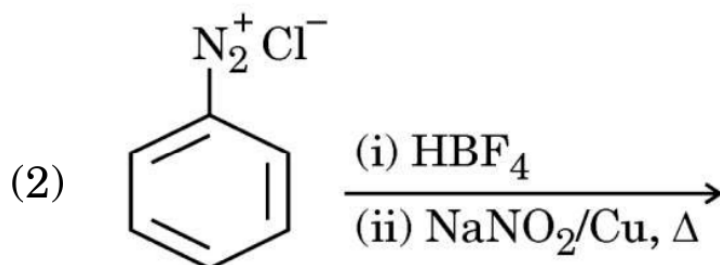
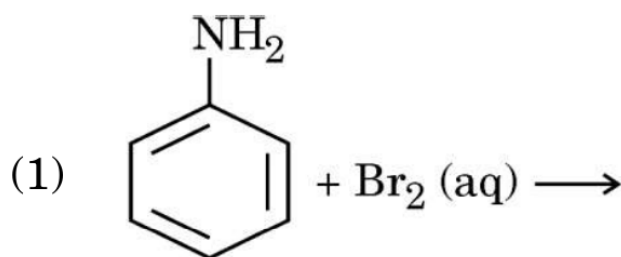
Step 4: Conclusion A: benzoic acid, $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{OH}$; B: benzamide, $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH}_2$; C: aniline, $\text{C}_6\text{H}_5 - \text{NH}_2$.

Quick Tip to Solve: Work backward from aniline: add a carbonyl group to its nitrogen precursor to obtain benzamide.

OR

32(iii). Complete the following reactions giving main products, as shown below.

[2 marks]

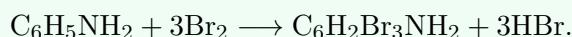


Solution:

Concept:

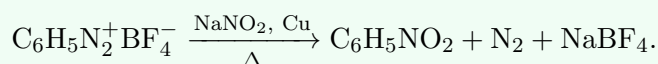
- The amino group activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- In aryl diazonium salts, the diazonium group can be replaced by other groups with liberation of nitrogen gas.

Step 1: Brominate aniline with bromine water The strongly activating $-\text{NH}_2$ group makes substitution occur at both ortho positions and the para position without a Lewis acid catalyst. Thus bromine water gives a white precipitate of 2,4,6-tribromoaniline:



The three bromine atoms occupy positions 2, 4 and 6 relative to the amino group at position 1; the amino group remains attached to the ring.

Step 2: Replace the diazonium group by a nitro group The starting compound in reaction (2) is benzenediazonium chloride, $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$. Treatment with HBF_4 first forms benzenediazonium tetrafluoroborate. Heating this salt with sodium nitrite in the presence of copper replaces the diazonium group by $-\text{NO}_2$, giving nitrobenzene and liberating N_2 :



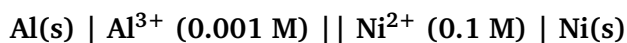
Heating the tetrafluoroborate alone would give fluorobenzene, but the printed second step specifically uses NaNO_2/Cu , so nitrobenzene is the main product here.

Step 3: Conclusion (1) 2,4,6-Tribromoaniline, $\text{C}_6\text{H}_2\text{Br}_3\text{NH}_2$, a white precipitate. (2) Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$.

Quick Tip to Solve: Read the reagents after tetrafluoroborate formation: sodium nitrite and copper introduce a nitro group.

Section E (15 marks)

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



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

(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:

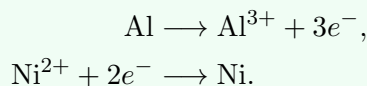
- The cell emf is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, using reduction potentials for both electrodes.
- At 298 K, the Nernst equation is $E = E^\circ - (0.0591/n) \log Q$, where n is the number of electrons

Quick Tip to Solve: Balance the electron transfer before writing Q: here the concentration powers are 2 and 3, and n is 6.

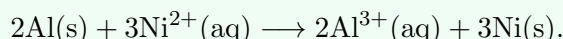
transferred in the balanced cell reaction and Q is its reaction quotient.

- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$. A weak electrolyte also changes its degree of ionisation significantly on dilution, giving a nonlinear curve.

Step 1: Identify the electrodes and balance the cell reaction Aluminium has the more negative reduction potential and is oxidised at the anode; nickel ions are reduced at the cathode:



Multiplying the first half-reaction by 2 and the second by 3 gives



Hence $n = 6$. Pure solid aluminium and nickel have unit activity and do not appear in the reaction quotient.

Step 2: Apply the Nernst equation to the stated concentrations The standard emf and reaction quotient are

$$\begin{aligned}E_{\text{cell}}^\circ &= -0.25 - (-1.66) = 1.41 \text{ V}, \\ Q &= \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = 10^{-3}.\end{aligned}$$

Using $\log Q = -3$,

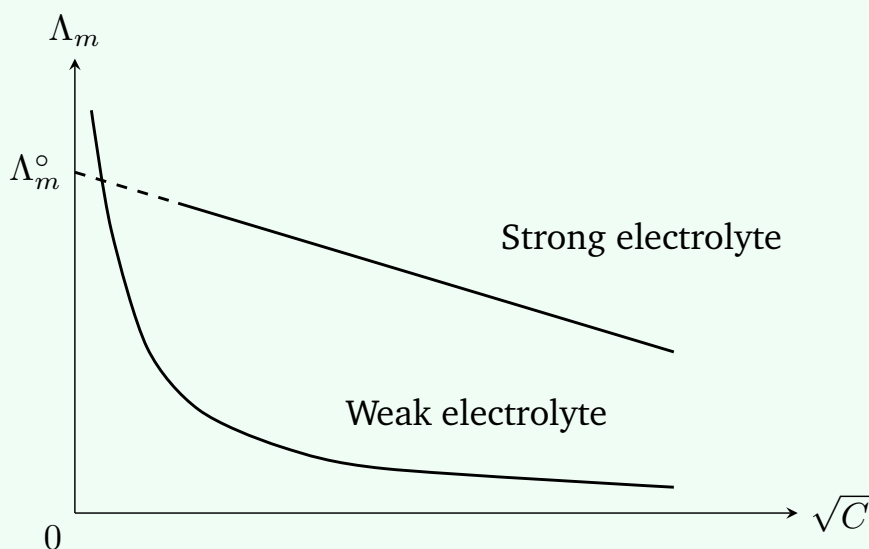
$$E_{\text{cell}} = 1.41 - \frac{0.0591}{6}(-3) = 1.43955 \text{ V}.$$

The small quotient increases the emf above its standard value, consistent with the low concentration of aluminium ions on the product side.

Step 3: Explain the conductivity graph A strong electrolyte is already almost completely dissociated. At sufficiently low concentration its molar conductivity decreases approximately linearly with $\sqrt{C}$, so extending its straight line to $\sqrt{C} = 0$ gives Λ_m° . A weak electrolyte, such as acetic acid, is only partially ionised at finite concentration. Dilution increases its degree of ionisation markedly, so Λ_m rises sharply as C approaches zero. Its Λ_m versus $\sqrt{C}$ curve is strongly curved; a straight-line extension of finite-concentration data therefore cannot determine a reliable intercept. The schematic graph illustrates these different shapes, with no numerical scale implied. Instead, obtain the limiting molar conductivity from independently migrating ions using Kohlrausch's law, for example

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{CH}_3\text{COONa}) - \Lambda_m^\circ(\text{NaCl}).$$

Quick Tip to Solve: Balance the electron transfer before writing Q : here the concentration powers are 2 and 3, and n is 6.



Schematic molar conductivity curves; dashed continuation shows strong-electrolyte extrapolation.

Step 4: Conclusion (i) The cell emf at 298 K is approximately 1.440 V . (ii) The weak-electrolyte conductivity curve is nonlinear because ionisation increases on dilution, so its limiting conductivity cannot be obtained by the straight-line extrapolation used for strong electrolytes.

Quick Tip to Solve: Balance the electron transfer before writing Q : here the concentration powers are 2 and 3, and n is 6.

OR

33(b). (i) The molar conductivities of NH_4^+ and Cl^- ion are $73.8 \text{ S cm}^2 \text{ mol}^{-1}$ and $76.2 \text{ S cm}^2 \text{ mol}^{-1}$ respectively. The conductivity of $0.1 \text{ M NH}_4\text{Cl}$ is $1.29 \times 10^{-2} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation.

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

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . The factor 1000 converts litres to cubic centimetres.
- Kohlrausch's law gives $\Lambda_m^\circ = \lambda_{\text{NH}_4^+}^\circ + \lambda_{\text{Cl}^-}^\circ$. Using the conductivity-ratio relation requested here, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- For a reduction half-cell, $E = E^\circ - (0.0591/n) \log Q$ at 298 K, where n is the number of electrons transferred and Q is the reaction quotient. A pure solid has unit activity.

Step 1: (i) Calculate the molar conductivity The solution has $c = 0.1 \text{ mol L}^{-1}$ and $\kappa = 1.29 \times$

Quick Tip to Solve: For a metal-ion reduction to a pure metal, write $Q = 1/[\text{metal ion}]$ first; this fixes the sign of the Nernst correction before substitution.

$10^{-2} \text{ S cm}^{-1}$. Substituting the given values,

$$\Lambda_m = \frac{1000(1.29 \times 10^{-2})}{0.1} = 129 \text{ S cm}^2 \text{ mol}^{-1}.$$

Step 2: (i) Obtain the limiting conductivity and dissociation ratio Each formula unit of NH_4Cl produces one ammonium ion and one chloride ion, so their limiting ionic conductivities are added with coefficients of unity:

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

The requested conductivity-based degree of dissociation is therefore

$$\alpha = \frac{129}{150} = 0.86, \quad 100\alpha = 86\%.$$

For this strong electrolyte, the ratio is the requested conductivity-based estimate; interionic effects also reduce mobility at finite concentration.

Step 3: (ii) Form the reaction quotient and apply the Nernst equation For $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn(s)}$, $n = 2$. Solid zinc has unit activity; electrons are excluded from Q . Thus,

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

Hence

$$E = -0.76 - \frac{0.0591}{2} \log 10 = -0.78955 \text{ V}.$$

Step 4: Conclusion (i) $\Lambda_m = 129 \text{ S cm}^2 \text{ mol}^{-1}$, and the requested conductivity-ratio degree of dissociation is $\alpha = 0.86 = 86\%$. (ii) The half-cell reduction potential is $E = -0.78955 \text{ V} \approx -0.790 \text{ V}$.

Quick Tip to Solve: For a metal-ion reduction to a pure metal, write $Q = 1/[\text{metal ion}]$ first; this fixes the sign of the Nernst correction before substitution.

34(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]

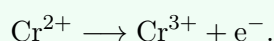
Solution:

Concept:

- Colour in common transition-metal salts arises when visible light promotes an electron between split d -orbital energy levels. A filled d^{10} subshell cannot undergo such $d-d$ transitions.
- A reducing agent donates electrons and is itself oxidised. Formation of a more stable electronic configuration can favour this oxidation.
- Transition-metal catalysts can use variable oxidation states to form intermediates; metal surfaces can adsorb reactants and lower the activation energy.
- In acidic medium permanganate is reduced from manganese in oxidation state +7 to Mn^{2+} :
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

Step 1: (i)(1) Explain the difference in colour Zinc has atomic number 30, so Zn^{2+} has the electronic configuration $[\text{Ar}]3d^{10}$. Its d subshell is completely filled. Consequently, no $d-d$ transition can occur, and its salts are colourless. Nickel has atomic number 28, and Ni^{2+} has configuration $[\text{Ar}]3d^8$. In a ligand field, its partially filled d orbitals split into levels of different energies. Absorption of visible light causes $d-d$ transitions; the remaining transmitted or reflected light gives nickel(II) salts their colour.

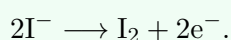
Step 2: (i)(2) Explain the reducing power of chromium(II) Cr^{2+} has configuration $[\text{Ar}]3d^4$. It readily loses an electron to form Cr^{3+} , with configuration $[\text{Ar}]3d^3$:



The d^3 configuration is particularly stable in an octahedral environment because its three electrons occupy the lower-energy t_{2g} orbitals. Thus oxidation to chromium(III) is favoured, and chromium(II) readily reduces other substances by donating an electron.

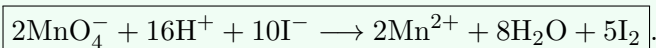
Step 3: (i)(3) Explain catalytic activity Transition metals and their compounds exhibit variable oxidation states, enabling them to form intermediate compounds with reactants and undergo reversible changes of oxidation state. These intermediates provide a reaction pathway with lower activation energy, after which the catalyst is regenerated. Solid transition metals also adsorb reactants on their surfaces. Adsorption brings reacting species close together and weakens bonds, facilitating reaction. These properties account for their catalytic activity.

Step 4: (ii)(1) Balance oxidation of iodide Iodide is oxidised to iodine, while acidic permanganate is reduced to manganese(II). The oxidation half-equation is



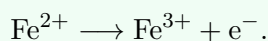
Quick Tip to Solve: In acidic permanganate reactions, start with its five-electron reduction to manganese(II), then multiply the oxidation half-equation to cancel electrons before checking atoms and charge.

Multiply the permanganate reduction half-equation by 2 and the iodide oxidation half-equation by 5, so that ten electrons cancel. The balanced ionic equation is

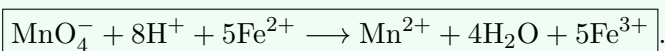


The net charge on each side is +4, and manganese, oxygen, hydrogen and iodine atoms are conserved.

Step 5: (ii) (2) Balance oxidation of iron(II) Iron(II) is oxidised to iron(III):



Multiply this half-equation by 5 and add it to the permanganate reduction half-equation. After cancellation of five electrons,



The net charge is +17 on both sides, and every element is balanced. Each permanganate ion therefore oxidises five iron(II) ions in acidic medium.

Step 6: Conclusion Zinc(II) is colourless because it is d^{10} , whereas nickel(II) is coloured because its d^8 configuration permits $d-d$ transitions. Chromium(II) reduces other species by forming stable Cr^{3+} ; variable oxidation states and adsorption explain catalytic activity. Acidic permanganate oxidises iodide to I_2 and iron(II) to Fe^{3+} , according to the balanced ionic equations above.

Quick Tip to Solve: In acidic permanganate reactions, start with its five-electron reduction to manganese(II), then multiply the oxidation half-equation to cancel electrons before checking atoms and charge.

OR

34(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 $\text{K}_2\text{Cr}_2\text{O}_7$?

(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 normally has oxidation state -2 ; the sum of oxidation states equals the ionic charge. Chromium belongs to group 6 and manganese to group 7.
- Chromate and dichromate are related by an acid-base equilibrium. Changing pH changes their relative amounts without changing chromium's oxidation state.
- Aqueous stability depends on the energy of hydration as well as electronic configuration. Half-filled and completely filled subshells also help explain the exceptional configurations of chromium and copper.

Quick Tip to Solve: For the oxoanions, calculate the metal oxidation state from oxygen's -2 value; for increasing pH, remember orange dichromate becomes yellow chromate.

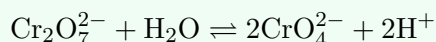
Step 1: (i) Identify the oxometal anions The required anions are chromate, CrO_4^{2-} , and permanganate, MnO_4^- . If the oxidation state of the metal is x , then

$$\text{CrO}_4^{2-} : x + 4(-2) = -2 \Rightarrow x = +6,$$

$$\text{MnO}_4^- : x + 4(-2) = -1 \Rightarrow x = +7.$$

Thus chromium and manganese exhibit oxidation states equal to their group numbers, 6 and 7 respectively.

Step 2: (ii) Increase the pH of dichromate solution Increasing pH means decreasing the concentration of H^+ , or adding alkali. The equilibrium



shifts to the right as hydrogen ions are removed. Equivalently, the reaction with alkali is



Orange dichromate is converted into yellow chromate, so the solution becomes yellow. Chromium remains in the +6 oxidation state; this is not a redox change.

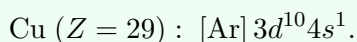
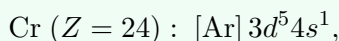
Step 3: (iii) Explain the instability of aqueous copper(I) In aqueous solution, Cu^+ undergoes disproportionation:



One copper(I) ion is oxidised and the other is reduced. The much more favourable hydration enthalpy of Cu^{2+} , compared with that of Cu^+ , compensates for the energy needed to remove a further electron. Consequently, the $3d^{10}$ configuration of Cu^+ alone does not ensure its stability in water.

Step 4: (iv) Name the lanthanoid with a well-known +4 state Cerium, Ce, is well-known to exhibit the +4 oxidation state. The Ce^{4+} ion has the noble-gas configuration $[\text{Xe}]$, with an empty $4f$ subshell, which helps explain the occurrence of this state in cerium compounds.

Step 5: (v) State the anomalous configurations The two elements are chromium and copper. Their actual ground-state electronic configurations are



These differ from the simple filling predictions $[\text{Ar}] 3d^4 4s^2$ and $[\text{Ar}] 3d^9 4s^2$. The close energies of the $3d$ and $4s$ orbitals and the extra stability associated with half-filled $3d^5$ and filled $3d^{10}$ subshells favour the observed configurations.

Step 6: Conclusion (i) Chromate and permanganate; (ii) orange dichromate changes to yellow chromate; (iii) Cu^+ disproportionates because aqueous Cu^{2+} gains much greater hydration stabilisation; (iv) cerium; (v) chromium and copper.

Quick Tip to Solve: For the oxoanions, calculate the metal oxidation state from oxygen's -2 value; for increasing pH, remember orange dichromate becomes yellow chromate.

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

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

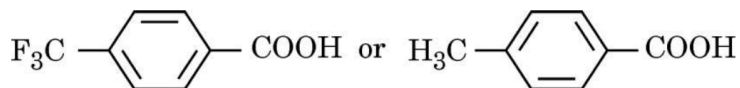
$\text{F}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$ or $\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{COOH}$

(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]

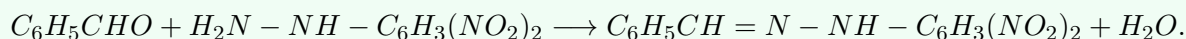


Solution:

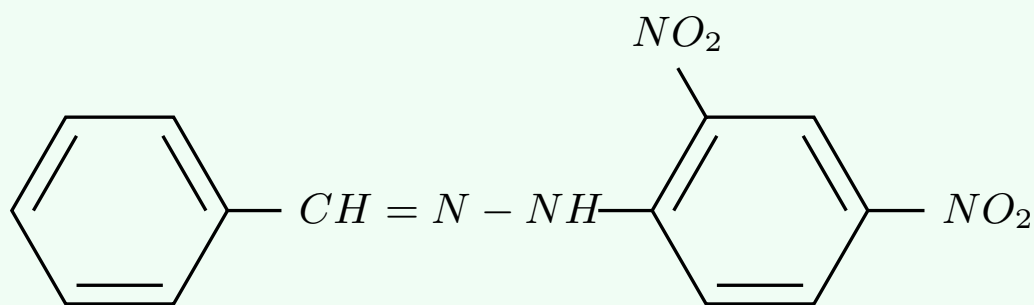
Concept:

- Aldehydes undergo condensation with 2,4-dinitrophenylhydrazine: the carbonyl oxygen is replaced by $=\text{N}-\text{NH}-\text{C}_6\text{H}_3(\text{NO}_2)_2$, with elimination of water.
- Electron-withdrawing groups stabilise a carboxylate ion and increase acidity; electron-donating groups have the opposite effect.
- Rosenmund reduction selectively converts an acyl chloride into an aldehyde using hydrogen and poisoned palladium supported on barium sulphate.
- Removal of an α -hydrogen from a carbonyl compound forms a resonance-stabilised enolate ion. Carboxylic acids also react with sodium hydrogen carbonate to liberate carbon dioxide.

Step 1: (a) Form the benzaldehyde derivative Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, reacts with 2,4-dinitrophenylhydrazine in acidic medium. The terminal $-\text{NH}_2$ group of the reagent condenses with the carbonyl group, eliminating water:



In the derivative, the two nitro groups occupy positions 2 and 4 relative to the ring carbon bonded to $-\text{NH}-$. The benzaldehyde carbon retains its hydrogen; the product therefore contains $\text{CH}=\text{N}$, not $\text{C}(=\text{O})$. Its structure is shown below.



Structure of benzaldehyde 2,4-dinitrophenylhydrazone

Step 2: (b) Compare the substituted benzoic acids The printed structures are para-substituted benzoic acids. The $-\text{CF}_3$ group exerts a strong electron-withdrawing inductive effect. It stabilises the negative charge of the carboxylate conjugate base and favours loss of H^+ . The $-\text{CH}_3$ group is electron-donating and makes the corresponding carboxylate less stable. Consequently, $p\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}$ is

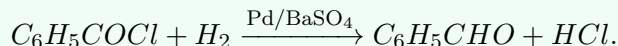
Quick Tip to Solve: For the hydrazone, replace the carbonyl oxygen by $=\text{N}-\text{NH}-\text{Ar}$ and retain the aldehydic hydrogen; place the nitro groups ortho and para to NH on the reagent ring.

stronger than $p\text{-CH}_3\text{C}_6\text{H}_4\text{COOH}$.

Step 3: (c) Write Rosenmund's reduction An acyl chloride is hydrogenated over poisoned palladium on barium sulphate:

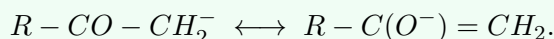


For example, benzoyl chloride gives benzaldehyde:



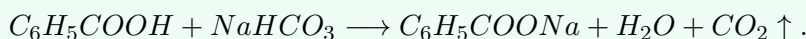
The reduced activity of the poisoned catalyst helps prevent further reduction of the aldehyde to the corresponding primary alcohol.

Step 4: (d) Explain acidity of alpha hydrogens An α -hydrogen is attached to the carbon immediately adjacent to the carbonyl carbon. The electron-withdrawing carbonyl group polarises these C-H bonds. When a base removes an α -hydrogen as a proton, the conjugate base is an enolate, whose negative charge is delocalised between the alpha carbon and the oxygen:



This resonance stabilisation makes proton removal easier than from an ordinary alkane. Here R can be hydrogen for an aldehyde or an alkyl group for a ketone. Benzaldehyde itself has no alpha hydrogen on its ring carbon bonded to $-\text{CHO}$.

Step 5: (e) Perform the sodium hydrogen carbonate test Add aqueous sodium hydrogen carbonate separately to the two samples. Benzoic acid gives brisk effervescence of carbon dioxide, whereas benzaldehyde gives no such effervescence:



Benzoic acid supplies the acidic proton required to displace carbonic acid from its salt; carbonic acid decomposes into water and carbon dioxide. Benzaldehyde lacks the carboxylic acid group and does not produce this reaction. The evolved gas turns limewater milky, confirming carbon dioxide.

Step 6: Conclusion (a) The derivative is $\text{C}_6\text{H}_5\text{CH} = \text{N} - \text{NH} - \text{C}_6\text{H}_3(\text{NO}_2)_2$, with nitro groups at positions 2 and 4. (b) $p\text{-CF}_3\text{C}_6\text{H}_4\text{COOH}$ is the stronger acid. (c) $\text{RCOCl} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{RCHO} + \text{HCl}$. (d) Alpha hydrogens are acidic because their removal produces a resonance-stabilised enolate. (e) Benzoic acid effervesces with NaHCO_3 ; benzaldehyde does not.

Quick Tip to Solve: For the hydrazone, replace the carbonyl oxygen by $=\text{N}-\text{NH}-\text{Ar}$ and retain the aldehydic hydrogen; place the nitro groups ortho and para to NH on the reagent ring.