

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-4-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **33** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** sections – **Section A, B, C, D and E**.
- (iii) **Section A** – questions number **1 to 16** are multiple choice type questions. Each question carries **1** mark.
- (iv) **Section B** – questions number **17 to 21** are very short answer type questions. Each question carries **2** marks.
- (v) **Section C** – questions number **22 to 28** are short answer type questions. Each question carries **3** marks.
- (vi) **Section D** – questions number **29 and 30** are case-based questions. Each question carries **4** marks.
- (vii) **Section E** – questions number **31 to 33** are long answer type questions. Each question carries **5** marks.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculator is not allowed.

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each. $16 \times 1 = 16$

1. Which property of transition metals enables them to form alloys?

[1 mark]

- (A) High ionization enthalpy
- (B) Similar atomic radii
- (C) Catalytic property
- (D) Complex formation

Correct Answer: (B) Similar atomic radii

Solution:

Concept:

- Similar atomic radii allow atoms of one transition metal to replace atoms of another in a metallic crystal lattice.
- An alloy is a metallic mixture that can retain the metallic bonding and lattice structure of its constituent metals.

Step 1: Identify the relevant structural property Transition metals often have comparable atomic sizes. Consequently, an atom of one metal can occupy a lattice site of another without causing excessive distortion. Such substitution gives a solid solution and explains why these metals readily form alloys.

Step 2: Check the remaining options High ionization enthalpy concerns the energy required to remove an electron, rather than whether atoms fit into a common lattice. Catalytic activity concerns reaction rates, while complex formation concerns bonding with ligands. None of these is the direct structural reason for alloy formation.

Step 3: Conclusion Similar atomic radii enable transition metals to form alloys. Hence, the correct option is (B).

Quick Tip to Solve: For an alloy question, ask whether atoms can replace one another in the same lattice; compare their atomic radii.

2. Which of the following d-orbitals experience more repulsion in the crystal field splitting of tetrahedral complex? [1 mark]

- (A) $d_{x^2-y^2}, d_{z^2}$
(B) $d_{x^2-y^2}, d_{xy}$
(C) d_{xy}, d_{yz}, d_{z^2}
(D) d_{xy}, d_{yz}, d_{zx}

Correct Answer: (D) d_{xy}, d_{yz}, d_{zx}

Solution:

Concept:

- In a tetrahedral complex, ligands approach between the coordinate axes rather than directly along them.
- The orbitals d_{xy}, d_{yz}, d_{zx} form the higher-energy t_2 set; $d_{x^2-y^2}, d_{z^2}$ form the lower-energy e set.

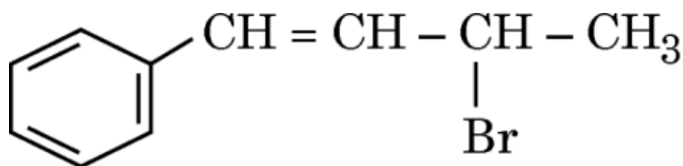
Step 1: Locate the ligand directions The lobes of the orbitals in the t_2 set point between the axes and lie relatively closer to the tetrahedral ligand directions. They therefore experience greater electrostatic repulsion and are raised in energy relative to the two orbitals directed along the axes.

Step 2: Match the complete orbital set The more strongly repelled set contains exactly d_{xy}, d_{yz}, d_{zx} , which is printed in option (D). Option (A) lists the less strongly repelled e set. Options (B) and (C) mix an orbital of the e set with members of the t_2 set, so neither is correct.

Step 3: Conclusion The d_{xy}, d_{yz}, d_{zx} orbitals experience more repulsion. Hence, the correct option is (D).

Quick Tip to Solve: For tetrahedral splitting, remember that the three orbitals with two different coordinate subscripts form the higher-energy set.

3. The position of -Br in the compound shown can be classified as: [1 mark]



- (A) Vinylic
(B) Allylic
(C) Benzylic
(D) Aryl

Correct Answer: (B) Allylic

Solution:**Concept:**

- An allylic halide has its halogen bonded to an sp^3 -hybridised carbon directly adjacent to a carbon-carbon double bond.
- A vinylic halogen is bonded directly to an alkene carbon; benzylic and aryl positions must instead be identified relative to an aromatic ring.

Step 1: Inspect the carbon bearing bromine The printed structure is $C_6H_5-CH=CH-CH(Br)-CH_3$. Bromine is attached to the saturated CH carbon immediately next to the $CH=CH$ unit. This carbon is not itself a member of the double bond and is therefore allylic.

Step 2: Exclude the other classifications Vinylic would require bromine on one of the two double-bond carbons. Benzylic would require its carbon to be directly attached to the benzene ring, whereas here the alkene lies between that ring and the brominated carbon. Aryl would require bromine directly on a ring carbon. All three alternatives fail these structural tests.

Step 3: Conclusion The position of bromine is allylic. Hence, the correct option is (B).

Quick Tip to Solve: First locate the carbon bonded to Br: beside a double bond means allylic; directly on the double bond means vinylic.

4. Williamson synthesis is an example of:

[1 mark]

- (A) Nucleophilic addition reaction
- (B) Electrophilic substitution reaction
- (C) Nucleophilic substitution reaction
- (D) Electrophilic addition reaction

Correct Answer: (C) Nucleophilic substitution reaction

Solution:**Concept:**

- Williamson synthesis prepares an ether by reacting an alkoxide ion with an alkyl halide.
- The alkoxide is a nucleophile and displaces the halide leaving group, generally through an S_N2 mechanism.

Step 1: Identify the reacting species The negatively charged oxygen of an alkoxide donates an electron pair to the electrophilic carbon bonded to a halogen. For example,



A new carbon-oxygen bond forms while the carbon-bromine bond breaks.

Step 2: Classify the bond changes Because a nucleophile replaces a leaving group, the process is nucleophilic substitution. It is not addition: the reaction does not add across a multiple bond. Electrophilic substitution and electrophilic addition are also excluded because the attacking species is the electron-rich alkoxide, not an electrophile.

Quick Tip to Solve: In Williamson synthesis, circle the alkoxide nucleophile and the departing halide; replacement of the latter identifies substitution.

Step 3: Conclusion Williamson synthesis is a nucleophilic substitution reaction. Hence, the correct option is (C).

Quick Tip to Solve: In Williamson synthesis, circle the alkoxide nucleophile and the departing halide; replacement of the latter identifies substitution.

5. Number of possible stereoisomers for the complex $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$ will be:

[1 mark]

- (A) 3
- (B) 4
- (C) 2
- (D) 1

Correct Answer: (A) 3

Solution:

Concept:

- In $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$, each en ligand is bidentate, so the coordination number of the complex cation is six.
- An octahedral $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ion has cis and trans geometrical arrangements; stereoisomers include any optical partners as separate isomers.

Step 1: Count the geometrical arrangements The two coordinated chloride ligands can occupy adjacent sites, giving the cis form, or opposite sites, giving the trans form. The chloride outside the coordination sphere is a counter-ion and does not provide another ligand position or another stereoisomer.

Step 2: Include the optical forms The cis arrangement is chiral and exists as two non-superimposable mirror-image forms, conventionally denoted Δ and Λ . The trans arrangement is achiral and contributes only one form. Thus the total is $2 + 1 = 3$. Option (C) counts only geometrical forms, while four and one do not match the full stereoisomer count.

Step 3: Conclusion There are three stereoisomers. Hence, the correct option is (A).

Quick Tip to Solve: For this octahedral complex, count cis as two optical partners and trans as one; do not stop after counting geometrical arrangements.

6. The correct order of decreasing basic strength of $\text{CH}_3\text{-NH}_2$, $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$ in aqueous solution is: [1 mark]

- (A) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{-NH}_2$
(B) $\text{CH}_3\text{-NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
(C) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{-NH}_2 > (\text{CH}_3)_3\text{N}$
(D) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{-NH}_2$

Correct Answer: (C) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{-NH}_2 > (\text{CH}_3)_3\text{N}$

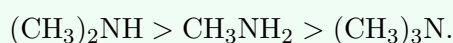
Solution:

Concept:

- Aqueous amine basicity depends on electron donation by alkyl groups and the solvation of the conjugate ammonium ion.
- For methylamines in water, the balance gives secondary amine greater basicity than primary amine, followed by tertiary amine.

Step 1: Balance electron donation and hydration Methyl groups increase electron density on nitrogen through their positive inductive effect, favouring proton acceptance. However, the protonated amine must also be stabilised by water. Increasing substitution reduces effective hydration of the ammonium ion, so the gas-phase trend cannot simply be carried over to aqueous solution.

Step 2: Compare the three given amines Dimethylamine combines strong electron donation with effective hydration of its conjugate acid and is the strongest of these three. Methylammonium is better hydrated than trimethylammonium, making methylamine stronger than trimethylamine in water. Therefore



Options (A) and (D) overrate trimethylamine; (B) incorrectly puts methylamine above dimethylamine.

Step 3: Conclusion The order is dimethylamine, methylamine, then trimethylamine. Hence, the correct option is (C).

Quick Tip to Solve: Check that the solvent is water: for methylamines use secondary, primary, tertiary; the inductive effect alone gives the wrong order.

7. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased: [1 mark]

- (A) vapour pressure of the solution increases
(B) heating occurs
(C) cooling occurs
(D) equilibrium remains unaffected

Correct Answer: (C) cooling occurs

Solution:

Concept:

- At liquid-vapour equilibrium, the rates of evaporation and condensation are equal.

Quick Tip to Solve: Track latent heat when pressure suddenly drops: increased evaporation takes heat from the liquid and produces cooling.

- Evaporation absorbs latent heat; lowering the pressure favours formation of more vapour from the liquid.

Step 1: Determine the immediate response A sudden pressure reduction disturbs the existing liquid-vapour equilibrium. More liquid evaporates to replenish vapour under the reduced pressure. The liquid-to-vapour change requires energy to overcome intermolecular attractions and is therefore an endothermic process.

Step 2: Trace the source of latent heat During this immediate evaporation, energy is taken from the liquid and its surroundings, so their temperature falls and cooling occurs. Heating has the opposite sign. Equilibrium cannot remain unaffected because pressure was disturbed. An increase of equilibrium vapour pressure is not the immediate consequence: vapour pressure is governed by temperature, which initially falls through evaporative cooling.

Step 3: Conclusion Cooling occurs on suddenly decreasing the pressure. Hence, the correct option is (C).

Quick Tip to Solve: Track latent heat when pressure suddenly drops: increased evaporation takes heat from the liquid and produces cooling.

8. The boiling point of one molal NaCl solution, assuming NaCl to be completely dissociated in water is: (K_b for water = $0.52 \text{ K kg mol}^{-1}$) [1 mark]

- (A) 100.52°C
- (B) 101.04°C
- (C) 100.04°C
- (D) 101.52°C

Correct Answer: (B) 101.04°C

Solution:

Concept:

- Boiling-point elevation is a colligative property: $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.
- Complete dissociation of NaCl gives one Na^+ ion and one Cl^- ion per formula unit; hence $i = 2$.

Step 1: Calculate the elevation Here $m = 1 \text{ mol kg}^{-1}$ and $K_b = 0.52 \text{ K kg mol}^{-1}$. Therefore

$$\Delta T_b = 2 \times 0.52 \times 1 = 1.04 \text{ K}.$$

A temperature rise of one kelvin equals a rise of one degree Celsius.

Step 2: Add the elevation to the boiling point of water Taking the normal boiling point of pure water as 100°C , the solution boils at $100 + 1.04 = 101.04^\circ\text{C}$. Option (A) ignores dissociation and uses $i = 1$. Options (C) and (D) give elevations of 0.04 and 1.52°C , neither of which follows from $iK_b m$.

Step 3: Conclusion The boiling point is 101.04°C . Hence, the correct option is (B).

Quick Tip to Solve: For a completely dissociated 1:1 electrolyte, double $K_b m$ before adding the elevation to the solvent boiling point.

9. The rate of a first order reaction is $5.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ when the concentration of reactant is 0.2 mol L^{-1} . The rate constant 'k' is: [1 mark]

(A) $5.6 \times 10^{-3} \text{ s}^{-1}$

(B) $2.8 \times 10^{-4} \text{ s}^{-1}$

(C) $2.8 \times 10^{-5} \text{ s}^{-1}$

(D) $2.8 \times 10^{-3} \text{ s}^{-1}$

Correct Answer: (D) $2.8 \times 10^{-3} \text{ s}^{-1}$

Solution:

Concept:

- For a first-order reaction, the instantaneous rate is $r = k[A]$, where $[A]$ is the reactant concentration and k is the rate constant.
- The units of a first-order rate constant are s^{-1} , obtained by dividing rate units by concentration units.

Step 1: Use the first-order rate law The given rate is $5.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ at $[A] = 0.2 \text{ mol L}^{-1}$. Rearranging $r = k[A]$ gives $k = r/[A]$. No integrated rate equation is needed because rate and concentration are given at the same instant.

Step 2: Substitute and compare the options

$$k = \frac{5.6 \times 10^{-4}}{0.2} = 28 \times 10^{-4} = 2.8 \times 10^{-3} \text{ s}^{-1}.$$

Division by 0.2 multiplies the numerical rate by five. Option (A) has the wrong coefficient; (B) and (C) are respectively ten and one hundred times too small. All four options have the appropriate units, so the numerical calculation decides the answer.

Step 3: Conclusion $k = 2.8 \times 10^{-3} \text{ s}^{-1}$. Hence, the correct option is (D).

Quick Tip to Solve: Dividing by 0.2 means multiplying by five; normalize the resulting power of ten only after this division.

10. Consider the following cell at 298 K:



How can we increase the emf of the cell using the same substances?

[1 mark]

- (A) By decreasing only the $[\text{Mg}^{2+}]$ to 0.1 M
- (B) By decreasing only the $[\text{Cu}^{2+}]$ to 0.1 M
- (C) By increasing both $[\text{Mg}^{2+}]$ and $[\text{Cu}^{2+}]$ to 2.0 M
- (D) By increasing only the $[\text{Mg}^{2+}]$ to 2.0 M

Correct Answer: (A) By decreasing only the $[\text{Mg}^{2+}]$ to 0.1 M

Solution:

Concept:

- The cell reaction is $\text{Mg(s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu(s)}$; two electrons are transferred, so $n = 2$.
- At 298 K, the Nernst equation is $E = E^\circ - \frac{0.0591}{2} \log Q$, with $Q = [\text{Mg}^{2+}]/[\text{Cu}^{2+}]$. Pure solids do not appear in Q .

Step 1: Determine which change raises the emf Initially both ionic concentrations are 1.0 M, so $Q = 1$ and $E = E^\circ$. To increase E , make $\log Q$ negative by decreasing Q . Decreasing only $[\text{Mg}^{2+}]$ to 0.1 M gives $Q = 0.1$, increasing the emf by 0.02955 V.

Step 2: Check all remaining concentration changes In (B), decreasing only $[\text{Cu}^{2+}]$ gives $Q = 10$, so the emf decreases. In (C), increasing both concentrations to 2.0 M keeps $Q = 1$, so the emf is unchanged. In (D), increasing only $[\text{Mg}^{2+}]$ gives $Q = 2$, so the emf again decreases. Only (A) reduces the reaction quotient.

Step 3: Conclusion Decrease only $[\text{Mg}^{2+}]$ to 0.1 M. Hence, the correct option is (A).

Quick Tip to Solve: Write the net cell reaction first: lowering product-ion concentration or raising reactant-ion concentration increases emf.

11. Which of the following reagent is used to convert benzene diazonium chloride to benzene?

[1 mark]

- (A) H_2O
- (B) LiAlH_4
- (C) $\text{C}_2\text{H}_5\text{OH}$
- (D) CuCN

Correct Answer: (C) $\text{C}_2\text{H}_5\text{OH}$

Solution:

Concept:

- Arenediazonium salts can undergo replacement of the diazonium group by hydrogen, releasing nitrogen gas.
- Ethanol reduces benzene diazonium chloride to benzene and is itself oxidised to ethanal.

Quick Tip to Solve: Remember the product pair: ethanol gives benzene from a diazonium salt and becomes ethanal in the same reaction.

Step 1: Identify the required replacement The conversion $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \rightarrow \text{C}_6\text{H}_6$ requires replacement of $-\text{N}_2^+$ by hydrogen. Ethanol supplies the reducing action in the standard reaction:



Step 2: Distinguish the other reagents Water hydrolyses benzene diazonium chloride to phenol, not benzene. Copper(I) cyanide replaces the diazonium group by $-\text{CN}$ to give benzonitrile. Lithium aluminium hydride is a general reducing agent but is not the standard reagent for this diazonium-to-benzene conversion among the listed choices. Ethanol is the specified textbook reagent that gives the required hydrogen replacement.

Step 3: Conclusion The reagent is $\text{C}_2\text{H}_5\text{OH}$. Hence, the correct option is (C).

Quick Tip to Solve: Remember the product pair: ethanol gives benzene from a diazonium salt and becomes ethanal in the same reaction.

12. Which of the following is a water-soluble vitamin?

[1 mark]

- (A) Vitamin K
- (B) Vitamin A
- (C) Vitamin B
- (D) Vitamin D

Correct Answer: (C) Vitamin B

Solution:

Concept:

- Vitamins are classified into water-soluble and fat-soluble groups according to their solubility.
- The B-group vitamins and vitamin C are water-soluble; vitamins A, D, E and K are fat-soluble.

Step 1: Locate vitamin B in the solubility classification The name vitamin B denotes the B-complex group. These vitamins belong to the water-soluble class, along with vitamin C. The question asks for classification by solubility, so their physiological roles are not needed to distinguish the options.

Step 2: Eliminate the fat-soluble alternatives Vitamin K in (A), vitamin A in (B) and vitamin D in (D) all belong to the fat-soluble group A, D, E, K. They therefore cannot be selected as the water-soluble vitamin here. Vitamin B in (C) is the only listed member of the water-soluble group, which makes the choice unique.

Step 3: Conclusion Vitamin B is water-soluble. Hence, the correct option is (C).

Quick Tip to Solve: Memorize A, D, E and K as the fat-soluble set; B-group vitamins and C form the water-soluble set.

13. Assertion (A): Alcohols act as Bronsted bases as well as Bronsted acids.

Reason (R): Alcohols react as both nucleophiles and electrophiles.

[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:

- A Bronsted acid donates a proton; a Bronsted base accepts a proton. Alcohols have an O–H proton and a lone pair on oxygen.
- Nucleophilic and electrophilic behaviour concerns electron-pair donation and acceptance during reactions; it does not by itself establish proton donation and acceptance.

Step 1: Judge the Assertion An alcohol can donate its O–H proton to a sufficiently strong base, forming an alkoxide RO^- . Its oxygen lone pair can also accept a proton from an acid, forming ROH_2^+ . Thus alcohols can act as both Bronsted acids and Bronsted bases, so Assertion (A) is true.

Step 2: Judge the Reason Alcohols can participate as nucleophiles through the lone pair on oxygen. They can also undergo reactions as electrophiles, especially after protonation makes water a suitable leaving group and allows a nucleophile to attack the carbon bearing oxygen. Thus Reason (R) is also true.

Step 3: Check the explanatory connection The Assertion is specifically about transfer of a proton: donation from the O–H group and acceptance by oxygen. The Reason states a different reaction classification and does not explain these two proton-transfer processes. Hence the Reason is true but is not the correct explanation. This excludes (A), while the truth of both statements excludes (C) and (D).

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

Quick Tip to Solve: For a Bronsted assertion, test donation and acceptance of H^+ ; do not replace this test with a general reaction label.

14. Assertion (A): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Reason (R): Diazonium salts of aromatic amines undergo resonance.

[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:

- Resonance delocalisation stabilises an ion by distributing its electronic structure over conjugated atoms.
- In an aromatic diazonium ion, the diazonium group is conjugated with the benzene ring; the corresponding aliphatic diazonium ion lacks this aromatic conjugation.

Step 1: Judge the Assertion Aromatic diazonium salts are relatively more stable than aliphatic diazonium salts. Arenediazonium salts can be maintained in cold aqueous solution, whereas aliphatic diazonium salts readily lose nitrogen and decompose. The statement compares their relative stability and does not claim that aromatic salts are indefinitely stable. Assertion (A) is true.

Step 2: Judge the Reason The diazonium group attached directly to an aromatic ring participates in resonance with the ring. Its electronic structure is delocalised through this conjugated system. Thus aromatic diazonium salts undergo resonance, and Reason (R) is true.

Step 3: Connect resonance with stability Resonance provides additional stabilisation to the aromatic diazonium ion that is absent in the aliphatic counterpart. It directly accounts for the greater stability asserted in A. Therefore (B) is excluded because the explanatory link exists, and (C) and (D) are excluded because neither statement is false.

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

Quick Tip to Solve: Check direct attachment to the aromatic ring: conjugation of the diazonium group provides the extra stabilisation.

15. Assertion (A): For complex reaction, order of reaction is given by the fast step.

Reason (R): Order of reaction is determined experimentally.

[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:

- Reaction order is the sum of the powers of concentration terms in the experimentally determined rate law.
- A complex reaction occurs through several elementary steps; the slow, rate-determining step controls the overall rate.

Step 1: Evaluate the assertion The assertion is false. A fast step does not generally determine the overall rate. The slow step limits the rate, and its rate expression, together with any necessary preceding equilibria, gives the observable rate law. Therefore the order cannot simply be assigned from the fast step.

Step 2: Evaluate the reason The reason is true. Reaction order is established experimentally by studying how the rate changes with reactant concentrations. If the observed rate law is $r = k[A]^m[B]^n$, the overall order is $m + n$; it need not equal the sum of coefficients in the overall balanced equation.

Step 3: Check the assertion-reason relationship Since the assertion is false while the reason is true, the reason cannot explain the assertion. Options (A) and (B) incorrectly treat the assertion as true, and option (C) also incorrectly treats the reason as false.

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

Quick Tip to Solve: In a multistep mechanism, look for the slow step when considering rate; obtain order from the experimentally verified rate law.

16. Assertion (A): $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ has positive value (+0.34 V).

Reason (R): It is due to its low $\Delta_{\text{hyd}}H^\circ$ and high $\Delta_{\text{a}}H^\circ$.

[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 standard reduction potential measures the tendency of an aqueous metal ion to be reduced relative to the standard hydrogen electrode.
- Formation of an aqueous metal ion involves atomisation and ionisation, requiring energy, followed by hydration, which releases energy. Their combined energetics influence the electrode potential.

Step 1: Evaluate the assertion The assertion is true. For the reduction half-reaction



This positive value indicates that aqueous copper(II) ions have a greater tendency to be reduced than hydrogen ions under standard conditions.

Step 2: Evaluate the reason The reason is true in the stated comparison of energy contributions. Copper has a high enthalpy of atomisation, whereas the hydration energy released is insufficient to compensate for the energy required for atomisation and ionisation. Thus the low hydration contribution mentioned here means relatively low compensating energy release, not a positive hydration enthalpy: hydration itself is exothermic.

Step 3: Check whether the reason explains the assertion This unfavourable energy balance for forming aqueous copper(II) ions from copper metal explains the positive standard reduction potential. Hence the reason explains the assertion; option (B) denies that connection, while (C) and (D) incorrectly declare one statement false.

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

Quick Tip to Solve: For copper's positive potential, compare the energy needed for atomisation and ionisation with the compensating energy released on hydration.

Section B (10 marks)

17(a). Explain the following with the help of Henry's law:

(i) Bends

(ii) Anoxia

[2 marks]

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the gas's partial pressure above the liquid, x its mole fraction dissolved in the liquid, and K_H Henry's law constant at a fixed temperature.
- Thus, at fixed temperature, gas solubility increases with its partial pressure and decreases when that pressure falls.

Step 1: Explain bends in divers At great depth, a diver breathes air at high pressure. The increased partial pressure of nitrogen causes more N_2 to dissolve in the blood, according to Henry's law. If the diver ascends too rapidly, the pressure falls suddenly and the dissolved nitrogen can no longer remain dissolved in the same amount. It escapes as gas bubbles in blood and tissues, causing painful decompression sickness called bends. Slow ascent allows nitrogen to leave gradually through the lungs.

Step 2: Explain anoxia at high altitude At high altitude, atmospheric pressure and hence the partial pressure of oxygen are low. Henry's law then predicts a smaller dissolved concentration of oxygen in the blood. The resulting oxygen deficiency in body tissues is called anoxia; it may cause weakness and difficulty thinking clearly. Thus low oxygen partial pressure, rather than a changed percentage of oxygen in air, is the relevant cause.

Step 3: Conclusion Bends arise from nitrogen bubbles formed after rapid decompression; anoxia at high altitude arises from insufficient dissolved oxygen due to its low partial pressure.

Quick Tip to Solve: Apply $x = p/K_H$: increased pressure dissolves more gas, while a sudden pressure drop releases gas; at altitude focus specifically on oxygen partial pressure.

OR

17(b). How does sprinkling of salt help in clearing the snow covered roads in hilly areas? Write the name of the colligative property involved in this process.

[2 marks]

Solution:

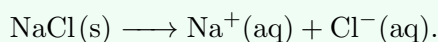
Concept:

- Adding a non-volatile solute to water lowers its freezing point. This colligative property is called depression of freezing point.
- For a dilute solution, $\Delta T_f = iK_f m$, where m is solute molality, K_f the solvent's freezing-point-depression constant, and i the van't Hoff factor accounting for dissolved particles.

Step 1: Describe how salt forms a solution A thin layer of liquid water is present on the snow or ice

Quick Tip to Solve: When salt is added to snow, identify the solvent as water and the relevant change as a lower freezing point, rather than a raised melting temperature.

surface under suitable conditions. Sprinkled salt dissolves in this water to form a salt solution. For common salt, dissolution produces ions:



These dissolved particles reduce the freezing point of the water relative to that of pure water.

Step 2: Relate the lower freezing point to melting Pure water freezes at 0°C , whereas the salt solution freezes at a lower temperature. If the road temperature is below 0°C but above the freezing point of the resulting brine, snow or ice melts into the solution and the brine remains liquid. This helps loosen and clear the snow. At extremely low temperatures, salt becomes less effective because the surroundings can also be below the brine's freezing point.

Step 3: Conclusion Salt helps clear snow by lowering the freezing point of water and promoting melting under suitable conditions. The colligative property involved is **depression of freezing point**.

Quick Tip to Solve: When salt is added to snow, identify the solvent as water and the relevant change as a lower freezing point, rather than a raised melting temperature.

18. Write the formulas for the following coordination compounds:

(a) Mercury(I) tetrathiocyanato-S-cobaltate(III)

(b) Dichloridobis(ethane-1,2-diamine) platinum(IV) nitrate

[2 marks]

Solution:

Concept:

- Determine a coordination ion's charge by adding the metal oxidation state and all ligand charges; choose counter-ions so the complete compound is electrically neutral.
- Thiocyanato-S is the monovalent SCN^- ligand bound through sulfur; chlorido is Cl^- , ethane-1,2-diamine (en) is neutral, and nitrate is NO_3^- .

Step 1: Write the cobaltate salt in part (a) Cobalt is in oxidation state +3, and four thiocyanato ligands contribute -4 . Hence the complex ion is $[\text{Co}(\text{SCN})_4]^-$, with charge

$$+3 + 4(-1) = -1.$$

The notation SCN puts sulfur next to the central metal to indicate S-coordination. Mercury(I) has oxidation state +1 per mercury atom and exists as the dimeric mercurous cation Hg_2^{2+} . Two singly charged cobaltate anions balance this cation, giving $\text{Hg}_2[\text{Co}(\text{SCN})_4]_2$. Its simplest empirical composition can also be written $\text{Hg}[\text{Co}(\text{SCN})_4]$.

Step 2: Write the platinum nitrate in part (b) Platinum(IV) contributes +4, the two chlorido ligands contribute -2 , and the two en ligands are neutral. Therefore

$$q_{\text{complex}} = +4 + 2(-1) + 2(0) = +2.$$

The coordination cation is $[\text{PtCl}_2(\text{en})_2]^{2+}$, and two nitrate anions are required outside the coordination

Quick Tip to Solve: First calculate the charge inside each bracket; remember that en is neutral and mercury(I) forms the dimeric ion Hg_2^{2+} .

brackets. The neutral salt is therefore $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$.

Step 3: Conclusion (a) $\text{Hg}_2[\text{Co}(\text{SCN})_4]_2$, with empirical formula $\text{Hg}[\text{Co}(\text{SCN})_4]$.

(b) $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$, where en denotes ethane-1,2-diamine.

Quick Tip to Solve: First calculate the charge inside each bracket; remember that en is neutral and mercury(I) forms the dimeric ion Hg_2^{2+} .

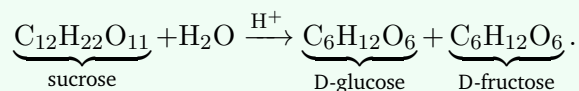
19. Name the sugar present in sugarcane. What are the hydrolysis products of this sugar? Is this sugar a reducing sugar? [2 marks]

Solution:

Concept:

- Sucrose is the principal sugar obtained from sugarcane. It is a disaccharide containing one glucose unit and one fructose unit.
- Hydrolysis cleaves the glycosidic linkage by adding water. A reducing sugar must have a free anomeric carbon that can provide an aldehyde or ketone group in its open-chain form.

Step 1: Identify the sugar and its hydrolysis products The sugar present in sugarcane is sucrose. In dilute acid or in the presence of invertase, it hydrolyses to an equimolar mixture of D-glucose and D-fructose:



Step 2: Explain the reducing nature In sucrose, the glycosidic bond joins C-1 of the glucose unit to C-2 of the fructose unit. These are the two anomeric carbons; both are involved in the linkage, so neither unit has a free hemiacetal or hemiketal group. Therefore sucrose cannot open to provide a free carbonyl group and does not reduce Tollens' reagent or Fehling's solution. Its hydrolysis products are reducing sugars, but sucrose itself is non-reducing.

Step 3: Conclusion Sugarcane contains sucrose; hydrolysis gives D-glucose and D-fructose in equal molar amounts. Sucrose is a non-reducing sugar.

Quick Tip to Solve: Check the anomeric carbons: if both are tied into the glycosidic bond, as in sucrose, the disaccharide is non-reducing.

20. (a) Reactions of which order will show the rate to be independent of the concentration of the reactant? Give one example of this order.

(b) State the condition under which a bimolecular reaction may be kinetically a first order reaction.

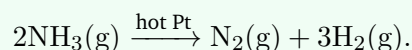
[2 marks]

Solution:

Concept:

- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law. For a zero-order reaction, $r = k[A]^0 = k$.
- Molecularity counts species participating in an elementary event. An excess reactant can have effectively constant concentration, producing a pseudo-first-order rate law.

Step 1: (a) Identify the order and give an example The rate is independent of the concentration of the reactant for a zero-order reaction, because raising the concentration to the power zero gives unity. Thus $r = k$. One example is the decomposition of ammonia on a hot platinum surface under conditions where the surface is saturated:



With the available surface sites occupied, increasing the ammonia concentration does not increase the rate.

Step 2: (b) State the condition for apparent first-order kinetics For a bimolecular reaction with rate law $r = k[A][B]$, take one reactant, say B , in large excess over A . The consumption of B during the reaction is then negligible compared with its initial amount, so $[B]$ remains practically constant:

$$r = k[A][B] \simeq k[B]_0[A] = k'[A], \quad k' = k[B]_0.$$

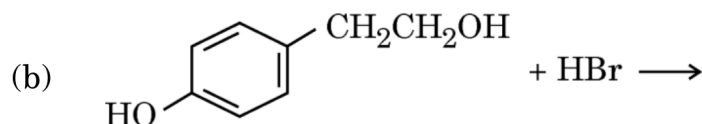
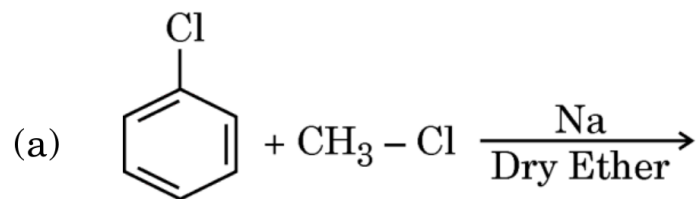
The rate is therefore proportional only to $[A]$, and the reaction is kinetically pseudo-first-order. Hydrolysis of an ester in a large excess of water illustrates this condition.

Step 3: Conclusion (a) Zero-order reactions have concentration-independent rates; ammonia decomposition on hot platinum is an example. (b) A bimolecular reaction becomes pseudo-first-order when one reactant is in large excess and its concentration is effectively constant.

Quick Tip to Solve: Absorb the nearly constant excess-reactant concentration into k' ; the remaining concentration power gives the observed order.

21. Draw the structures of major products in each of the following reactions:

[2 marks]

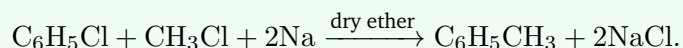


Solution:

Concept:

- The Wurtz–Fittig reaction couples an aryl halide and an alkyl halide with sodium in dry ether, forming an alkylbenzene.
- Hydrogen bromide converts an aliphatic alcohol group into an alkyl bromide. A phenolic hydroxyl group attached directly to an aromatic ring is not replaced by bromide under these conditions.

Step 1: (a) Couple the phenyl and methyl groups The Wurtz–Fittig reaction forms a bond between the phenyl group and the methyl group, producing methylbenzene (toluene):

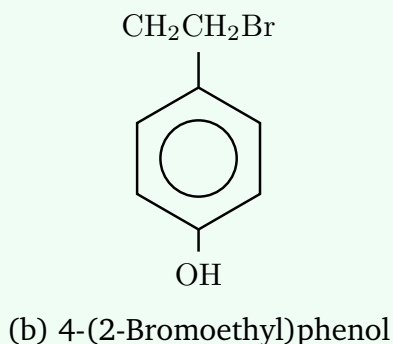
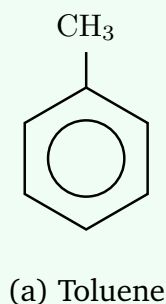


The chlorine atoms leave as sodium chloride.

Step 2: (b) Replace the side-chain hydroxyl group The reactant is $p\text{-HO-C}_6\text{H}_4\text{-CH}_2\text{CH}_2\text{OH}$. HBr replaces the terminal alcoholic hydroxyl group by bromide after protonation:



The phenolic -OH remains unchanged: resonance strengthens its aryl carbon–oxygen bond, preventing ordinary substitution by HBr. The product is 4-(2-bromoethyl)phenol.



Structures of (a) toluene and (b) 4-(2-bromoethyl)phenol

Step 3: Conclusion The products are (a) toluene and (b) 4-(2-bromoethyl)phenol, as drawn above.

Quick Tip to Solve: In part (b), replace only the terminal alcoholic -OH by Br; retain the phenolic -OH on the ring.

Section C (21 marks)

22. What happens when:

(a) Propanenitrile is treated with phenyl magnesium bromide followed by hydrolysis?

(b) p-fluorotoluene is treated with CrO_3 in the presence of acetic anhydride followed by hydrolysis with aqueous acid.

(c) Phthalic acid is treated with NH_3 followed by heating?

Write chemical reactions in support of your answer.

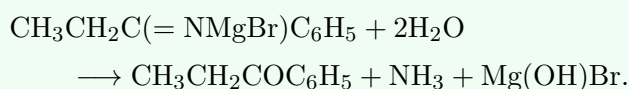
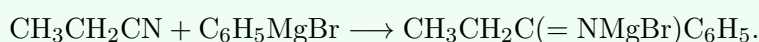
[3 marks]

Solution:

Concept:

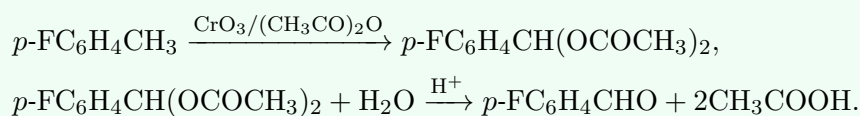
- A Grignard reagent adds once to the carbon of a nitrile group. Hydrolysis of the resulting imine magnesium salt gives a ketone.
- Chromium trioxide in acetic anhydride oxidises an aromatic methyl group to a protected aldehyde derivative; acidic hydrolysis releases the aldehyde.
- Ortho-dicarboxylic acids react with ammonia and undergo dehydration on heating to form a cyclic imide.

Step 1: (a) Add phenylmagnesium bromide to propanenitrile Addition to the nitrile gives an imine magnesium salt; hydrolysis forms a ketone:



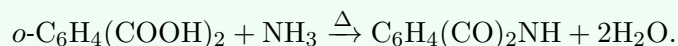
The product is propiophenone (1-phenylpropan-1-one); its carbonyl carbon is the original nitrile carbon.

Step 2: (b) Oxidise the methyl side chain of p-fluorotoluene CrO_3 in acetic anhydride converts the methyl group into the corresponding benzylidene diacetate, $p\text{-FC}_6\text{H}_4\text{CH}(\text{OCOCH}_3)_2$. Hydrolysis with aqueous acid gives p-fluorobenzaldehyde. The fluorine substituent remains attached to the ring:



The diacetate protects the aldehyde from further oxidation until hydrolysis.

Step 3: (c) Form the cyclic imide from phthalic acid The ammonium salt of phthalic acid dehydrates on heating to form a five-membered imide ring:



Phthalimide has an NH group bonded to both carbonyl carbons; the ortho arrangement permits ring closure.

Step 4: Conclusion (a) Propanenitrile gives propiophenone, $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$. (b) p-Fluorotoluene

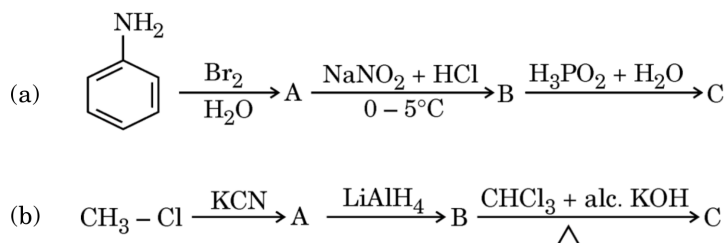
Quick Tip to Solve: Track the reactive group in each part: nitrile carbon becomes a ketone, the aromatic methyl group becomes CHO, and adjacent COOH groups form a cyclic imide.

gives *p*-fluorobenzaldehyde, *p*-FC₆H₄CHO. (c) Phthalic acid gives phthalimide, C₆H₄(CO)₂NH, on reaction with ammonia followed by heating.

Quick Tip to Solve: Track the reactive group in each part: nitrile carbon becomes a ketone, the aromatic methyl group becomes CHO, and adjacent COOH groups form a cyclic imide.

23. Give the structures of A, B and C in the following reactions:

[3 marks]

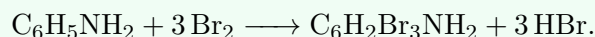


Solution:

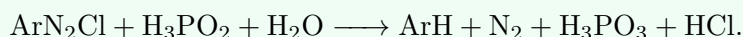
Concept:

- Aniline activates its two ortho positions and its para position, so bromine water produces 2,4,6-tribromoaniline.
- Diazotisation gives a diazonium salt at 0–5 °C; hypophosphorous acid replaces the diazonium group with hydrogen.
- KCN extends the chain by one carbon. Nitrile reduction gives a primary amine; the carbylamine reaction gives an isocyanide.

Step 1: Identify the products in sequence (a) Bromine water substitutes at both ortho positions and the para position, giving A, 2,4,6-tribromoaniline:

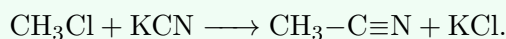


Diazotisation of A with the printed cold acidified nitrite gives B, 2,4,6-tribromobenzenediazonium chloride, 2,4,6-Br₃C₆H₂-N₂⁺ Cl⁻. Finally, H₃PO₂ replaces the diazonium group by hydrogen:



Here Ar is the tribromophenyl group. C is 1,3,5-tribromobenzene, C₆H₃Br₃, with the ring numbered afresh after amino-group removal.

Step 2: Identify the products in sequence (b) Cyanide substitutes for chloride through its carbon end:

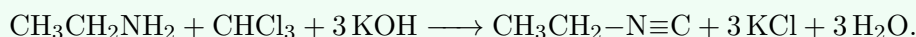


A is ethanenitrile; reduction gives the primary amine B, ethanamine:



Quick Tip to Solve: Track the cyanide carbon through reduction: methyl chloride gives a two-carbon amine. In the carbylamine product, write the ethyl group bonded to nitrogen, not carbon.

Heating B with the printed chloroform and alcoholic alkali gives C:



C is ethyl isocyanide, with the ethyl group bonded to nitrogen.

Step 3: Conclusion (a) A: 2,4,6-tribromoaniline; B: 2,4,6-tribromobenzenediazonium chloride; C: 1,3,5-tribromobenzene.

(b) A: $\text{CH}_3\text{C}\equiv\text{N}$; B: $\text{CH}_3\text{CH}_2\text{NH}_2$; C: $\text{CH}_3\text{CH}_2\text{N}\equiv\text{C}$.

Quick Tip to Solve: Track the cyanide carbon through reduction: methyl chloride gives a two-carbon amine. In the carbylamine product, write the ethyl group bonded to nitrogen, not carbon.

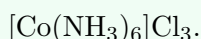
24(a). When a coordination compound $\text{CoCl}_3 \cdot 6\text{NH}_3$ is mixed with excess of AgNO_3 solution, 3 moles of AgCl are precipitated per mole of the compound. Write the structural formula of the complex, IUPAC name, its hybridisation and magnetic behaviour on the basis of valence bond theory. [3 marks]

Solution:

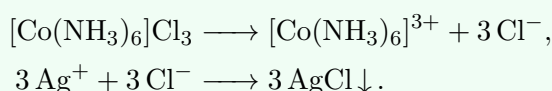
Concept:

- Excess AgNO_3 precipitates chloride ions outside the coordination sphere as AgCl . A chloride ligand coordinated to the metal is not counted as a freely ionisable chloride ion.
- Ammonia is a neutral monodentate ligand. Six ammonia ligands give coordination number six and an octahedral complex.
- In valence bond theory, low-spin d^6 cobalt(III) pairs its six electrons in three $3d$ orbitals, leaving two $3d$ orbitals available for d^2sp^3 hybridisation.

Step 1: Determine the coordination sphere and name One mole of the compound yields three moles of AgCl , so all three chloride ions must lie outside the coordination sphere. The six ammonia molecules are coordinated to cobalt, giving the structural formula



Its dissociation and precipitation are



Since ammonia carries no charge, cobalt has oxidation state +3. The cation is named hexaamminecobalt(III), and the counter-ion is chloride. The complete IUPAC name is therefore hexaamminecobalt(III) chloride. The double m in “ammine” distinguishes a coordinated ammonia ligand from an organic amine.

Step 2: Explain hybridisation and magnetism using VBT Cobalt has atomic number 27 and the ground-state configuration $[\text{Ar}] 3d^7 4s^2$. Removing the two $4s$ electrons and one $3d$ electron gives Co^{3+} the configuration $[\text{Ar}] 3d^6$. In this cobalt(III) complex, the ligand field is strong enough to pair the

Quick Tip to Solve: First place all three chloride ions outside the bracket using the AgCl result; then use neutral ammonia to obtain cobalt(III), a paired d^6 inner orbital complex.

six $3d$ electrons in three orbitals. Thus two inner $3d$ orbitals are empty. These two $3d$ orbitals, one $4s$ orbital and three $4p$ orbitals hybridise to form six equivalent d^2sp^3 orbitals, each accepting a lone pair from an ammonia ligand. The resulting complex is an inner orbital, octahedral complex. All six metal d electrons are paired, so the number of unpaired electrons is $n = 0$. Accordingly, its spin-only magnetic moment is

$$\mu = \sqrt{n(n+2)} \mu_B = 0,$$

and the compound is diamagnetic.

Step 3: Conclusion Structural formula: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$; IUPAC name: hexaamminecobalt(III) chloride; hybridisation: d^2sp^3 , with octahedral geometry; magnetic behaviour: diamagnetic because there are no unpaired electrons.

Quick Tip to Solve: First place all three chloride ions outside the bracket using the AgCl result; then use neutral ammonia to obtain cobalt(III), a paired d^6 inner orbital complex.

OR

24(b). (i) How many geometrical isomers are possible in each of the following complexes?

(I) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

(II) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex. Why? [Atomic number: Co = 27, Ni = 28]

(iii) Write the formula of Wilkinson catalyst and its use.

[3 marks]

Solution:

Concept:

- In octahedral MA_3B_3 , identical ligands occupy one face (fac) or a meridian (mer).
- Octahedral hybridisation is inner orbital d^2sp^3 using $3d$, or outer orbital sp^3d^2 using $4d$.
- Wilkinson's rhodium(I) catalyst contains three triphenylphosphine ligands and catalyses alkene hydrogenation.

Step 1: Count the geometrical arrangements in part (i) (I) In $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, all three oxalate ligands are identical bidentate ligands. Each chelates two adjacent sites. There is one geometrical arrangement and no geometrical isomerism. Its mirror-image forms are optical isomers, so do not count them here.

(II) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ has two geometrical isomers. In fac, all three chlorides occupy one face and are mutually cis. In mer, they lie in a plane through the metal, with two trans to each other.

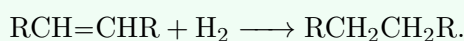
Step 2: Explain the orbital choice in part (ii) In $[\text{Co}(\text{NH}_3)_6]^{3+}$, cobalt(III) has configuration $[\text{Ar}] 3d^6$. Pairing in three $3d$ orbitals leaves two vacant. These combine with $4s$ and three $4p$ orbitals for d^2sp^3 hybridisation: an inner orbital complex.

In $[\text{Ni}(\text{NH}_3)_6]^{2+}$, nickel(II) has configuration $[\text{Ar}] 3d^8$. Eight electrons require at least four $3d$ orbitals, so two vacant inner orbitals are impossible. One $4s$, three $4p$ and two vacant $4d$ orbitals are used instead, giving sp^3d^2 hybridisation and an outer orbital complex. This nickel complex has two

Quick Tip to Solve: Separate optical isomers from geometrical isomers for the tris-oxalato complex. For the inner versus outer orbital comparison, ask whether the electron count can leave two $3d$ orbitals vacant.

unpaired electrons.

Step 3: State Wilkinson's catalyst and its use in part (iii) The formula is $[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$, commonly written $[\text{RhCl}(\text{PPh}_3)_3]$, where Ph denotes the phenyl group C_6H_5 . It catalyses homogeneous hydrogenation of alkenes to alkanes:



Step 4: Conclusion (i) $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$: one geometrical arrangement, hence no geometrical isomerism; $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$: two geometrical isomers, fac and mer.

(ii) Co^{3+} , d^6 , provides two vacant inner $3d$ orbitals after pairing; Ni^{2+} , d^8 , cannot, and uses outer $4d$ orbitals.

(iii) Wilkinson's catalyst is $[\text{RhCl}(\text{PPh}_3)_3]$, used for hydrogenation of alkenes.

Quick Tip to Solve: Separate optical isomers from geometrical isomers for the tris-oxalato complex. For the inner versus outer orbital comparison, ask whether the electron count can leave two $3d$ orbitals vacant.

25. Answer the following questions:

- (a) Why is direct current (DC) not used to measure the resistance of an ionic solution?
- (b) Why are the products of electrolysis different for the electrolysis of aqueous solution of AgNO_3 with silver electrodes and electrolysis of aqueous solution of AgNO_3 with platinum electrodes?
- (c) Why are magnesium blocks fixed to the iron pipelines carrying water? [3 marks]

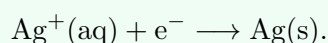
Solution:

Concept:

- The resistance of an ionic solution depends on its ion concentration and the state of the electrodes; an applied current must not appreciably change these during measurement.
- At the cathode reduction occurs, whereas the anode reaction depends on whether the electrode is an active metal or an inert conductor.
- A metal more easily oxidised than iron can protect iron by acting as a sacrificial anode.

Step 1: (a) Effect of direct current on the solution Direct current drives ions continuously towards the same electrodes and causes electrolysis. The resulting deposition or discharge changes the ionic concentrations near the electrodes and produces electrode polarisation. Hence the measured resistance would change during the measurement and would not represent the original solution accurately. Alternating current is used because its rapidly reversing direction minimises electrolysis and polarisation.

Step 2: (b) Compare silver and platinum anodes In both cases, silver ions are reduced at the cathode:

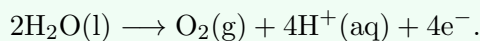


Quick Tip to Solve: For electrolysis, write the cathode reaction first and then ask whether the anode itself can oxidise; for corrosion protection, choose a metal more reactive than iron.

A silver anode is active and dissolves instead of water being oxidised:

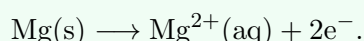


Thus silver is transferred from the anode to the cathode. Platinum is inert, so water is oxidised at its anode:



Therefore oxygen is evolved at a platinum anode, while silver is deposited at the cathode. The different anode behaviour accounts for the different products.

Step 3: (c) Sacrificial protection by magnesium Magnesium is more reactive than iron and oxidises preferentially when electrically connected to the pipeline:



It supplies electrons to the iron, keeping the pipe cathodic and suppressing the oxidation of iron that starts corrosion. Magnesium is gradually consumed, so the blocks must be replaced periodically.

Step 4: Conclusion (a) DC causes electrolysis and polarisation. (b) A silver anode dissolves, whereas an inert platinum anode liberates oxygen. (c) Magnesium acts as a sacrificial anode and protects the iron pipeline from corrosion.

Quick Tip to Solve: For electrolysis, write the cathode reaction first and then ask whether the anode itself can oxidise; for corrosion protection, choose a metal more reactive than iron.

26. Answer the following:

- (a) Which isomer of $\text{C}_4\text{H}_9\text{Br}$ is most reactive towards $\text{S}_{\text{N}}1$ reaction?
- (b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.
- (c) Although chlorine shows strong -I effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why?

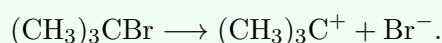
[3 marks]

Solution:

Concept:

- An $\text{S}_{\text{N}}1$ reaction involves slow ionisation to a carbocation, so a more stable carbocation gives a faster reaction.
- Dehydrohalogenation removes a β -hydrogen and the halogen from adjacent carbon atoms. By Saytzeff's rule, the more substituted alkene is generally the major product.
- Chlorine withdraws electron density through its $-I$ effect but donates a lone pair to the benzene ring through resonance; activation and orientation must be considered separately.

Step 1: (a) Select the isomer forming the most stable carbocation Among the isomers of $\text{C}_4\text{H}_9\text{Br}$, 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, forms the tertiary tert-butyl carbocation on loss of bromide:



Quick Tip to Solve: Rank carbocation stability for $\text{S}_{\text{N}}1$, count alkyl groups on each possible double bond for elimination, and separate chlorine's deactivation from its resonance-controlled orientation.

Three methyl groups stabilise this carbocation by their electron-releasing inductive effect and hyper-conjugation. The other isomers form secondary or primary carbocations, which are less stable. Hence 2-bromo-2-methylpropane is the most reactive towards S_N1 .

Step 2: (b) Identify the major elimination product In 1-bromo-1-methylcyclohexane, the carbon bearing bromine is carbon 1. Removal of a hydrogen from either adjacent ring carbon, carbon 2 or carbon 6, together with bromine from carbon 1, creates a double bond inside the ring. The two positions are equivalent and give 1-methylcyclohexene. This alkene has a trisubstituted double bond and is the major product under the usual dehydrohalogenation conditions. Elimination from the methyl group would give the less substituted, exocyclic methylenecyclohexane as a minor product.

Step 3: (c) Explain orientation by chlorine Chlorine's strong $-I$ effect lowers the overall electron density of the ring, making chlorobenzene less reactive than benzene towards electrophilic substitution. However, a chlorine lone pair can overlap with the ring's π system and donate electron density by resonance. This donation particularly favours the ortho and para positions. The arenium-ion intermediates formed by ortho or para attack receive additional resonance stabilisation through lone-pair donation from chlorine; the meta intermediate lacks this stabilisation. Consequently chlorine directs substitution to ortho and para positions despite deactivating the ring overall.

Step 4: Conclusion (a) 2-Bromo-2-methylpropane is most reactive towards S_N1 . (b) The major alkene is 1-methylcyclohexene. (c) Chlorine's resonance donation favours ortho and para attack, although its strong $-I$ effect deactivates the ring.

Quick Tip to Solve: Rank carbocation stability for S_N1 , count alkyl groups on each possible double bond for elimination, and separate chlorine's deactivation from its resonance-controlled orientation.

27. Calculate the vapour pressure of a solution containing 61 g of benzoic acid (molar mass = 122 g mol⁻¹) dissolved in 500 g of benzene when the vapour pressure of pure benzene at this temperature of experiment is 66 torr. Assume complete dimerization of benzoic acid in benzene. [3 marks]

Solution:

Concept:

- For a solution of a non-volatile solute, Raoult's law gives $p = x_{\text{benzene}} p^\circ$, where p° is the vapour pressure of pure benzene and x_{benzene} is its mole fraction in the solution.
- Benzoic acid associates in benzene: $2 \text{C}_6\text{H}_5\text{COOH} \rightleftharpoons (\text{C}_6\text{H}_5\text{COOH})_2$. Complete dimerisation halves the number of dissolved solute particles, giving a van't Hoff factor $i = 1/2$.
- The mole fraction uses the effective moles of solute particles after association, together with the moles of solvent; it does not use the original acid moles unchanged.

Step 1: Find moles of acid and benzene The moles of benzoic acid before association are

$$n_{\text{acid}} = \frac{61 \text{ g}}{122 \text{ g mol}^{-1}} = 0.500 \text{ mol.}$$

Quick Tip to Solve: Halve the benzoic-acid moles before forming the solvent mole fraction, and keep both solvent and dimer moles in the denominator of Raoult's law.

Benzene has formula C_6H_6 , so its molar mass is $6(12) + 6(1) = 78 \text{ g mol}^{-1}$. Hence

$$n_{\text{benzene}} = \frac{500}{78} = 6.41026 \text{ mol.}$$

Step 2: Account for complete dimerisation Every two acid molecules combine into one dimer, so the effective amount of solute particles is

$$n_{\text{dimer}} = \frac{0.500}{2} = 0.250 \text{ mol.}$$

Therefore the solvent mole fraction is

$$x_{\text{benzene}} = \frac{6.41026}{6.41026 + 0.250} = 0.96246.$$

Although association leaves the total mass of benzoic acid unchanged, it reduces the number of solute particles. This makes the lowering of vapour pressure smaller than it would be without association.

Step 3: Apply Raoult's law With pure benzene vapour pressure $p^\circ = 66 \text{ torr}$,

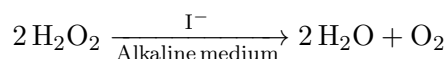
$$p = 66 \left(\frac{500/78}{500/78 + 0.250} \right) = 63.5226 \text{ torr.}$$

As a check, the effective solute mole fraction is $1 - 0.96246 = 0.03754$, so the pressure lowering is $66(0.03754) \approx 2.4774 \text{ torr}$. Subtracting this from 66 torr gives the same solution pressure.

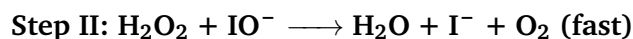
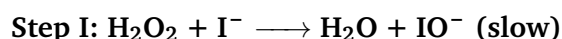
Step 4: Conclusion The vapour pressure of the solution, allowing for complete dimerisation of benzoic acid, is $p \approx 63.52 \text{ torr}$.

Quick Tip to Solve: Halve the benzoic-acid moles before forming the solvent mole fraction, and keep both solvent and dimer moles in the denominator of Raoult's law.

28. Consider the decomposition of hydrogen peroxide (H_2O_2) as per the equation given below:



The mechanism for this reaction was found to be:



(a) Write the rate law expression.

(b) Determine the order of reaction with respect to H_2O_2 , I^- and overall order of reaction.

(c) What is the molecularity of the reaction in Step II?

[3 marks]

Solution:

Concept:

- The slow elementary step determines the rate of a reaction proceeding through a multistep mechanism.
- For an elementary step, the rate law contains the concentrations of its reactants raised to their stoichiometric powers. Reaction order is the sum of these powers.
- Molecularity counts the reacting particles in a single elementary step; it is a positive integer and is distinct from the overall reaction order.

Step 1: Identify the rate-determining step and write the rate law (a) Step I, $\text{H}_2\text{O}_2 + \text{I}^- \longrightarrow \text{H}_2\text{O} + \text{IO}^-$, is slow. One molecule of H_2O_2 and one I^- ion participate in this elementary step, so its rate is proportional to both concentrations:

$$r = k[\text{H}_2\text{O}_2][\text{I}^-].$$

Here k is the rate constant and square brackets denote molar concentration. The fast second step follows the formation of IO^- ; it does not set the rate law. On adding the steps, IO^- cancels as an intermediate and I^- is regenerated as a catalyst.

Step 2: Read the partial and overall orders (b) Each concentration in the rate law has exponent 1. Therefore, the order with respect to H_2O_2 is 1 and the order with respect to I^- is 1. Adding these exponents gives

$$n = 1 + 1 = 2.$$

The coefficient 2 of H_2O_2 in the overall equation must not be used to assign its partial order: the overall equation is not a single elementary step.

Step 3: Count the reacting particles in Step II (c) Step II is $\text{H}_2\text{O}_2 + \text{IO}^- \longrightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2$. Its reactant side contains one H_2O_2 molecule and one IO^- ion. Thus two reacting particles take part in this elementary step, making it bimolecular. Product particles are not counted in molecularity.

Step 4: Conclusion (a) $r = k[\text{H}_2\text{O}_2][\text{I}^-]$. (b) The partial orders are 1 in H_2O_2 and 1 in I^- ; the overall order is 2. (c) Step II has molecularity 2 (bimolecular).

Quick Tip to Solve: Use the slow elementary step for the rate law, then count only the reactant particles in the specific step asked for molecularity.

Section D (8 marks)

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

29(a). Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron releasing groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to yield alkyl halides. Dehydration of alcohols gives alkenes. On oxidation, primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents, while secondary alcohols yield ketones. Tertiary alcohols are resistant to oxidation. The presence of -OH group in phenols activates the aromatic ring towards electrophilic substitution and directs the incoming group to ortho and para positions due to resonance effect.

(a) Write the mechanism of acid dehydration of ethanol to yield ethene.

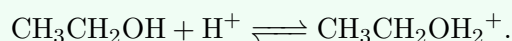
[2 marks]

Solution:

Concept:

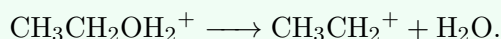
- Acid-catalysed dehydration removes water from ethanol to form ethene. Concentrated H_2SO_4 and heating at 443 K favour alkene formation.
- Protonation converts the poor leaving group $-\text{OH}$ into an oxonium group from which neutral water can leave. Loss of a proton subsequently regenerates the acid catalyst.

Step 1: Protonate the oxygen of ethanol An oxygen lone pair accepts a proton from the acid, giving protonated ethanol (an ethyloxonium ion):



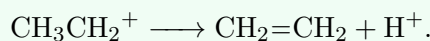
The positive charge is on oxygen. This activation is essential because an unprotonated hydroxyl group would have to leave as the strongly basic OH^- ion.

Step 2: Eliminate water from protonated ethanol In the conventional CBSE stepwise mechanism, cleavage of the carbon–oxygen bond in the protonated alcohol releases neutral water and is the slow step:



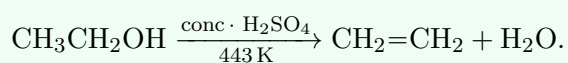
The electron pair in the carbon–oxygen bond moves to oxygen. The resulting ethyl carbocation is the intermediate in this textbook representation.

Step 3: Remove a proton to create the double bond Loss of a proton from the adjacent methyl carbon allows the carbon–hydrogen bond electrons to form the carbon–carbon double bond:



A base in the medium, such as water, accepts the proton. Regeneration of H^+ shows that acid acts as a catalyst rather than a net reactant.

Step 4: Conclusion Protonation, elimination of water and deprotonation convert ethanol to ethene:



Quick Tip to Solve: Show protonation before water leaves and regenerate the proton in the last step; these two features identify acid-catalysed dehydration.

29(b). Why are tertiary alcohols resistant to oxidation?

[1 mark]

Solution:

Concept:

- Normal oxidation of an alcohol to a carbonyl compound removes the hydrogen of the hydroxyl group and a hydrogen attached to the carbon bearing that group.
- In a tertiary alcohol, R_3C-OH , the hydroxyl-bearing carbon is bonded to three carbon groups and has no hydrogen attached to it.

Step 1: Examine the hydroxyl-bearing carbon All four bonds of this carbon are already accounted for: three carbon-carbon bonds and one carbon-oxygen bond. It therefore lacks the hydrogen on the carbinol carbon that is present in primary and secondary alcohols.

Step 2: Explain the resistance to ordinary oxidation Formation of a carbonyl group without breaking the carbon skeleton is consequently impossible by the usual removal of two hydrogens. Tertiary alcohols resist ordinary oxidation. Under vigorous conditions they can undergo oxidative carbon-carbon bond cleavage, giving smaller products; resistance does not mean that oxidation is impossible under every condition.

Step 3: Conclusion Tertiary alcohols resist oxidation because the carbon bearing $-OH$ has no hydrogen; oxidation requires cleavage of a carbon-carbon bond.

Quick Tip to Solve: Check for a hydrogen directly on the carbon bonded to oxygen, rather than counting hydrogens elsewhere in the alcohol.

OR

29(b). Write the structure of the major product expected from the dinitration of 3-methylphenol.

[1 mark]

Solution:

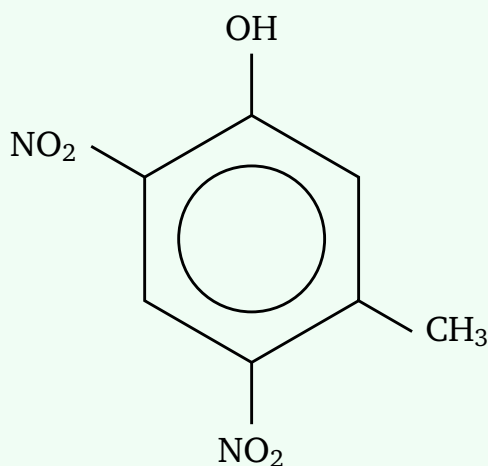
Concept:

- The phenolic $-OH$ group activates the benzene ring and directs electrophilic substitution to its ortho and para positions.
- In 3-methylphenol, take the hydroxyl-bearing carbon as C1 and the methyl-bearing carbon as C3. The methyl group is also an ortho/para director.

Step 1: Identify the favoured positions for nitration The positions C2, C4 and C6 are activated by both substituents: they are ortho or para to the hydroxyl group and also ortho or para to the methyl group. However, C2 lies between the two existing groups and is sterically crowded.

Step 2: Place the two nitro groups and write the structure The major dinitration product has nitro groups at C4 and C6, leaving the crowded C2 position unsubstituted. The hydroxyl and methyl groups retain their original positions. The structure shown below therefore represents 3-methyl-4,6-dinitrophenol, equivalently numbered as 5-methyl-2,4-dinitrophenol.

Quick Tip to Solve: Number from the hydroxyl carbon, mark positions activated by both groups, and avoid C2 because it lies between hydroxyl and methyl.



Major dinitration product of 3-methylphenol

Step 3: Conclusion The major product is 3-methyl-4,6-dinitrophenol: -OH at C1, -CH_3 at C3, and -NO_2 at C4 and C6.

Quick Tip to Solve: Number from the hydroxyl carbon, mark positions activated by both groups, and avoid C2 because it lies between hydroxyl and methyl.

29(c). Why is ortho-nitrophenol more acidic than ortho-methoxyphenol?

[1 mark]

Solution:

Concept:

- Phenol acidity depends on the stability of its conjugate base, the phenoxide ion. Greater stabilisation of the negative charge favours loss of H^+ .
- An ortho nitro group withdraws electrons by both inductive and resonance effects; an ortho methoxy group donates electrons by resonance.

Step 1: Assess the effect of the nitro substituent After ortho-nitrophenol loses its phenolic proton, the electron-withdrawing -NO_2 group stabilises the phenoxide ion. At the ortho position it can withdraw electron density through resonance as well as through its negative inductive effect, dispersing the negative charge.

Step 2: Compare the methoxy substituent The -OCH_3 group in ortho-methoxyphenol donates electron density to the aromatic ring through resonance. This donation makes the negatively charged conjugate base less favourable relative to the nitro-substituted phenoxide. Although methoxy also has an electron-withdrawing inductive effect, its resonance donation provides the relevant contrast here.

Step 3: Conclusion Ortho-nitrophenol is more acidic because -NO_2 stabilises its phenoxide conjugate base by electron withdrawal, whereas the resonance donation of -OCH_3 opposes that stabilisation.

Quick Tip to Solve: Compare the substituted phenoxide ions: an ortho nitro group withdraws charge, while methoxy donates electron density by resonance.

30(a). Carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. They have been broadly classified into three groups - monosaccharides, oligosaccharides and polysaccharides. The carbohydrates may also be classified as either reducing or non-reducing sugars. An important monosaccharide glucose is an aldohexose and is correctly named as D(+)-glucose. It was assigned the open structure on the basis of its reactions with HI, NH_2OH , Br_2 water, $(\text{CH}_3\text{CO})_2\text{O}$ and nitric acid. Despite having the $-\text{CHO}$ group, glucose does not give Schiff's test and hydrogen sulphite addition product with NaHSO_3 . It was found that glucose forms a six-membered ring in which one of the $-\text{OH}$ groups add to the $-\text{CHO}$ group and form a cyclic hemiacetal structure.

(a) How do you explain the following?

(i) Presence of a carbonyl group in glucose

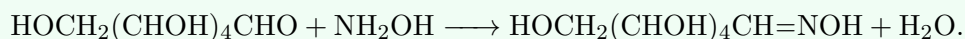
(ii) Presence of five $-\text{OH}$ groups in glucose which are attached to different carbon atoms. [2 marks]

Solution:

Concept:

- A carbonyl group, $\text{C}=\text{O}$, reacts with hydroxylamine, NH_2OH , to form an oxime. This reaction identifies the carbonyl functionality in glucose.
- Each alcoholic $-\text{OH}$ group can be acetylated by acetic anhydride, $(\text{CH}_3\text{CO})_2\text{O}$. The number of acetyl groups introduced gives the number of hydroxyl groups.

Step 1: Identify the carbonyl group through oxime formation Glucose reacts with hydroxylamine to form glucose oxime. For its open-chain form, the reaction is



The conversion of the terminal carbonyl group into $-\text{CH}=\text{NOH}$ provides experimental evidence for a carbonyl group. Oxime formation alone identifies a carbonyl group; the aldehydic nature is additionally supported by oxidation with bromine water.

Step 2: Count the hydroxyl groups through acetylation On treatment with acetic anhydride, glucose forms glucose pentaacetate. Five hydroxyl hydrogens are replaced by acetyl groups, giving five $-\text{OCOCH}_3$ groups. Thus, glucose contains five $-\text{OH}$ groups. The stable nature of the pentaacetate supports their attachment to five different carbon atoms: the corresponding arrangement with two hydroxyl groups on one carbon is generally unstable. In the open-chain structure, the hydroxyl groups occur at carbon atoms 2 through 6.

Step 3: Conclusion (i) Formation of glucose oxime with NH_2OH establishes a carbonyl group. (ii) Formation of stable glucose pentaacetate with acetic anhydride establishes five hydroxyl groups attached to different carbon atoms.

Quick Tip to Solve: Link hydroxylamine to oxime and the carbonyl group; link pentaacetate to five hydroxyl groups, using its stability to explain their positions on different carbon atoms.

30(b). What type of carbohydrates are called reducing sugars?

[1 mark]

Solution:

Concept:

- Reducing sugars are carbohydrates that reduce Fehling's solution or Tollens' reagent.
- A free anomeric centre permits ring opening to a reactive carbonyl form; the sugar is oxidised while the reagent is reduced.

Step 1: State the chemical criterion A carbohydrate is a reducing sugar when it can reduce Fehling's solution or Tollens' reagent. Thus, classification depends on its chemical reducing action, rather than simply on whether it is a monosaccharide or disaccharide.

Step 2: Connect the criterion to the structure Sugars with a free aldehydic or ketonic group, or a free anomeric hydroxyl group that allows a reactive open-chain form, show this behaviour. Glucose and fructose are examples. Fructose reduces these alkaline reagents through conversion to aldoses; therefore, reducing sugars are not restricted to aldoses.

Step 3: Conclusion Carbohydrates which reduce Fehling's solution or Tollens' reagent are called reducing sugars.

Quick Tip to Solve: Define reducing sugars by their action on Fehling's solution or Tollens' reagent; do not exclude fructose merely because it is a ketose.

30(c). In D(+)-glucose, what do the letter 'D' and sign '(+)' represent?

[1 mark]

Solution:

Concept:

- D and L describe relative configuration with reference to D- and L-glyceraldehyde.
- The signs (+) and (–) describe the experimentally observed direction of optical rotation; they are independent of D/L configuration.

Step 1: Interpret the letter D D indicates that glucose has the same relative configuration as D-glyceraldehyde at its penultimate carbon atom. In its standard Fischer projection, with the aldehyde group at the top, the hydroxyl group on carbon 5 is on the right.

Step 2: Interpret the positive sign (+) indicates that glucose is dextrorotatory: it rotates the plane of plane-polarised light to the right. This sign is determined experimentally. The letter D itself does not specify the direction of optical rotation, so D and (+) convey different information.

Step 3: Conclusion D specifies configuration relative to D-glyceraldehyde, whereas (+) means dextrorotatory, or rotation of plane-polarised light to the right.

Quick Tip to Solve: Read D as a configuration label and (+) as an optical-rotation label; never infer the sign of rotation from D alone.

30(c). Draw the six-membered ring structure of α -D(+)-glucose.

[1 mark]

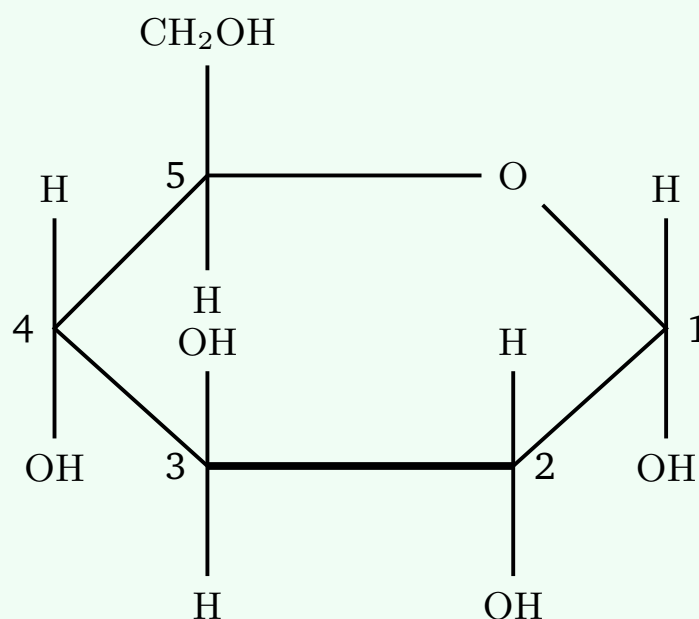
Solution:

Concept:

- The six-membered cyclic hemiacetal of glucose is glucopyranose: the ring contains five carbon atoms and one oxygen atom.
- In the standard Haworth projection of a D sugar, the CH_2OH group at carbon 5 lies above the ring. The α anomer has its anomeric hydroxyl group on the opposite side.

Step 1: Form the pyranose ring The hydroxyl group on carbon 5 adds to the aldehyde group on carbon 1. The resulting ring contains the oxygen from that hydroxyl group and carbon atoms 1 to 5. Carbon 6 remains outside the ring as a CH_2OH substituent.

Step 2: Place the substituents in the Haworth projection Place CH_2OH above the ring at carbon 5. The hydroxyl groups at carbon atoms 2, 3 and 4 point down, up and down, respectively. For the α anomer, place the hydroxyl group at carbon 1 down, opposite to CH_2OH . Each hydrogen points to the opposite side from its hydroxyl or hydroxymethyl substituent.



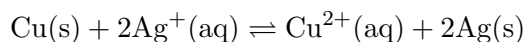
Haworth projection of α -D(+)-glucopyranose

Step 3: Conclusion The diagram shows α -D(+)-glucopyranose, with the anomeric OH below the ring and the CH_2OH group above it.

Quick Tip to Solve: For D-glucose, keep CH_2OH up; then make the carbon-1 hydroxyl point down to obtain the α anomer.

Section E (15 marks)

31(a). (i) Calculate E_{cell}° for the following reaction which is at equilibrium:



Equilibrium constant (K_c) for the cell is 10^{15} . [Given: $\log 10 = 1$]

(ii) Write anode, cathode and overall reaction of lead storage battery when it is in use.

(iii) How much electricity is required in coulombs for the oxidation of 1 mol of FeO to Fe_2O_3 ? [5 marks]

Solution:

Concept:

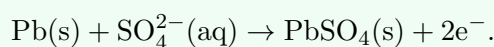
- At equilibrium, the actual cell potential is zero, but the standard cell potential is related to the equilibrium constant by $E_{\text{cell}}^{\circ} = (0.0591/n) \log K_c$ at 298 K. Here n is the number of electrons exchanged per balanced cell reaction.
- During discharge of a lead storage battery, oxidation occurs at the lead anode and reduction at the lead dioxide cathode. Sulphuric acid supplies the sulphate ions and hydrogen ions required in the reactions.
- Faraday's law gives $Q = n_e F$, where n_e is the amount of electrons transferred in moles and $F = 96485 \text{ C mol}^{-1}$ is the Faraday constant.

Step 1: (i) Identify the electron transfer and use the equilibrium constant Copper is oxidised according to $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$, while two silver ions each gain one electron. Thus, $n = 2$ for the cell reaction as written. Combining $\Delta_r G^{\circ} = -nFE_{\text{cell}}^{\circ}$ and $\Delta_r G^{\circ} = -RT \ln K_c$ gives

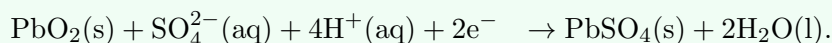
$$E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log(10^{15}) = \frac{0.0591}{2} \times 15 = 0.44325 \text{ V}.$$

The printed superscript asks for the standard potential. The equilibrium condition makes $E_{\text{cell}} = 0$, because the Nernst correction exactly cancels the standard potential when the reaction quotient equals K_c ; it does not make E_{cell}° zero.

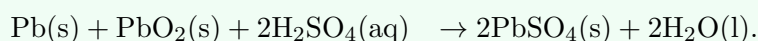
Step 2: (ii) Write the electrode reactions during discharge At the anode, metallic lead undergoes oxidation and forms lead sulphate:



At the cathode, lead dioxide is reduced in the acidic electrolyte:



Adding the two half-reactions cancels the electrons. Expressing the hydrogen and sulphate ions as sulphuric acid gives the overall discharge reaction:



Both plates become coated with lead sulphate, and sulphuric acid is consumed as the battery supplies

Quick Tip to Solve: Read the superscript on the potential carefully; for the charge calculation, count electrons per mole of the stated reactant, not per product formula unit.

electrical energy.

Step 3: (iii) Calculate the charge for oxidation of iron(II) oxide Iron has oxidation state +2 in FeO and +3 in Fe₂O₃. Each iron atom therefore loses one electron. Since one mole of FeO contains one mole of iron atoms, its oxidation involves one mole of electrons:

$$Q = (1 \text{ mol})F = 96485 \text{ C} \simeq 9.65 \times 10^4 \text{ C}.$$

Although the product contains two iron atoms per formula unit, one mole of the reactant forms half a mole of the product. This does not double the charge required for the stated amount of FeO.

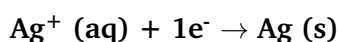
Step 4: Conclusion (i) $E_{\text{cell}}^{\circ} \simeq +0.443 \text{ V}$. (ii) During discharge, lead is oxidised at the anode and lead dioxide is reduced at the cathode, with both forming lead sulphate; the balanced electrode and overall reactions are given in part (ii) above. (iii) $Q \simeq 9.65 \times 10^4 \text{ C}$.

Quick Tip to Solve: Read the superscript on the potential carefully; for the charge calculation, count electrons per mole of the stated reactant, not per product formula unit.

OR

31(b). (i) Conductivity of 0.0024 M acetic acid is $7.2 \times 10^{-5} \text{ S cm}^{-1}$. If Λ_m° for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, then calculate the degree of dissociation (α) of acetic acid.

(ii) Calculate the cell potential for the following half cell reaction at 25°C:



Given that: $[\text{Ag}^+] = 0.01 \text{ M}$ and $E_{\text{Ag}^+/\text{Ag}}^{\circ} = +0.80 \text{ V}$ [$\log 10 = 1$]

(iii) Write the name of the electrolyte used in:

(I) Dry cell

(II) Fuel cell (H₂-O₂)

[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 of 1000 converts litres to cubic centimetres.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^{\circ}$, where Λ_m° is the molar conductivity at infinite dilution, corresponding to complete dissociation.
- For $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$, the Nernst equation at 298 K is $E = E^{\circ} + 0.0591 \log[\text{Ag}^+]$, taking the activity of pure solid silver as unity and dilute-solution activity as concentration relative to the standard concentration.

Step 1: (i) Calculate the molar conductivity of acetic acid The given values are $\kappa = 7.2 \times 10^{-5} \text{ S cm}^{-1}$ and $c = 0.0024 \text{ mol L}^{-1}$. Therefore,

$$\Lambda_m = \frac{1000(7.2 \times 10^{-5})}{0.0024} = 30.0 \text{ S cm}^2 \text{ mol}^{-1}.$$

Quick Tip to Solve: First convert conductivity into molar conductivity before finding dissociation; in the silver half-cell, dilute Ag⁺ lowers the reduction potential.

Acetic acid is a weak electrolyte: only the dissociated fraction provides ions that carry current. Comparing its molar conductivity with the limiting value gives

$$\alpha = \frac{30.0}{390.5} = 0.0768246 \simeq 0.0768.$$

This ratio is dimensionless because the conductivity units cancel. Its percentage dissociation is $100\alpha \simeq 7.68\%$, so only a small fraction of the acid is ionised at the stated concentration.

Step 2: (ii) Apply the Nernst equation to the silver reduction half-cell One electron is involved in the reduction of each silver ion, so $n = 1$. For the reaction as written, the reaction quotient is $Q = 1/[\text{Ag}^+]$, because solid silver has unit activity. Thus,

$$\begin{aligned} E &= E^\circ - \frac{0.0591}{1} \log \frac{1}{[\text{Ag}^+]} \\ &= 0.80 + 0.0591 \log(0.01) \\ &= 0.80 + 0.0591(-2) \\ &= 0.6818 \text{ V.} \end{aligned}$$

Here $0.01 = 10^{-2}$, so the given $\log 10 = 1$ implies $\log 0.01 = -2$. The lower silver-ion concentration decreases the tendency for reduction relative to standard conditions, consistent with a potential below $+0.80 \text{ V}$.

Step 3: (iii) Identify the electrolytes in the two cells (I) A dry cell uses a moist paste containing ammonium chloride, NH_4Cl , and zinc chloride, ZnCl_2 , as its electrolyte. The paste permits ionic conduction while allowing the cell to be used without a free-flowing electrolyte solution. Manganese dioxide is a cathode material and is not the electrolyte.

(II) The hydrogen–oxygen fuel cell uses concentrated aqueous potassium hydroxide, KOH , as its electrolyte. It supplies hydroxide ions for ionic conduction between the electrodes. Hydrogen and oxygen are the continuously supplied reactants; the electrode catalyst is not the electrolyte.

Step 4: Conclusion (i) $\alpha = 0.0768$, or approximately 7.68% dissociation. (ii) $E = +0.682 \text{ V}$. (iii) Dry cell: moist NH_4Cl – ZnCl_2 paste; hydrogen–oxygen fuel cell: concentrated aqueous KOH .

Quick Tip to Solve: First convert conductivity into molar conductivity before finding dissociation; in the silver half-cell, dilute Ag^+ lowers the reduction potential.

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

(I) MnO is basic while Mn_2O_7 is acidic.

(II) Iron has higher enthalpy of atomization than that of copper.

(III) Mn^{3+} is a stronger oxidising agent than Cr^{3+} .

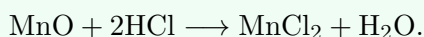
(ii) How do you prepare potassium dichromate from sodium chromate? Write balanced chemical equation for each step. [5 marks]

Solution:

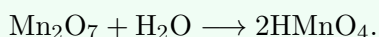
Concept:

- The acid-base character of a metal oxide depends on the metal's oxidation state: low oxidation states generally give basic oxides, while very high oxidation states give acidic oxides.
- Enthalpy of atomization is the enthalpy needed to form isolated gaseous atoms from the element. Stronger metallic bonding gives a larger atomization enthalpy.
- A stable electronic configuration can favour reduction. A half-filled d^5 configuration and a d^3 configuration are especially stable in the relevant manganese and chromium ions.
- Acidification converts chromate into dichromate; potassium dichromate can then be crystallised because it is less soluble than sodium dichromate.

Step 1: (i)(I) Explain the acid-base character of the manganese oxides In MnO , manganese has oxidation state +2. Its bonding is predominantly ionic and the oxide behaves as a base, reacting with an acid to form a salt and water:



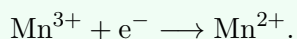
In Mn_2O_7 , manganese has oxidation state +7. The high oxidation state favours covalent bonding and acidic character. It is the acid anhydride of permanganic acid:



Thus, the increase in oxidation state from +2 to +7 explains the change from a basic to an acidic oxide.

Step 2: (i)(II) Compare the metallic bonding in iron and copper The atomic configurations are Fe : $[\text{Ar}] 3d^6 4s^2$ and Cu : $[\text{Ar}] 3d^{10} 4s^1$. Iron has more unpaired electrons available to participate in metallic bonding, whereas copper has a completely filled $3d$ subshell. Metallic bonding is therefore stronger in iron. More energy is required to separate iron atoms into isolated gaseous atoms, so iron has a higher enthalpy of atomization than copper.

Step 3: (i)(III) Compare the reduction of the trivalent ions Mn^{3+} has configuration $3d^4$. On accepting one electron, it forms Mn^{2+} , with the particularly stable half-filled $3d^5$ configuration:



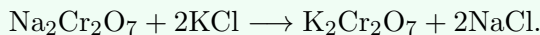
By contrast, Cr^{3+} already has a stable $3d^3$ configuration. Its reduction would form Cr^{2+} , with configuration $3d^4$, and is less favourable. Hence Mn^{3+} accepts an electron more readily and is a stronger oxidising agent than Cr^{3+} .

Quick Tip to Solve: For the oxide comparison, calculate manganese's oxidation state first; for the oxidant comparison, write both the ion and its one-electron reduction product configurations.

Step 4: (ii) Prepare potassium dichromate from sodium chromate First acidify an aqueous solution of sodium chromate with sulphuric acid. The yellow chromate solution changes to orange as sodium dichromate forms:



Then treat the sodium dichromate solution with potassium chloride:



Concentrate the solution and allow it to cool. The less soluble potassium dichromate separates as orange crystals, which are collected by filtration. The different solubilities make this final isolation possible.

Step 5: Conclusion MnO is basic because manganese is in the low +2 state, while Mn_2O_7 is acidic because it is in the +7 state. Stronger metallic bonding explains iron's higher atomization enthalpy. Reduction to stable $3d^5$ makes Mn^{3+} the stronger oxidant. Acidification of sodium chromate, followed by treatment with KCl and crystallisation, gives $\text{K}_2\text{Cr}_2\text{O}_7$.

Quick Tip to Solve: For the oxide comparison, calculate manganese's oxidation state first; for the oxidant comparison, write both the ion and its one-electron reduction product configurations.

OR

32(b). Answer the following questions:

(i) Why is chemistry of actinoids more complicated as compared to lanthanoids?

(ii) $E^\circ_{\text{M}^{2+}/\text{M}}$ values are not regular for first row transition elements (3d series). Why?

(iii) Identify the following:

(I) Oxoanion of chromium which is stable in acidic medium.

(II) The lanthanoid element that exhibits +4 oxidation state.

(iv) Write the products obtained on heating KMnO_4 .

(v) Predict which of the following ions will be coloured in aqueous solution:

Cu^+ , Sc^{3+} , Fe^{2+} , Ti^{3+} , Zn^{2+}

[5 marks]

Solution:

Concept:

- Comparable orbital energies allow several oxidation states. Actinoids involve $5f$, $6d$ and $7s$ orbitals, while lanthanoids predominantly show the +3 oxidation state.
- The standard reduction potential $E^\circ_{\text{M}^{2+}/\text{M}}$ depends on the net energy change involving atomization, the first two ionizations and hydration of M^{2+} .
- Chromate and dichromate interconvert with a change in acidity. Partially filled d orbitals allow visible-light absorption through $d-d$ transitions in many transition-metal aqua ions.

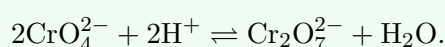
Step 1: (i) Explain the more complicated chemistry of actinoids The $5f$, $6d$ and $7s$ orbitals of actinoids have comparable energies, so differing numbers of electrons can participate in bonding.

Quick Tip to Solve: Remove the metal's $4s$ electrons before $3d$ electrons when finding ionic configurations; among these ions, select the partially filled d subshells for aqueous colour.

Actinoids therefore exhibit a wider range of oxidation states than lanthanoids, whose chemistry is dominated by the +3 state. Their greater variation in bonding and oxidation state makes their chemistry more complicated. In addition, all actinoids are radioactive, which also complicates their study and handling.

Step 2: (ii) Explain the irregular standard reduction potentials Formation of an aqueous divalent ion from the metal involves atomization of the metal, removal of two electrons from the gaseous atom, and hydration of the resulting gaseous ion. Thus the electrode potential reflects the combined effects of atomization enthalpy, the first and second ionization enthalpies, and hydration enthalpy. These contributions do not vary uniformly across the 3d series. Changes in electronic configuration, including the special stability of half-filled and filled subshells, affect the ionization energies. Their combined balance therefore produces irregular $E_{M^{2+}/M}^\circ$ values, rather than a smooth trend.

Step 3: (iii) Identify the chromium oxoanion and the lanthanoid (I) The chromium oxoanion favoured in acidic medium is the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$. Addition of acid shifts the following equilibrium to the right:



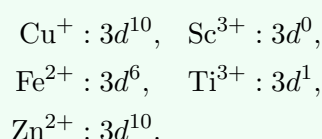
(II) Cerium, Ce, exhibits the +4 oxidation state. The Ce^{4+} ion has the stable [Xe] configuration, which helps explain the occurrence of this state in cerium compounds.

Step 4: (iv) Write the products of heating potassium permanganate On heating, potassium permanganate decomposes to potassium manganate, manganese dioxide and oxygen. The balanced thermal decomposition is



The solid products are K_2MnO_4 and MnO_2 , while O_2 is evolved as a gas. The equation conserves two potassium atoms, two manganese atoms and eight oxygen atoms on each side.

Step 5: (v) Predict the coloured aqueous ions Determine the *d*-electron configuration of each ion by removing the 4*s* electrons before the 3*d* electrons:



Fe^{2+} and Ti^{3+} have partially filled *d* subshells and are coloured in aqueous solution, typically pale green and violet respectively. Their aqua complexes can absorb visible light in *d-d* transitions. Cu^+ , Sc^{3+} and Zn^{2+} have d^{10} , d^0 and d^{10} configurations respectively and are colourless in this comparison because such transitions are unavailable.

Step 6: Conclusion (i) Comparable 5*f*, 6*d* and 7*s* energies and variable oxidation states complicate actinoid chemistry. (ii) Irregular combined atomization, ionization and hydration energies cause irregular electrode potentials. (iii) The answers are $\text{Cr}_2\text{O}_7^{2-}$ and cerium. (iv) Heating gives K_2MnO_4 , MnO_2 and O_2 . (v) The coloured ions are Fe^{2+} and Ti^{3+} .

Quick Tip to Solve: Remove the metal's 4*s* electrons before 3*d* electrons when finding ionic configurations; among these ions, select the partially filled *d* subshells for aqueous colour.

33(a). (i) How will you bring about the following conversions:

(I) Bromobenzene to 1-phenylethanol

(II) Benzene to m-nitroacetophenone

(ii) An organic compound with the molecular formula C_8H_8O forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation with acidic or alkaline $KMnO_4$ it gives Benzene-1,2-dicarboxylic acid. Identify the compound and write the products when it undergoes Cannizzaro reaction.

(iii) Arrange the following compounds in increasing order of their acid strength:

C_6H_5COOH , O_2N-CH_2-COOH , CF_3-COOH , $HCOOH$

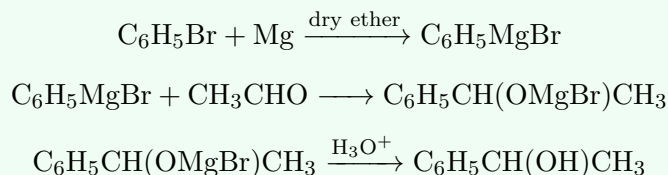
[5 marks]

Solution:

Concept:

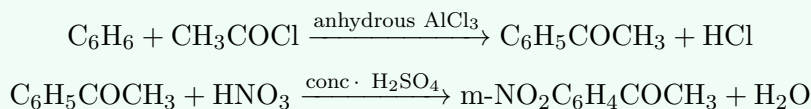
- A Grignard reagent adds to an aldehyde; hydrolysis of its magnesium alkoxide gives an alcohol. Ethanal (acetaldehyde) gives a secondary alcohol with an aryl Grignard reagent.
- In electrophilic aromatic substitution, the acetyl group, $-COCH_3$, deactivates the ring and directs an incoming nitro group predominantly to the meta position.
- Aldehydes lacking an alpha hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.
- Electron-withdrawing substituents stabilise a carboxylate conjugate base and increase acid strength through the inductive effect.

Step 1: (i)(I) Form the Grignard reagent and add ethanal Treat bromobenzene with magnesium in dry ether to obtain phenylmagnesium bromide. Add ethanal in dry ether, then hydrolyse with dilute acid. The phenyl group adds to the carbonyl carbon, giving the required two-carbon alcohol side chain.



The final compound is 1-phenylethanol. Dry conditions are essential before hydrolysis because water destroys the Grignard reagent.

Step 2: (i)(II) Acetylate benzene before nitrating it Carry out Friedel–Crafts acylation with acetyl chloride and anhydrous aluminium chloride to form acetophenone. Nitrate this with concentrated nitric acid and concentrated sulphuric acid; the acetyl group directs substitution mainly to the meta position.



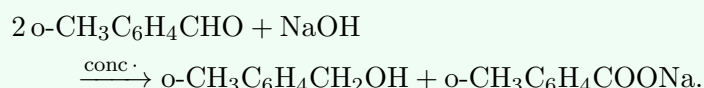
This order is necessary: nitration first would give strongly deactivated nitrobenzene, which does not undergo the required Friedel–Crafts acylation.

Step 3: (ii) Identify the carbonyl compound from all the tests Formation of a 2,4-DNP derivative

Quick Tip to Solve: Install the meta-directing acetyl group before nitration. In the identification problem, the positions of the two carboxyl groups after oxidation reveal the original positions of the methyl and aldehyde groups.

establishes a carbonyl group, and reduction of Tollens' reagent identifies an aldehyde. Cannizzaro reaction indicates the absence of an alpha hydrogen. With molecular formula C_8H_8O , a methylbenzaldehyde fits these requirements. Vigorous oxidation changes both the aldehyde and the ring methyl side chain into carboxyl groups. Since the resulting acid is benzene-1,2-dicarboxylic acid, the two original substituents must be adjacent. Thus the compound is 2-methylbenzaldehyde (o-tolualdehyde), $o\text{-CH}_3C_6H_4CHO$.

Step 4: (ii) Write the Cannizzaro products In concentrated sodium hydroxide, one molecule of 2-methylbenzaldehyde is reduced to 2-methylbenzyl alcohol, and another is oxidised to sodium 2-methylbenzoate (sodium o-toluate):



On acidification, the carboxylate gives 2-methylbenzoic acid. The salt, rather than the free acid, is the immediate oxidation product in alkaline reaction medium.

Step 5: (iii) Compare stabilisation of the conjugate bases Formic acid is stronger than benzoic acid. The strongly electron-withdrawing nitro group makes nitroacetic acid stronger than formic acid, and the combined inductive effect of three fluorine atoms makes trifluoroacetic acid the strongest of the four. Therefore the increasing order is



Step 6: Conclusion Bromobenzene gives 1-phenylethanol through phenylmagnesium bromide and ethanal; benzene gives m-nitroacetophenone by acetylation followed by nitration. The unknown is 2-methylbenzaldehyde, whose Cannizzaro products are 2-methylbenzyl alcohol and a 2-methylbenzoate salt. Acid strength increases as $C_6H_5COOH < HCOOH < O_2N-CH_2-COOH < CF_3-COOH$.

Quick Tip to Solve: Install the meta-directing acetyl group before nitration. In the identification problem, the positions of the two carboxyl groups after oxidation reveal the original positions of the methyl and aldehyde groups.

33(b). (i) Write the products formed when benzaldehyde reacts with the following reagents:

(I) 2,4-Dinitrophenylhydrazine

(II) Acetophenone in the presence of dilute NaOH followed by heating

(ii) Give reasons for the following:

(I) Benzoic acid does not undergo Friedel-Crafts reaction.

(II) Carboxylic acids have higher boiling point than alcohols of comparable molecular mass.

(iii) Write simple chemical test to distinguish between propanal and propanone.

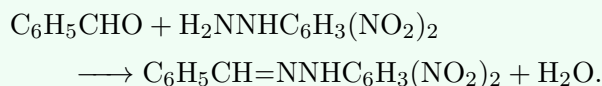
[5 marks]

Solution:

Concept:

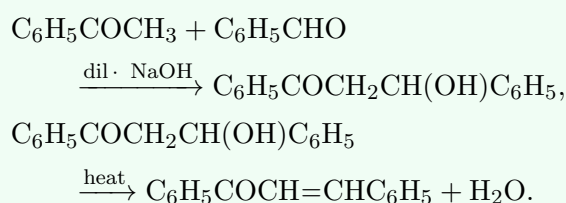
- Aldehydes condense with 2,4-dinitrophenylhydrazine to form 2,4-dinitrophenylhydrazones, eliminating water.
- In a crossed aldol condensation, an enolate from a carbonyl compound having alpha hydrogens adds to another carbonyl compound. Heating the aldol product eliminates water to give an unsaturated carbonyl compound.
- The carboxyl group withdraws electron density from an aromatic ring. Carboxylic acids also form dimers through two intermolecular hydrogen bonds.
- Tollens' reagent oxidises an aldehyde to a carboxylate and is reduced to metallic silver; ordinary ketones do not give this test.

Step 1: (i)(I) Form the benzaldehyde hydrazone Benzaldehyde reacts with the terminal amino group of 2,4-dinitrophenylhydrazine, replacing the carbonyl oxygen by the hydrazone group with elimination of water:



The product is benzaldehyde 2,4-dinitrophenylhydrazone, obtained as a yellow-orange precipitate. The two nitro groups remain at positions 2 and 4 on the phenyl ring attached to the hydrazine nitrogen.

Step 2: (i)(II) Condense benzaldehyde with acetophenone Acetophenone has alpha hydrogens on its methyl group, whereas benzaldehyde has none. Dilute sodium hydroxide generates the acetophenone enolate, which attacks benzaldehyde to form the beta-hydroxy ketone $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{OH})\text{C}_6\text{H}_5$. Heating causes dehydration:



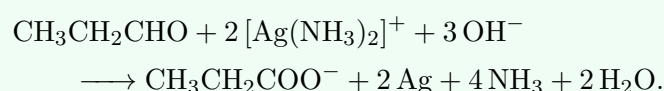
The final product is chalcone (1,3-diphenylprop-2-en-1-one), predominantly the trans isomer. Its carbon-carbon double bond is conjugated with the ketone carbonyl group.

Quick Tip to Solve: For the crossed aldol reaction, keep the acetophenone carbonyl and join its alpha carbon to the benzaldehyde carbonyl carbon; heating places the double bond between those two carbons.

Step 3: (ii)(I) Explain the failure of Friedel–Crafts reaction In benzoic acid, the $-\text{COOH}$ group withdraws electron density by both inductive and resonance effects. It strongly deactivates the benzene ring toward the electrophilic attack required for Friedel–Crafts alkylation or acylation. In addition, the carboxyl group complexes with the Lewis-acid catalyst AlCl_3 , interfering with its role in the reaction. Benzoic acid therefore does not undergo the normal Friedel–Crafts reaction.

Step 4: (ii)(II) Explain the higher boiling points of carboxylic acids Two carboxylic acid molecules associate as a cyclic dimer through two intermolecular hydrogen bonds: each molecule supplies an $\text{O}-\text{H}$ hydrogen-bond donor and a carbonyl oxygen acceptor. These strongly associated dimers require more energy to separate during vaporisation. Alcohols also form hydrogen bonds, but carboxylic acids show particularly strong dimeric association. Thus carboxylic acids have higher boiling points than alcohols of comparable molecular mass.

Step 5: (iii) Apply Tollens' test to the two samples Add freshly prepared Tollens' reagent separately to propanal and propanone and warm gently in a water bath. Propanal gives a silver mirror because it reduces the silver(I) complex to metallic silver while being oxidised to propanoate. Propanone gives no silver mirror under these conditions.



The contrasting visible observations distinguish the aldehyde from the ketone; a 2,4-DNP test alone would not distinguish them because both contain a carbonyl group.

Step 6: Conclusion Benzaldehyde gives its 2,4-dinitrophenylhydrazone with 2,4-DNP and chalcone with acetophenone, dilute alkali and heat. Benzoic acid resists Friedel–Crafts reaction because its ring is strongly deactivated and its carboxyl group complexes the catalyst. Hydrogen-bonded dimers explain the higher boiling points of carboxylic acids. Propanal gives a silver mirror with Tollens' reagent; propanone does not.

Quick Tip to Solve: For the crossed aldol reaction, keep the acetophenone carbonyl and join its alpha carbon to the benzaldehyde carbonyl carbon; heating places the double bond between those two carbons.