

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-4-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

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

Section A (16 marks)

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

1. Which of the following is not correct for S_N1 reaction?

[1 mark]

- (A) Follows first order kinetics
- (B) Favoured by polar protic solvents
- (C) Proceeds through the formation of carbocation
- (D) Results in inversion of configuration

Correct Answer: (D) Results in inversion of configuration

Solution:

Concept:

- An S_N1 substitution has slow unimolecular ionisation, giving the rate law $r = k[RX]$.
- The carbocation intermediate is planar; nucleophilic attack can occur from either face, giving both retention and inversion at a chiral reaction centre.

Step 1: Check the kinetic and solvent statements Only the substrate participates in the rate-determining step, so first-order kinetics in (A) is correct. Polar protic solvents stabilise the carbocation and leaving-group ion and facilitate ionisation, so (B) is also correct. The two-step mechanism explicitly contains a carbocation, making (C) correct.

Step 2: Check the stereochemical statement The planar carbocation admits attack from both sides and therefore leads to racemisation, often with some excess inversion owing to ion-pair effects. Exclusive inversion is characteristic of backside attack in S_N2 , and is not the general stereochemical outcome of S_N1 .

Step 3: Conclusion The statement that S_N1 results in inversion of configuration is the incorrect general description. Hence, the correct option is (D).

Quick Tip to Solve: For an S_N1 stereochemistry question, draw a planar carbocation mentally and allow attack from both faces.

2. Dehydration of tertiary alcohols with Cu at 573 K gives:

[1 mark]

- (A) Ketones
- (B) Alkenes
- (C) Aldehydes
- (D) Carboxylic acid

Correct Answer: (B) Alkenes

Solution:

Concept:

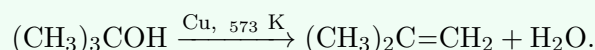
- Alcohol vapour passed over heated copper at 573 K gives different products depending on the class of alcohol.

Quick Tip to Solve: Before predicting the hot-copper product, check whether the carbon bearing $-OH$ has a hydrogen; a tertiary alcohol does not.

- A tertiary alcohol lacks a hydrogen on the carbon carrying —OH ; it undergoes dehydration, losing water to form an alkene.

Step 1: Identify the available reaction Formation of an aldehyde or ketone by dehydrogenation requires removal of a hydrogen from the carbon bonded to the hydroxyl group. That hydrogen is absent in a tertiary alcohol, because this carbon is attached to three other carbon atoms. Dehydration instead eliminates the hydroxyl group and a hydrogen from an adjacent carbon.

Step 2: Compare the product classes Loss of water creates a carbon-carbon double bond. For example, tert-butyl alcohol gives 2-methylpropene:



Ketones in (A) and aldehydes in (C) are the usual dehydrogenation products of secondary and primary alcohols, respectively. A carboxylic acid in (D) would require oxidation, not this dehydration.

Step 3: Conclusion Tertiary alcohols undergo dehydration to form alkenes. Hence, the correct option is (B).

Quick Tip to Solve: Before predicting the hot-copper product, check whether the carbon bearing —OH has a hydrogen; a tertiary alcohol does not.

3. The coordination number of Co in $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is:

[1 mark]

- (A) 4
- (B) 3
- (C) 6
- (D) 2

Correct Answer: (C) 6

Solution:

Concept:

- Coordination number counts the donor atoms directly bonded to the central metal, rather than the number of ligand molecules or the charge on the complex.
- Ethane-1,2-diamine (en) is bidentate, donating through two nitrogen atoms; each chlorido ligand is monodentate.

Step 1: Count donors from each ligand In $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, the two en ligands provide $2 \times 2 = 4$ nitrogen donor atoms. Both chlorido ligands lie inside the coordination brackets and are directly bonded to cobalt, contributing another $2 \times 1 = 2$ donor atoms.

Step 2: Add the contributions

$$\text{Coordination number} = 2(2) + 2(1) = 6.$$

The value 4 in (A) merely counts ligand entities and ignores the bidentate nature of en. The value 3 in (B) is cobalt's oxidation state here, since $x - 2 = +1$; it is not the coordination number. The value

Quick Tip to Solve: Replace each en ligand by two donor sites before counting; complex charge is irrelevant to coordination number.

2 in (D) counts only one kind of ligand and omits the remaining donors.

Step 3: Conclusion Cobalt has six directly bonded donor atoms and coordination number 6. Hence, the correct option is (C).

Quick Tip to Solve: Replace each en ligand by two donor sites before counting; complex charge is irrelevant to coordination number.

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

(A) d_{xy} , d_{yz} , d_{xz}

(B) $d_{x^2-y^2}$, d_{z^2}

(C) d_{xy} , $d_{x^2-y^2}$

(D) d_{xz} , d_{z^2}

Correct Answer: (B) $d_{x^2-y^2}$, d_{z^2}

Solution:

Concept:

- In an octahedral complex, the six ligands approach the central ion along the positive and negative coordinate axes.
- Orbitals directed along these axes experience greater electrostatic repulsion than orbitals whose lobes lie between the axes.

Step 1: Identify the orbitals facing the ligands The $d_{x^2-y^2}$ orbital has lobes directed along the x and y axes, while d_{z^2} has its principal lobes along the z axis. They point toward the incoming ligands, so their energies increase more. Together they form the higher-energy e_g set.

Step 2: Exclude the orbitals between the axes The d_{xy} , d_{yz} and d_{xz} orbitals point between the axes and form the lower-energy t_{2g} set. Thus (A) gives the less-repelled set, while (C) and (D) each mix an orbital of that set with one of the more-repelled set. Only (B) contains both orbitals directly facing the ligands.

Step 3: Conclusion The $d_{x^2-y^2}$ and d_{z^2} orbitals experience greater repulsion in an octahedral field. Hence, the correct option is (B).

Quick Tip to Solve: For octahedral splitting, remember that ligands lie on the axes: orbitals pointing along the axes form the higher e_g pair.

5. Which of the following transition metals shows +1 and +2 oxidation states?

[1 mark]

- (A) Zn
- (B) Cu
- (C) Fe
- (D) Cr

Correct Answer: (B) Cu

Solution:

Concept:

- Transition metals can lose outer s electrons and then d electrons because these subshells have comparable energies.
- Copper has configuration $[\text{Ar}] 3d^{10}4s^1$; its familiar oxidation states are +1 and +2.

Step 1: Form the two copper ions Removing the single $4s$ electron gives Cu^+ , with configuration $[\text{Ar}] 3d^{10}$. Removing one additional $3d$ electron gives Cu^{2+} , with configuration $[\text{Ar}] 3d^9$. Thus copper exhibits both oxidation states named in the question, as in Cu_2O and CuO .

Step 2: Compare the other choices Zinc usually forms Zn^{2+} and, with a completely filled d subshell in its atom and common ion, is not classified as a transition element. Iron's characteristic common pair is +2, +3, while chromium commonly exhibits +2, +3, +6. These alternatives do not give the characteristic +1, +2 pair asked here.

Step 3: Conclusion Copper is the transition metal characteristically showing +1 and +2 oxidation states. Hence, the correct option is (B).

Quick Tip to Solve: Recall copper's exceptional $3d^{10}4s^1$ configuration: remove the $4s$ electron first, then one $3d$ electron.

6. 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 $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.
- Complete dissociation of NaCl gives two ions per formula unit, so $i = 2$. The solution boiling point is the pure-solvent boiling point plus ΔT_b .

Step 1: Calculate the elevation The dissociation is $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$. For $m = 1 \text{ mol kg}^{-1}$ and

Quick Tip to Solve: Count the two ions of fully dissociated NaCl, double $K_b m$, then add the elevation to 100°C .

$$K_b = 0.52 \text{ K kg mol}^{-1},$$

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

A temperature difference of 1.04 K equals a difference of 1.04 °C.

Step 2: Add the elevation to water's boiling point At normal atmospheric pressure, pure water boils at 100 °C, giving

$$T_b = 100 + 1.04 = 101.04 \text{ °C}.$$

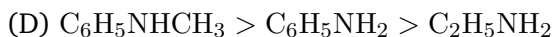
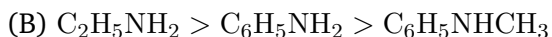
Option (A) ignores dissociation by taking $i = 1$. Options (C) and (D) give elevations of 0.04 and 1.52 °C, neither equal to the calculated $iK_b m$.

Step 3: Conclusion The solution boils at 101.04 °C. Hence, the correct option is (B).

Quick Tip to Solve: Count the two ions of fully dissociated NaCl, double $K_b m$, then add the elevation to 100 °C.

7. The correct order of decreasing order of pK_b values is:

[1 mark]



Correct Answer: (A) $\text{C}_6\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{NHCH}_3 > \text{C}_2\text{H}_5\text{NH}_2$

Solution:

Concept:

- $pK_b = -\log K_b$; therefore a stronger base has a larger K_b and a smaller pK_b .
- Delocalisation of the nitrogen lone pair into a benzene ring reduces basicity, whereas an alkyl group's electron-releasing effect increases electron availability at nitrogen.

Step 1: Compare the basic strengths In aniline, $\text{C}_6\text{H}_5\text{NH}_2$, resonance makes the lone pair less available to accept a proton. The methyl group in N-methylaniline, $\text{C}_6\text{H}_5\text{NHCH}_3$, donates electron density, making it more basic than aniline. Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, has no aromatic delocalisation of its lone pair and is the strongest base of these three. Thus basicity increases as aniline, N-methylaniline, ethylamine.

Step 2: Reverse the basicity order for pK_b Since greater basic strength means smaller pK_b , the decreasing order is



Option (B) wrongly gives ethylamine the highest pK_b . Option (C) also fails to place ethylamine last. Option (D) reverses the relative order of aniline and N-methylaniline.

Step 3: Conclusion The decreasing pK_b order is aniline, N-methylaniline, ethylamine. Hence, the correct option is (A).

Quick Tip to Solve: First rank the amines by basicity using resonance and alkyl donation; reverse that order when the question asks for pK_b .

8. 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 $\text{Mg (s)} + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Mg}^{2+}(\text{aq}) + \text{Cu (s)}$, transferring two electrons.
- At 298 K, the Nernst equation is $E = E^\circ - \frac{0.0591}{2} \log Q$, where $Q = [\text{Mg}^{2+}]/[\text{Cu}^{2+}]$. Pure solids do not enter Q .

Step 1: Identify the change needed Initially both ion concentrations are 1.0 M, so $Q = 1$ and $E = E^\circ$. To increase the emf using the same electrodes, decrease Q ; a negative $\log Q$ then adds to the standard emf.

Step 2: Compare all four concentration changes In (A), $Q = 0.1/1 = 0.1$, so the emf increases by 0.02955 V. In (B), $Q = 1/0.1 = 10$, so the emf decreases. In (C), $Q = 2/2 = 1$, so the emf is unchanged. In (D), $Q = 2/1 = 2$, so the emf decreases.

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

Quick Tip to Solve: Write the ion concentration ratio as product over reactant: lowering the numerator raises the emf of this cell.

9. 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, evaporation and condensation occur at equal rates.
- Vaporisation absorbs latent heat; a sudden reduction in pressure disturbs the equilibrium and favours formation of vapour.

Step 1: Determine the immediate response When pressure is suddenly decreased, the existing liquid–vapour equilibrium is disturbed. More liquid evaporates as the system responds to the lower

Quick Tip to Solve: When a pressure drop promotes evaporation, follow the latent heat: energy leaves the liquid, so its temperature falls.

pressure. Thus the equilibrium cannot remain unaffected, ruling out (D).

Step 2: Trace the heat required for evaporation The additional evaporation needs energy to overcome intermolecular attractions. It draws latent heat from the liquid and its immediate surroundings, lowering the temperature rather than heating the liquid. At fixed temperature the equilibrium vapour pressure is a property of the liquid, so simply lowering the external pressure does not increase it. These observations rule out (A) and (B).

Step 3: Conclusion The sudden pressure decrease promotes evaporation, producing cooling. Hence, the correct option is (C).

Quick Tip to Solve: When a pressure drop promotes evaporation, follow the latent heat: energy leaves the liquid, so its temperature falls.

10. Each polypeptide in a protein has amino acids linked with each other in a specific sequence and it is this sequence of amino acids that is said to be: [1 mark]

- (A) primary structure of proteins
- (B) secondary structure of proteins
- (C) tertiary structure of proteins
- (D) quaternary structure of proteins

Correct Answer: (A) primary structure of proteins

Solution:

Concept:

- The primary structure of a protein is the specific linear sequence of amino acid residues in each polypeptide chain.
- Amino acids are joined by peptide bonds, $-\text{CO}-\text{NH}-$; higher structural levels describe folding or association of these chains.

Step 1: Identify what the question describes The defining words are "specific sequence" of amino acids in a polypeptide. This describes the order of residues along the chain, without specifying its folding in space.

Step 2: Distinguish the other structural levels Secondary structure refers to local arrangements such as the α -helix and β -pleated sheet. Tertiary structure describes the overall three-dimensional folding of one polypeptide. Quaternary structure describes how multiple polypeptide subunits associate. Thus (B), (C) and (D) describe levels beyond the amino acid sequence.

Step 3: Conclusion The amino acid sequence is the primary structure of the protein. Hence, the correct option is (A).

Quick Tip to Solve: Match "sequence" to primary, local helix or sheet to secondary, complete folding to tertiary, and subunit association to quaternary.

11. 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 rate law is $r = k[A]$, where r is reaction rate and $[A]$ is reactant concentration.
- The first order rate constant is $k = r/[A]$ and has units s^{-1} .

Step 1: Substitute in the first order rate law Divide the given rate by the concentration, rather than multiplying them:

$$k = \frac{5.6 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}}{0.2 \text{ mol L}^{-1}}.$$

Step 2: Simplify the number and check the units Since $0.2 = 2 \times 10^{-1}$,

$$k = \frac{5.6}{2} \times 10^{-4-(-1)} = 2.8 \times 10^{-3} \text{ s}^{-1}.$$

The concentration units cancel. Option (A) has the wrong coefficient, while (B) and (C) retain incorrect powers of ten. As a check, multiplying 2.8×10^{-3} by 0.2 reproduces the given rate.

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

Quick Tip to Solve: Dividing by 0.2 multiplies by five; use this quick check to avoid losing a power of ten.

12. Benzene diazonium chloride on reaction with phenol in weakly basic medium gives: [1 mark]

- (A) Benzene
- (B) Anisole
- (C) p-hydroxyazobenzene
- (D) Benzophenone

Correct Answer: (C) p-hydroxyazobenzene

Solution:

Concept:

- An aromatic diazonium ion undergoes electrophilic coupling with an activated aromatic ring to form an azo compound containing $-\text{N}=\text{N}-$.
- In weakly basic medium, phenol is activated through phenoxide formation, and coupling occurs mainly at the available para position.

Quick Tip to Solve: For diazonium salt plus phenol in weak base, look for an azo linkage at the para position of phenol.

Step 1: Locate the coupling position The hydroxy group activates the ortho and para positions of the phenol ring. The para position is free and is favoured over the more crowded ortho position. The benzene diazonium ion therefore links to this position through an azo group.

Step 2: Identify the product and reject alternatives The product has the condensed structure $C_6H_5-N=N-C_6H_4-OH$, with the hydroxy group para to the azo linkage on the phenol ring. Benzene would require removal of the diazonium group, anisole would require methylation of phenol, and benzophenone would require formation of a carbonyl linkage. None describes this azo-coupling reaction.

Step 3: Conclusion The product is *p*-hydroxyazobenzene. Hence, the correct option is (C).

Quick Tip to Solve: For diazonium salt plus phenol in weak base, look for an azo linkage at the para position of phenol.

13. Assertion (A): $(CH_3)_3C-O-CH_3$ gives $(CH_3)_3C-I$ and CH_3OH on reaction with HI.

Reason (R): The reaction occurs by S_N1 mechanism.

[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:

- An ether reacts with HI after protonation of its oxygen, making carbon–oxygen bond cleavage possible.
- A tertiary alkyl group can form a relatively stable carbocation, so cleavage of a tertiary alkyl ether proceeds by the S_N1 pathway.

Step 1: Evaluate the assertion Protonation of $(CH_3)_3C-O-CH_3$ is followed by cleavage of the bond between oxygen and the tertiary carbon. This releases methanol, CH_3OH , and forms the tert-butyl carbocation. Iodide then gives $(CH_3)_3C-I$. The stated products are therefore correct, so Assertion (A) is true.

Step 2: Evaluate the reason The carbon–oxygen bond ionises to produce the relatively stable tertiary carbocation, $(CH_3)_3C^+$, before attack by I^- . This stepwise substitution is the S_N1 mechanism. Reason (R) is therefore true.

Step 3: Check the explanatory connection The S_N1 pathway explains why iodide attaches to the tertiary group and methanol is released. The usual S_N2 preference for attack at a less hindered methyl carbon does not determine this tertiary-ether cleavage. Thus the reason directly accounts for the

Quick Tip to Solve: Before applying the less-hindered-carbon rule to ether cleavage, check for a tertiary group that can undergo S_N1 cleavage.

products in the assertion, ruling out (B), (C) and (D).

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

Quick Tip to Solve: Before applying the less-hindered-carbon rule to ether cleavage, check for a tertiary group that can undergo S_N1 cleavage.

14. Assertion (A): Diazonium salts of aromatic amines are less 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- Aromatic diazonium salts have a diazonium group directly attached to an aromatic ring and are resonance stabilised.
- Aliphatic diazonium salts lack the corresponding aromatic conjugation and readily decompose with loss of N_2 .

Step 1: Evaluate the assertion The assertion reverses the stability comparison. Aromatic diazonium salts are more stable than aliphatic diazonium salts. Although aromatic diazonium salts are still normally prepared and used at low temperature, their relative stability is greater. Assertion (A) is therefore false.

Step 2: Evaluate the reason The diazonium group in an aromatic diazonium salt participates in resonance with the attached aromatic ring. This delocalisation stabilises the aromatic diazonium ion. Reason (R) is therefore true.

Step 3: Relate the statements and select the code The true reason supports the opposite of the assertion: resonance increases relative stability rather than making aromatic diazonium salts less stable. Options (A), (B) and (C) all require a true assertion, so none of them applies. The required code combines a false assertion with a true reason.

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

Quick Tip to Solve: For this comparison, link aromatic resonance to greater stability; check carefully whether the assertion says "more" or "less".

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

Reason (R): Order of reaction is not applicable for the complex reaction.

[1 mark]

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

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

Solution:

Concept:

- The order of a reaction is the sum of the concentration powers in its experimentally determined rate law.
- A complex reaction proceeds through elementary steps. Its slowest, rate-determining step controls the observed rate.

Step 1: Evaluate the assertion The slowest step acts as the bottleneck of a multistep reaction. The overall rate law, and hence its order, is determined using this step, with any intermediate concentration expressed in terms of reactant concentrations when needed. Thus Assertion (A) is true in the stated textbook sense.

Step 2: Evaluate the reason Order applies to both simple and complex reactions because both can have an experimentally measured rate law. It is molecularity that is assigned to an elementary step rather than to an overall complex reaction. Therefore Reason (R) is false.

Step 3: Check the explanatory link A false statement cannot explain the true assertion. Options (A) and (B) incorrectly treat the reason as true, while (D) incorrectly treats the assertion as false.

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

Quick Tip to Solve: Distinguish order from molecularity: order comes from the observed rate law; molecularity counts species in one elementary step.

16. Assertion (A): $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ value is highly negative.

Reason (R): Because Mn^{2+} is highly stable due to half-filled $3d^5$ configuration.

[1 mark]

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

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

Solution:

Concept:

- A negative standard reduction potential indicates that reduction of the ion to the metal is unfavourable relative to the standard hydrogen electrode.
- A half-filled $3d^5$ subshell has extra stability because of its symmetrical occupancy and exchange energy.

Step 1: Evaluate the assertion The relevant reduction is $\text{Mn}^{2+} + 2e^- \longrightarrow \text{Mn}$. Its standard reduction potential is highly negative, so the assertion is true. The ion does not readily gain electrons to form the metal under standard conditions relative to the hydrogen electrode.

Step 2: Evaluate the reason Manganese has configuration $[\text{Ar}] 3d^5 4s^2$. Loss of the two $4s$ electrons gives Mn^{2+} , with the particularly stable half-filled configuration $[\text{Ar}] 3d^5$. The reason is therefore true.

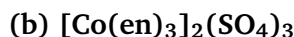
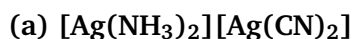
Step 3: Relate stability to the potential The extra stability of the divalent ion favours its formation and opposes its reduction to the metal, explaining the unusually negative reduction potential. Thus the reason explains the assertion; (B) misses this link, while (C) and (D) wrongly declare one statement 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: Write the reduction half-reaction first: stabilising the ion on its left makes reduction less favourable and its potential more negative.

Section B (10 marks)

17. Write IUPAC names of the following compounds:



[2 marks]

Solution:

Concept:

- Name the complex cation before the anion. Give the oxidation state of the central metal in Roman numerals after its name.
- Neutral NH_3 is named ammine; anionic CN^- is cyanido. In an anionic silver complex the metal name becomes argentate.
- The neutral bidentate ligand en is ethane-1,2-diamine; three such ligands take the multiplier tris.

Step 1: Name the silver salt in part (a) The compound consists of $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Ag}(\text{CN})_2]^-$. In the cation, both ammine ligands are neutral, so silver is in oxidation state +1. In the anion, if the silver oxidation state is x , then $x + 2(-1) = -1$, giving $x = +1$. Hence the two ions are diamminesilver(I) and dicyanidoargentate(I), respectively.

Step 2: Name the cobalt salt in part (b) Three sulphate ions contribute total charge -6 , so the two complex cations together have charge $+6$. Each $[\text{Co}(\text{en})_3]^{3+}$ ion therefore has charge $+3$. As en is neutral, cobalt is in oxidation state $+3$. The ligand name contains a numerical term, so use tris(ethane-1,2-diamine) rather than adding the simple prefix tri. The cation is named before sulphate.

Step 3: Conclusion (a) Diamminesilver(I) dicyanidoargentate(I).
(b) Tris(ethane-1,2-diamine)cobalt(III) sulphate.

Quick Tip to Solve: Find each complex ion's charge first; use argentate only for the anionic silver complex, and tris for three en ligands.

18. What is the effect of denaturation on the structure of proteins? What are the common types of secondary structures of proteins?

[2 marks]

Solution:

Concept:

- A protein's primary structure is its amino-acid sequence held together by covalent peptide bonds. Secondary and tertiary structures describe its folding.
- Hydrogen bonding and other interactions stabilise the folded structure. Heating or changing pH can disrupt these interactions and cause denaturation.

Step 1: Explain the structural effect of denaturation On denaturation, the protein loses its native folded form: its secondary and tertiary structures are disrupted, and any quaternary association can also be affected. The polypeptide unfolds and generally loses its characteristic biological activity. Peptide bonds are not hydrolysed in ordinary denaturation, so the primary structure, namely the order of amino acids in the chain, remains intact. Coagulation of egg white on heating is a familiar example.

Quick Tip to Solve: For denaturation, distinguish loss of folding from peptide-bond hydrolysis: folding is disrupted, but the amino-acid sequence remains unchanged.

Step 2: Identify the common secondary structures The common forms are the α -helix and the β -pleated sheet. In an α -helix, the chain coils and is stabilised by hydrogen bonds within that chain. In a β -pleated sheet, extended chain segments lie alongside one another, with hydrogen bonds between neighbouring strands. In both, peptide carbonyl and N-H groups provide the hydrogen-bonding sites.

Step 3: Conclusion Denaturation disrupts secondary and tertiary folding without changing the primary amino-acid sequence. The common secondary structures are the α -helix and the β -pleated sheet.

Quick Tip to Solve: For denaturation, distinguish loss of folding from peptide-bond hydrolysis: folding is disrupted, but the amino-acid sequence remains unchanged.

19. (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:

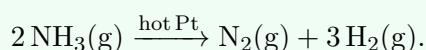
Concept:

- For a rate law $r = k[A]^n$, r is the reaction rate, k is the rate constant and n is the order with respect to reactant A.
- If one reactant is present in a large excess, its concentration changes negligibly and can be absorbed into an observed rate constant.

Step 1: Identify the order and give an example for part (a) A zero-order reaction has a rate independent of reactant concentration because

$$r = k[A]^0 = k.$$

One example is the decomposition of ammonia on a hot platinum surface at sufficiently high pressure, when the catalyst surface is saturated:



Under these conditions, increasing ammonia concentration does not provide more available catalytic sites, so the rate remains constant.

Step 2: State the pseudo-first-order condition for part (b) For a bimolecular reaction obeying $r = k[A][B]$, take B in a very large excess over A. Its concentration then stays effectively constant during the reaction. Defining $k' = k[B]$, the rate becomes

$$r = k'[A].$$

It is therefore kinetically first order with respect to the changing concentration of A and is called a pseudo-first-order reaction. Hydrolysis of an ester in excess water is an example under fixed catalytic conditions.

Quick Tip to Solve: Write the rate law first: a zero exponent removes concentration dependence; a constant excess-reactant concentration is absorbed into k' .

Step 3: Conclusion (a) Zero-order reactions show concentration-independent rates; decomposition of ammonia on a saturated hot platinum surface is an example.

(b) A bimolecular reaction behaves as a pseudo-first-order reaction when one reactant is in such large excess that its concentration is effectively constant.

Quick Tip to Solve: Write the rate law first: a zero exponent removes concentration dependence; a constant excess-reactant concentration is absorbed into k' .

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

(i) Bends

(ii) Anoxia

[2 marks]

Solution:

Concept:

- Henry's law states that, at constant temperature, the partial pressure p of a gas above a liquid is proportional to its mole fraction x in the liquid: $p = K_H x$, where K_H is Henry's law constant.
- Thus $x = p/K_H$: a larger gas partial pressure increases its solubility, while a smaller partial pressure reduces it.

Step 1: Explain bends during rapid ascent Under the high pressure at depth, more nitrogen from the breathing mixture dissolves in a diver's blood. If the diver rises rapidly, the surrounding pressure falls suddenly and the equilibrium solubility of N_2 decreases. Dissolved nitrogen comes out as bubbles, which can obstruct capillaries and cause severe pain; this condition is called bends. A gradual ascent allows the excess dissolved gas to leave more slowly.

Step 2: Explain anoxia at high altitude At high altitude the atmospheric pressure, and hence the partial pressure of oxygen, is lower. By Henry's law, less O_2 dissolves in the blood. This reduces oxygen supply to body tissues and can cause weakness and difficulty in thinking clearly. This oxygen-deficiency condition is called anoxia.

Step 3: Conclusion Bends results from nitrogen bubbles forming after a rapid pressure decrease; anoxia at high altitude results from inadequate oxygen availability at low oxygen partial pressure.

Quick Tip to Solve: Link bends to a sudden fall in nitrogen solubility, but link altitude anoxia to the lower partial pressure of oxygen.

20(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:

- A dissolved non-volatile solute lowers the freezing point of a solvent. For a dilute solution, $\Delta T_f = iK_f m$, where K_f is the solvent's cryoscopic constant, m is molality and i is the van't Hoff factor.
- The effect is colligative: it depends on the number of dissolved solute particles. Salt produces ions in water, increasing the dissolved particle concentration.

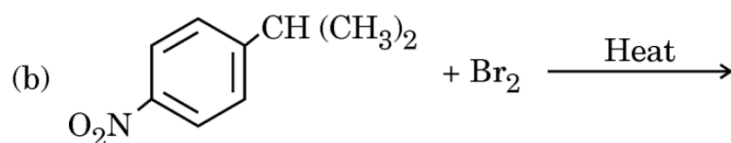
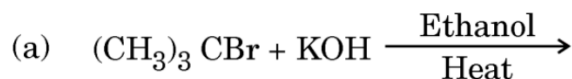
Step 1: Form a salt solution on the snow Salt dissolves in the thin layer of liquid water present on the snow or ice, forming brine. For common salt the dissolution is represented by $\text{NaCl} \longrightarrow \text{Na}^+ + \text{Cl}^-$. These dissolved ions lower the vapour pressure of liquid water and shift the ice-liquid equilibrium to a lower temperature.

Step 2: Relate the lower freezing point to melting The brine freezes below 0°C , whereas pure water freezes at 0°C at ordinary pressure. When the road temperature lies above the brine's freezing point, ice melts to produce liquid brine and the accumulated snow can be cleared more easily. Thus salt does not need to heat the snow; it changes the temperature at which the liquid freezes.

Step 3: Conclusion Sprinkling salt lowers the freezing point of the water in contact with the snow, promoting melting. The colligative property involved is **depression in freezing point**.

Quick Tip to Solve: For salt on icy roads, identify freezing-point depression and explain that the liquid brine remains unfrozen below the freezing point of pure water.

21. Draw the structures of major products of each of the following reactions: [2 marks]



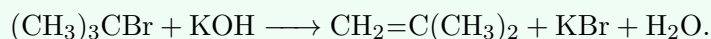
Solution:

Concept:

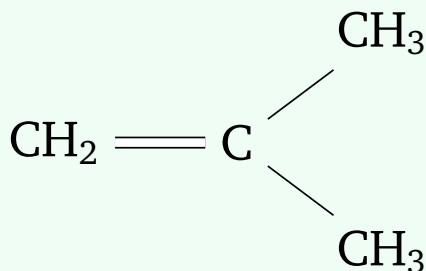
- Hot alcoholic KOH favours beta-elimination: a hydrogen on a neighbouring carbon and the halogen leave, producing a carbon-carbon double bond.
- Bromine with heat causes free-radical substitution at the benzylic carbon of an alkylbenzene. The benzylic radical is stabilised by resonance with the aromatic ring.

Quick Tip to Solve: Read the conditions first: ethanolic hydroxide plus heat means elimination; bromine plus heat on an alkylbenzene targets a benzylic hydrogen.

Step 1: Eliminate hydrogen bromide in part (a) The carbon bonded to bromine in $(\text{CH}_3)_3\text{CBr}$ is attached to three equivalent methyl groups. Removal of a beta-hydrogen from any one of them gives the same alkene. With ethanolic KOH and heat, the reaction is

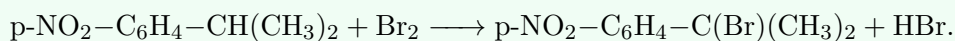


The structure is shown below. Aqueous hydroxide would favour alcohol formation, but the printed alcoholic, heated conditions favour elimination.

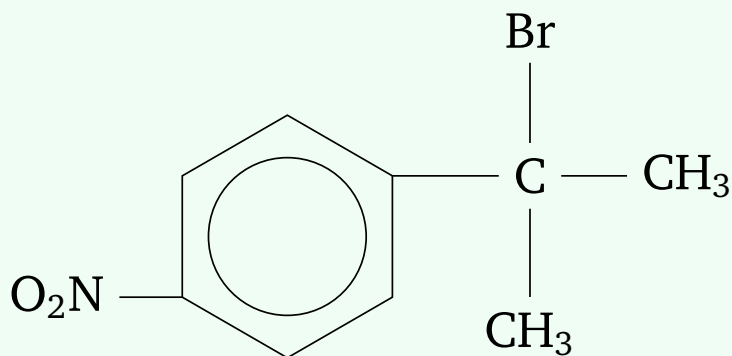


Product (a): 2-methylpropene

Step 2: Substitute the benzylic hydrogen in part (b) The side chain is $-\text{CH}(\text{CH}_3)_2$, so it has one hydrogen on the carbon directly attached to the benzene ring. With Br_2 and heat, this benzylic hydrogen is replaced by bromine. The aromatic ring and its para nitro group remain unchanged:



Bromination at a terminal methyl carbon would involve a less stable radical; ring bromination is not the reaction selected by these conditions.



Product (b): bromine replaces the single benzylic hydrogen

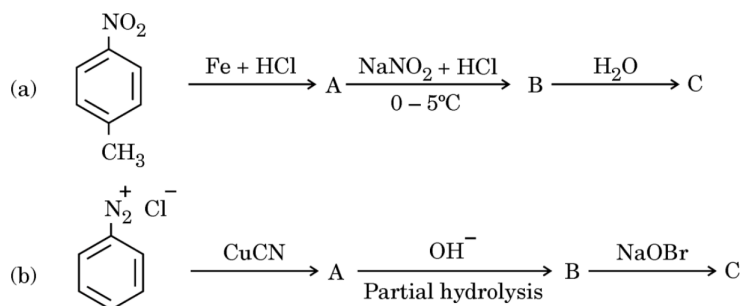
Step 3: Conclusion The major products are (a) 2-methylpropene, $\text{CH}_2=\text{C}(\text{CH}_3)_2$, and (b) $\text{p-NO}_2-\text{C}_6\text{H}_4-\text{C}(\text{Br})(\text{CH}_3)_2$, formed by benzylic bromination.

Quick Tip to Solve: Read the conditions first: ethanolic hydroxide plus heat means elimination; bromine plus heat on an alkylbenzene targets a benzylic hydrogen.

Section C (21 marks)

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

[3 marks]

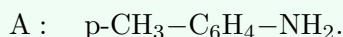


Solution:

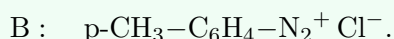
Concept:

- Fe/HCl reduces an aromatic nitro group to an amino group. A primary aromatic amine reacts with NaNO_2/HCl at $0-5^\circ\text{C}$ to form an arenediazonium salt, which is hydrolysed to a phenol.
- In the Sandmeyer reaction, CuCN replaces the diazonium group by $-\text{CN}$. Partial hydrolysis of a nitrile gives an amide; Hofmann bromamide degradation with NaOBr converts that amide to an amine with one fewer carbon atom.

Step 1: Identify the reduction and diazotisation products in (a) The starting compound has NO_2 and CH_3 para to one another. Reduction changes only $-\text{NO}_2$ to $-\text{NH}_2$; the methyl group is retained. Therefore A is 4-methylaniline (p-toluidine):

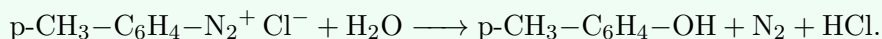


Cold NaNO_2/HCl generates nitrous acid and converts the primary aromatic amino group to a diazonium chloride group. Thus B is 4-methylbenzenediazonium chloride:



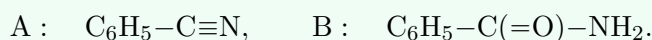
In both condensed structures, the two substituents occupy the 1,4-positions on the benzene ring.

Step 2: Hydrolyse the diazonium salt in (a) Water replaces the diazonium group by $-\text{OH}$, releasing nitrogen. The methyl substituent stays para to the hydroxyl group:



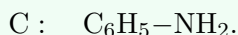
Hence C is 4-methylphenol (p-cresol), with condensed structure $\text{p-CH}_3-\text{C}_6\text{H}_4-\text{OH}$.

Step 3: Replace the diazonium group and partially hydrolyse in (b) The starting ring in this sequence has no methyl substituent. CuCN replaces its diazonium group with a cyano group, giving benzonitrile. Partial hydrolysis then converts the nitrile to benzamide; the instruction “partial” means stopping at the amide rather than continuing to a carboxylate:



Quick Tip to Solve: Keep the para methyl group throughout (a). In (b), stop nitrile hydrolysis at the amide and remove its carbonyl carbon when applying Hofmann degradation.

Step 4: Apply Hofmann degradation in (b) NaOBr brings about Hofmann bromamide degradation of benzamide. The carbonyl carbon is removed from the organic product and the phenyl group becomes directly attached to $-\text{NH}_2$. Thus the product is aniline, not benzylamine:



Step 5: Conclusion (a) $\text{A} = \text{p-CH}_3-\text{C}_6\text{H}_4-\text{NH}_2$, $\text{B} = \text{p-CH}_3-\text{C}_6\text{H}_4-\text{N}_2^+ \text{Cl}^-$, $\text{C} = \text{p-CH}_3-\text{C}_6\text{H}_4-\text{OH}$.
(b) $\text{A} = \text{C}_6\text{H}_5-\text{C}\equiv\text{N}$, $\text{B} = \text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}_2$, $\text{C} = \text{C}_6\text{H}_5-\text{NH}_2$.

Quick Tip to Solve: Keep the para methyl group throughout (a). In (b), stop nitrile hydrolysis at the amide and remove its carbonyl carbon when applying Hofmann degradation.

23. Answer the following:

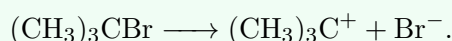
- (a) Which isomer of $\text{C}_4\text{H}_9\text{Br}$ is most reactive towards $\text{S}_{\text{N}}1$ reaction?
(b) Predict the alkene that would be formed by dehydrohalogenation of 1-Bromo-1-methylcyclohexane.
(c) Although chlorine shows strong $-I$ effect, yet it is ortho- and para-directing in electrophilic aromatic substitution reactions. Why? [3 marks]

Solution:

Concept:

- An $\text{S}_{\text{N}}1$ substitution proceeds through a carbocation; greater carbocation stability gives faster ionisation and a faster reaction.
- Dehydrohalogenation removes a halogen and a hydrogen from adjacent carbon atoms. Saytzeff's rule favours the more substituted alkene under the usual conditions.
- Chlorine withdraws electron density by the inductive effect but donates a lone pair into the aromatic ring by resonance; these effects influence reactivity and orientation differently.

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



Three alkyl groups stabilise this carbocation through their electron-releasing inductive effect and hyperconjugation. The other isomers form secondary or primary carbocations, so their $\text{S}_{\text{N}}1$ ionisation is less favourable.

Step 2: (b) Apply Saytzeff's rule to the ring compound In 1-bromo-1-methylcyclohexane, bromine is on carbon 1. Removal of a beta hydrogen from carbon 2 or the equivalent carbon 6 produces the same endocyclic double bond, giving 1-methylcyclohexene. This is a trisubstituted alkene. Elimination of a hydrogen from the methyl group would instead form the less substituted methylenecyclohexane; hence the endocyclic alkene is the major product.

Step 3: (c) Separate deactivation from directing influence Chlorine's strong $-I$ effect withdraws electron density and makes chlorobenzene less reactive than benzene. However, overlap of its lone pair with the ring's pi system donates electron density by resonance, particularly at the ortho and

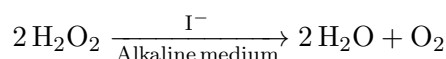
Quick Tip to Solve: For these three parts, compare carbocation stability, alkene substitution and resonance stabilisation separately; chlorine's deactivation does not imply meta direction.

para positions. The intermediates for ortho and para electrophilic attack receive additional resonance stabilisation through chlorine donation; the meta intermediate does not receive this stabilisation. Thus chlorine deactivates the ring overall while directing substitution mainly to ortho and para positions.

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 substitution despite its deactivating $-I$ effect.

Quick Tip to Solve: For these three parts, compare carbocation stability, alkene substitution and resonance stabilisation separately; chlorine's deactivation does not imply meta direction.

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



The mechanism for this reaction was found to be:

Step I: $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ (slow)

Step II: $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ (fast)

(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:

- In a multistep reaction, the slow elementary step controls the overall rate. Its reactant stoichiometry supplies the powers in its rate law.
- The order with respect to a species is its exponent in the rate law; overall order is the sum of these exponents. Molecularity counts the reacting particles in one elementary step.

Step 1: (a) **Use the slow step to write the rate law** Step I, $H_2O_2 + I^- \longrightarrow H_2O + IO^-$, is slow, whereas Step II consumes its intermediate rapidly. The rate therefore depends on a collision involving one hydrogen peroxide molecule and one iodide ion in Step I:

$$r = k[H_2O_2][I^-].$$

Here k is the rate constant and square brackets denote molar concentrations. Iodide appears in the rate law even though it is regenerated in Step II and cancels from the overall equation: it acts as a catalyst. The intermediate IO^- does not appear in this rate law because it is not a reactant of the slow step.

Step 2: (b) **Read the individual and overall orders** The exponent of $[H_2O_2]$ is 1, so the reaction is first order with respect to hydrogen peroxide. The exponent of $[I^-]$ is also 1, so it is first order with respect to iodide. Adding these exponents gives

$$n_{\text{overall}} = 1 + 1 = 2.$$

Quick Tip to Solve: Circle the slow step to obtain the rate law, but count reactants in Step II when answering its molecularity; these are two separate tasks.

The coefficient 2 of hydrogen peroxide in the overall balanced equation must not be used as its order; the mechanism, specifically the slow elementary step here, determines the rate law.

Step 3: (c) Count reacting particles in Step II 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 hydrogen peroxide molecule and one hypoiodite ion, giving two reacting particles. It is therefore bimolecular. The three product species do not enter the molecularity count, and the fact that this step is fast does not change its molecularity.

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

Quick Tip to Solve: Circle the slow step to obtain the rate law, but count reactants in Step II when answering its molecularity; these are two separate tasks.

25. 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:

- Raoult's law gives the solvent vapour pressure as $p = x_{\text{benzene}}p^\circ$, where p° is the pure solvent's vapour pressure and x_{benzene} is its mole fraction in solution.
- Complete dimerisation combines two solute molecules into one particle. The effective solute amount is therefore half its initial molecular amount, corresponding to van't Hoff factor $i = 1/2$.

Step 1: Calculate the initial amounts of solute and solvent Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, has the given molar mass 122 g mol⁻¹. Its initial amount is

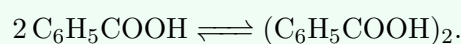
$$n_{\text{acid}} = \frac{61}{122} = 0.500 \text{ mol.}$$

The molar mass of benzene, C_6H_6 , is $6(12) + 6(1) = 78 \text{ g mol}^{-1}$, so

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

The solvent amount is unaffected by association of the solute.

Step 2: Account for complete dimerisation In benzene, two benzoic acid molecules associate by hydrogen bonding to form one dimer:



Since the dimerisation is complete, no unassociated acid remains. The amount of solute particles to use in the mole fraction is

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

Using the original 0.500 mol would double the solute particle count and overestimate the lowering of

Quick Tip to Solve: Halve the moles of benzoic acid for complete dimerisation before calculating the solvent mole fraction; keep the solvent moles unchanged.

vapour pressure.

Step 3: Apply Raoult's law with the corrected mole fraction Treating benzoic acid as a nonvolatile solute, the vapour pressure of the solution is the benzene partial pressure. Its mole fraction is

$$x_{\text{benzene}} = \frac{500/78}{500/78 + 0.250} = \frac{1000}{1039} = 0.962464.$$

Hence

$$p = 66 \times \frac{1000}{1039} = 63.5226 \text{ torr}.$$

The calculation uses the total effective amount in the denominator and therefore does not require the dilute-solution approximation. As expected, the result is below the pure benzene vapour pressure of 66 torr.

Step 4: Conclusion The vapour pressure of the solution is approximately 63.52 torr.

Quick Tip to Solve: Halve the moles of benzoic acid for complete dimerisation before calculating the solvent mole fraction; keep the solvent moles unchanged.

26(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:

- Chloride ions outside the coordination sphere are ionisable and precipitate as AgCl with AgNO_3 . Ligands inside the square brackets remain coordinated to the metal.
- In valence bond theory, an octahedral inner orbital complex uses two vacant $3d$, one $4s$ and three $4p$ orbitals for d^2sp^3 hybridisation. Magnetic behaviour depends on unpaired electrons.

Step 1: Locate the chloride ions One mole of the compound gives three moles of AgCl , so all three chloride ions are outside the coordination sphere. The six neutral ammonia molecules are coordinated to cobalt. Thus the coordination formula is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, which dissociates as



The three free chloride ions then undergo $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl(s)}$.

Step 2: Name the compound and find the metal configuration Since ammonia is neutral and the complex cation has charge +3, cobalt has oxidation state +3. The IUPAC name is **hexaamminecobalt(III) chloride**. Cobalt has atomic number 27 and configuration $[\text{Ar}] 3d^7 4s^2$; removal of two $4s$ electrons and one $3d$ electron gives Co^{3+} the configuration $[\text{Ar}] 3d^6$.

Step 3: Apply valence bond theory In this cobalt(III) complex, the ligand field due to the six ammonia ligands causes the six $3d$ electrons to pair in three $3d$ orbitals. Two $3d$ orbitals are left vacant. These combine with one $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrid orbitals, each accepting an ammonia lone pair. The complex is octahedral and uses inner orbitals. There are no unpaired

Quick Tip to Solve: Use the moles of precipitated silver chloride to count chloride counterions first; then determine the metal oxidation state before filling its orbitals.

electrons, so it is diamagnetic.

Step 4: Conclusion The structural formula is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$; its name is hexaamminecobalt(III) chloride. It is an octahedral, d^2sp^3 -hybridised inner orbital complex and is diamagnetic.

Quick Tip to Solve: Use the moles of precipitated silver chloride to count chloride counterions first; then determine the metal oxidation state before filling its orbitals.

OR

26(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:

- Geometrical isomers differ in the relative positions of ligands. Octahedral complexes of type MA_3B_3 have facial and meridional arrangements; optical isomerism is a different classification.
- An inner orbital octahedral complex uses d^2sp^3 hybridisation involving 3d orbitals; an outer orbital octahedral complex uses sp^3d^2 involving 4d orbitals.

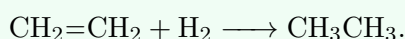
Step 1: Count the geometrical arrangements in part (i) (I) In $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$, three identical bidentate oxalate ligands occupy all six coordination positions. It exhibits **no geometrical isomerism**: there is only one geometrical arrangement. Its two optical forms are not counted as geometrical isomers.

(II) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$ has **two geometrical isomers**, *fac* and *mer*. In the facial form, the three identical ligands occupy one face of the octahedron and are mutually cis. In the meridional form, they lie in a plane through the metal and one pair of identical ligands is trans.

Step 2: Explain the orbital choice in part (ii) Cobalt(III) is $3d^6$. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, the 3d electrons pair in three orbitals, leaving two 3d orbitals vacant. These participate with 4s and 4p orbitals in d^2sp^3 hybridisation, making it an inner orbital complex.

Nickel(II) is $3d^8$. Eight electrons cannot fit into only three 3d orbitals, so two vacant 3d orbitals cannot be made available, even by pairing. Hence $[\text{Ni}(\text{NH}_3)_6]^{2+}$ uses the 4s, three 4p and two 4d orbitals for sp^3d^2 hybridisation and is an outer orbital complex.

Step 3: Identify the catalyst and its use in part (iii) Wilkinson catalyst is $[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$, chloridotris(triphenylphosphine)rhodium(I). Each phosphorus ligand is triphenylphosphine. It is a homogeneous catalyst used for the hydrogenation of alkenes to alkanes, for example



Step 4: Conclusion (i) The chromium complex has no geometrical isomerism (one arrangement);

Quick Tip to Solve: Keep optical and geometrical isomerism separate. For inner orbital hybridisation, explicitly check whether two vacant 3d orbitals can exist.

the cobalt complex has two forms, *fac* and *mer*. (ii) The cobalt complex is inner orbital, d^2sp^3 , and the nickel complex is outer orbital, sp^3d^2 . (iii) Wilkinson catalyst, $[\text{RhCl}(\text{P}(\text{C}_6\text{H}_5)_3)_3]$, hydrogenates alkenes.

Quick Tip to Solve: Keep optical and geometrical isomerism separate. For inner orbital hybridisation, explicitly check whether two vacant $3d$ orbitals can exist.

27. 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]

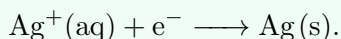
Solution:

Concept:

- Passing direct current through an electrolyte can cause electrolysis and electrode polarisation, changing the solution and the measured potential difference.
- Electrolysis products depend on the electrolyte and on whether the electrodes participate in the reactions. A more readily oxidised metal can protect iron as a sacrificial anode.

Step 1: Explain the use of alternating current in part (a) Direct current causes electrolysis, changing the concentration near the electrodes. Electrode polarisation also introduces an opposing potential, so the measured resistance is unreliable. Alternating current of suitable frequency reverses direction rapidly, minimising net electrolysis and polarisation, and is used instead.

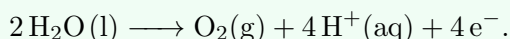
Step 2: Compare the electrode reactions in part (b) At the cathode in both cases, silver ions are reduced:



Silver electrodes are active. The silver anode itself is oxidised, replenishing silver ions in solution:

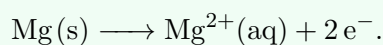


Silver is transferred from anode to cathode. Platinum is inert: instead of the anode dissolving, water is oxidised and oxygen is evolved:



Thus the anode material changes the anodic product. Nitrate remains a spectator ion.

Step 3: Explain magnesium protection in part (c) Magnesium is more readily oxidised than iron. When the magnesium blocks are electrically connected to the iron pipeline in the presence of water, magnesium becomes the sacrificial anode:



Quick Tip to Solve: For electrolysis, write the cathode and anode reactions separately. For corrosion protection, make the more reactive metal the anode and the protected iron the cathode.

The electrons make iron the cathode and suppress its oxidation. Magnesium corrodes preferentially, protecting the pipe; the blocks are replaced as they are consumed.

Step 4: Conclusion (a) DC changes the solution and polarises electrodes, giving an unreliable resistance measurement. (b) Silver anodes dissolve, while inert platinum anodes evolve oxygen; silver deposits at either cathode. (c) Magnesium blocks act as sacrificial anodes and provide cathodic protection to iron.

Quick Tip to Solve: For electrolysis, write the cathode and anode reactions separately. For corrosion protection, make the more reactive metal the anode and the protected iron the cathode.

28. 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.

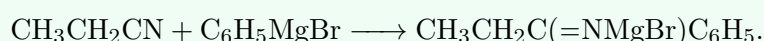
[3 marks]

Solution:

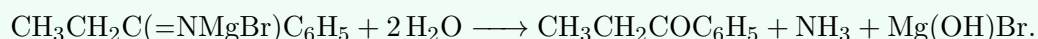
Concept:

- A Grignard reagent adds to the carbon of a nitrile group. Hydrolysis of the resulting magnesium imine salt gives a ketone.
- Chromium trioxide in acetic anhydride oxidises an aromatic methyl group to a protected aldehyde, the geminal diacetate; acidic hydrolysis releases the aldehyde.
- Adjacent carboxyl groups of phthalic acid react with ammonia and lose water on heating to form a cyclic imide.

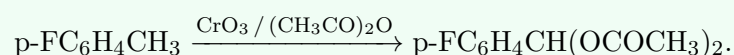
Step 1: (a) Add phenylmagnesium bromide to propanenitrile The phenyl group bonds to the nitrile carbon. Thus the carbonyl carbon in the final ketone is attached to an ethyl group and a phenyl group:



Hydrolysis of the magnesium imine salt gives propiophenone (1-phenylpropan-1-one):

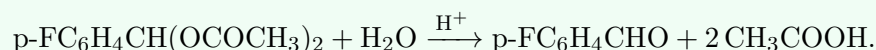


Step 2: (b) Oxidise the methyl side chain under protecting conditions The fluorine substituent remains unchanged. Acetic anhydride traps the aldehyde as its geminal diacetate, preventing further oxidation to the acid:



Quick Tip to Solve: In nitrile-Grignard reactions, retain the nitrile carbon as the ketone carbonyl carbon. For oxidation in acetic anhydride, show the protected diacetate before hydrolysis.

Acidic hydrolysis then produces 4-fluorobenzaldehyde:



Step 3: (c) Form the cyclic imide on heating Ammonia first forms an ammonium salt. Heating causes dehydration and ring closure:



In phthalimide, the two carbonyl groups and the same NH group form a five-membered ring fused to benzene.

Step 4: Conclusion The products are (a) propiophenone, $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$; (b) 4-fluorobenzaldehyde, $\text{p-FC}_6\text{H}_4\text{CHO}$; and (c) phthalimide, $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$.

Quick Tip to Solve: In nitrile–Grignard reactions, retain the nitrile carbon as the ketone carbonyl carbon. For oxidation in acetic anhydride, show the protected diacetate before hydrolysis.

Section D (8 marks)

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

29(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:

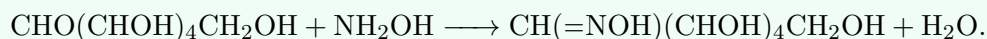
Concept:

- Hydroxylamine, NH_2OH , reacts with a carbonyl group to form an oxime by condensation with loss of water.
- Acetic anhydride converts an alcoholic $-\text{OH}$ group into an acetate ester. The number of acetyl groups introduced counts the hydroxyl groups.

Step 1: (i) Identify the carbonyl group through oxime formation Glucose reacts with hydroxylamine

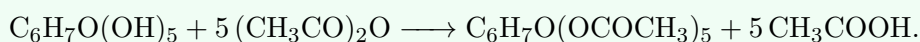
Quick Tip to Solve: Associate oxime formation with the carbonyl group and the prefix penta- in pentaacetate with five hydroxyl groups; acetylation does not count the carbonyl oxygen.

to give glucose oxime. Using its open-chain formula, the reaction is



This characteristic reaction establishes the presence of a carbonyl group in glucose. Oxime formation alone distinguishes a carbonyl compound from an alcohol but does not distinguish an aldehyde from a ketone; that distinction is established by other reactions.

Step 2: (ii) Count the hydroxyl groups by acetylation Glucose reacts with acetic anhydride to form glucose pentaacetate. Each of its five hydroxyl groups forms one acetate ester:



The pentaacetate therefore confirms five $-\text{OH}$ groups. In the standard structural argument, the stability of glucose supports their attachment to different carbon atoms: structures with multiple hydroxyl groups on the same carbon are generally unstable. In the open-chain structure these groups occur at C2, C3, C4, C5 and C6.

Step 3: Conclusion Oxime formation with hydroxylamine establishes a carbonyl group. Formation of glucose pentaacetate establishes five hydroxyl groups, and glucose's stability supports their attachment to different carbon atoms.

Quick Tip to Solve: Associate oxime formation with the carbonyl group and the prefix penta- in pentaacetate with five hydroxyl groups; acetylation does not count the carbonyl oxygen.

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

[1 mark]

Solution:

Concept:

- Reducing sugars reduce mild oxidising reagents such as Tollens' reagent and Fehling's solution, while the sugar itself is oxidised.
- A free anomeric hemiacetal or hemiketal group allows a cyclic sugar to open to a reactive carbonyl form.

Step 1: State the chemical test defining reducing sugars Carbohydrates that reduce Tollens' reagent or Fehling's solution are called reducing sugars. They produce metallic silver with Tollens' reagent or a brick-red precipitate of Cu_2O with Fehling's solution.

Step 2: Connect this behaviour to their structure Glucose is an example: its cyclic hemiacetal can open to expose an aldehyde group. Ketose sugars such as fructose also give these tests because they rearrange to aldoses in the alkaline test medium. Thus reducing sugars include both aldoses and ketoses; the term does not mean that every reducing sugar initially has a free aldehyde group.

Step 3: Conclusion Reducing sugars are carbohydrates that reduce Tollens' reagent or Fehling's solution, for example glucose and fructose.

Quick Tip to Solve: Define reducing sugars by their reaction with Tollens' or Fehling's reagent; remember that fructose also responds after rearrangement in alkaline solution.

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

[1 mark]

Solution:

Concept:

- The D/L designation states the relative configuration of a sugar compared with the corresponding glyceraldehyde.
- The signs (+) and (–) describe the experimentally observed direction of rotation of plane-polarised light, independently of the D/L designation.

Step 1: Interpret the letter D D means that the configuration at the highest-numbered chiral carbon, C5 in glucose, corresponds to that of D-glyceraldehyde. In the standard Fischer projection with the aldehyde at the top, the hydroxyl group on C5 lies on the right.

Step 2: Interpret the sign plus The sign (+) means glucose is dextrorotatory: it rotates plane-polarised light to the right (clockwise). This sign is measured experimentally. The letter D alone does not imply positive optical rotation; configuration and the direction of rotation are separate properties.

Step 3: Conclusion D denotes configuration relative to D-glyceraldehyde, while (+) denotes dextrorotation of plane-polarised light.

Quick Tip to Solve: Read D from the last chiral centre in the Fischer projection; read (+) as an experimental optical-rotation sign, never as the meaning of D.

OR

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

[1 mark]

Solution:

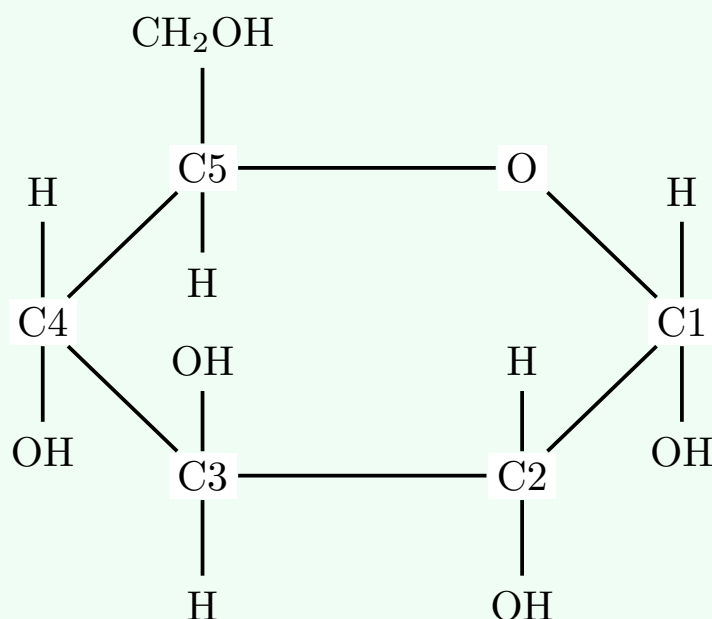
Concept:

- Glucose forms a six-membered cyclic hemiacetal when its C5 hydroxyl group adds to the C1 aldehyde group; the ring contains five carbon atoms and one oxygen atom.
- In the Haworth projection of a D-sugar, the C5 CH₂OH group is above the ring. The α anomer has its C1 hydroxyl group on the opposite side.

Step 1: Place the glucose hydroxyl groups on the pyranose ring Draw the ring oxygen between C5 and C1. For D-glucose the hydroxyl groups at C2, C3 and C4 point down, up and down, respectively, while the CH₂OH group attached to C5 points up. The sixth carbon is in this side group, outside the ring.

Step 2: Select the alpha anomer Place the hydroxyl group on the anomeric carbon C1 below the ring, opposite to the upward CH₂OH group at C5. The hydrogens occupy the opposite positions at each carbon. The resulting Haworth projection is shown below; C1–C5 label the five ring carbon atoms.

Quick Tip to Solve: For D-glucose, keep CH₂OH up; alpha means the anomeric OH is down. The C2–C4 hydroxyl pattern is down–up–down.



Haworth projection of α -D-glucopyranose

Step 3: Conclusion The structure is α -D-glucopyranose, with the C1 hydroxyl group down and the C5 CH_2OH group up.

Quick Tip to Solve: For D-glucose, keep CH_2OH up; alpha means the anomeric OH is down. The C2–C4 hydroxyl pattern is down–up–down.

30(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:

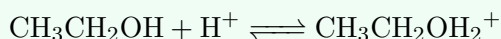
Concept:

- Acid-catalysed dehydration removes water from an alcohol to form an alkene. Ethanol is heated with concentrated sulphuric acid at about 443 K.
- Protonation converts the poor leaving group $-\text{OH}$ into water. The acid catalyst is regenerated when a proton is eliminated and the carbon–carbon double bond forms.

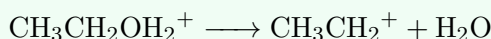
Step 1: Protonate the oxygen of ethanol An oxygen lone pair accepts a proton from the acid to form protonated ethanol, an oxonium ion. The positively charged oxygen now bears two hydrogen atoms,

Quick Tip to Solve: Remember the order: protonate oxygen, remove water, then remove the adjacent carbon's proton to create the double bond and regenerate acid.

allowing the group to leave as neutral water.

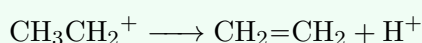


Step 2: Show loss of water In the standard stepwise acid-dehydration mechanism, protonated ethanol loses a water molecule in the slow step to give the carbocation intermediate.

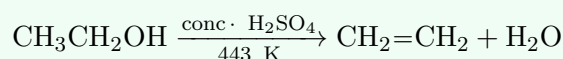


The carbon–oxygen bond electrons leave with oxygen; this is why protonation must precede departure of the leaving group.

Step 3: Eliminate a proton to form the double bond A proton is removed from the carbon adjacent to the positively charged carbon. The electrons of that carbon–hydrogen bond form the carbon–carbon π bond, regenerating the acid catalyst.



Step 4: Conclusion Ethanol undergoes acid-catalysed dehydration to ethene:



Quick Tip to Solve: Remember the order: protonate oxygen, remove water, then remove the adjacent carbon's proton to create the double bond and regenerate acid.

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

[1 mark]

Solution:

Concept:

- Oxidation of an alcohol to a carbonyl compound removes hydrogen from oxygen and from the carbon bearing the hydroxyl group.
- A tertiary alcohol has the general structure R_3COH : the carbon bonded to $-\text{OH}$ is also bonded to three carbon groups and has no hydrogen atom.

Step 1: Inspect the hydroxyl-bearing carbon In a tertiary alcohol all four bonds of the hydroxyl-bearing carbon connect it to oxygen or carbon atoms. Hence it lacks the required hydrogen on that carbon, although the hydroxyl group itself still contains hydrogen.

Step 2: Apply the requirement for ordinary oxidation Without a hydrogen on the hydroxyl-bearing carbon, a carbonyl group cannot form by the usual removal of two hydrogen atoms. Oxidation would require carbon–carbon bond cleavage, which needs vigorous conditions.

Step 3: Conclusion Tertiary alcohols resist ordinary oxidation because the carbon bearing $-\text{OH}$ has no hydrogen atom; oxidation under harsh conditions involves carbon–carbon bond cleavage.

Quick Tip to Solve: Look for hydrogen on the carbon bonded to hydroxyl, not merely for hydrogen in the hydroxyl group or elsewhere in the molecule.

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

[1 mark]

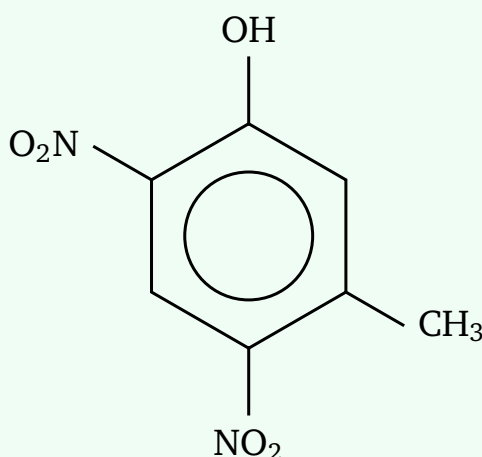
Solution:

Concept:

- Both hydroxyl and methyl groups direct electrophilic aromatic substitution towards their ortho and para positions.
- Dinitration replaces two ring hydrogens by two $-\text{NO}_2$ groups. Steric crowding disfavors substitution between two existing substituents.

Step 1: Locate the jointly directed positions Number the starting phenol ring with hydroxyl at carbon 1 and methyl at carbon 3. Both groups direct nitration towards carbons 2, 4 and 6: these are ortho or para to each group.

Step 2: Avoid the crowded site between the groups Carbon 2 lies between hydroxyl and methyl and is the most sterically crowded of the available sites. The two nitro groups therefore enter positions 4 and 6 of the starting ring. The structure below shows these positions, with hydroxyl at the top and methyl at the lower right.



Major dinitration product of 3-methylphenol

Step 3: Conclusion The major product is 3-methyl-4,6-dinitrophenol (using the starting ring numbering), equivalently named 5-methyl-2,4-dinitrophenol.

Quick Tip to Solve: For 3-methylphenol, mark positions 2, 4 and 6 first; exclude position 2 because it lies between hydroxyl and methyl, then nitrate at 4 and 6.

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

[1 mark]

Solution:

Concept:

- Phenol acidity depends on the stability of the phenoxide conjugate base: greater stabilisation after loss of H^+ favours ionisation.
- Nitro is electron withdrawing by inductive and resonance effects; methoxy donates electron density to the ring by resonance, despite its inductive withdrawal.

Step 1: Examine the nitro-substituted conjugate base On ionisation, ortho-nitrophenol gives ortho-nitrophenoxide. The $-NO_2$ group withdraws electron density by its $-I$ and $-R$ effects and permits additional delocalisation of the negative charge. This stabilises the conjugate base and favours proton loss.

Step 2: Compare the methoxy-substituted conjugate base In ortho-methoxyphenol, the $-OCH_3$ group supplies electron density to the ring through its $+R$ effect. It does not provide the strong resonance stabilisation of negative charge supplied by nitro, so proton loss is less favourable than in ortho-nitrophenol.

Step 3: Conclusion Ortho-nitrophenol is more acidic because its electron-withdrawing nitro group stabilises the phenoxide ion much more effectively than the resonance-donating methoxy group.

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

Section E (15 marks)

31(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:

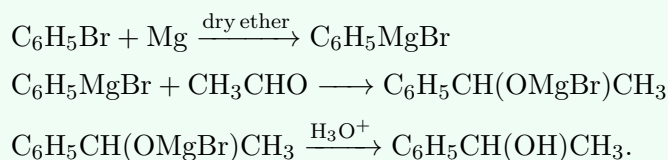
- Grignard reagents add to aldehydes; acidic hydrolysis of the magnesium alkoxide gives an alcohol. Addition to ethanal gives a secondary alcohol.
- The acetyl group, $-COCH_3$, is meta-directing. Introduce it by Friedel-Crafts acylation before nitration, because nitrobenzene does not undergo ordinary Friedel-Crafts acylation.
- An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated

Quick Tip to Solve: Install the meta-directing acetyl group before nitration. For the identification, the 1,2-diacid fixes the relative positions of the two oxidisable side chains.

alkali, producing a carboxylate and a primary alcohol.

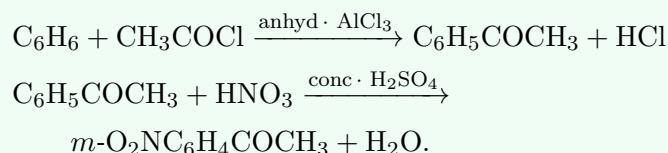
- Electron-withdrawing groups stabilise the carboxylate ion and increase carboxylic-acid strength; their inductive effect becomes stronger with greater electron withdrawal and shorter distance.

Step 1: (i)(I) Form the Grignard reagent and add ethanal Treat bromobenzene with magnesium in dry ether to form phenylmagnesium bromide. Add ethanal under anhydrous conditions, then hydrolyse the addition product with dilute acid:



The new carbon–carbon bond joins the phenyl group to the carbonyl carbon of ethanal. This gives 1-phenylethanol after hydrolysis; water must be excluded until that last step because it destroys the Grignard reagent.

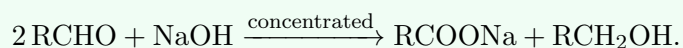
Step 2: (i)(II) Acylate benzene before nitration First prepare acetophenone by treating benzene with acetyl chloride and anhydrous aluminium chloride. Then nitrate with concentrated nitric and sulphuric acids:



The acetyl group withdraws electrons and directs the incoming nitro group mainly to the meta position, furnishing m-nitroacetophenone. Reversing this order would first form strongly deactivated nitrobenzene.

Step 3: (ii) Identify the aldehyde from the chemical tests Formation of a 2,4-DNP derivative indicates a carbonyl group. Reduction of Tollens' reagent establishes an aldehyde here, while the Cannizzaro reaction shows that the aldehyde lacks an alpha-hydrogen. The molecular formula $\text{C}_8\text{H}_8\text{O}$ and oxidation to benzene-1,2-dicarboxylic acid together identify the compound as 2-methylbenzaldehyde (o-tolualdehyde), $o\text{-CH}_3\text{C}_6\text{H}_4\text{CHO}$. Both the methyl and aldehyde side chains are oxidised to carboxyl groups by vigorous permanganate oxidation. Their adjacent positions explain the 1,2-dicarboxylic acid product. The methyl hydrogens are not alpha to the aldehyde carbonyl; the carbon directly attached to $-\text{CHO}$ is a ring carbon with no hydrogen.

Step 4: (ii) Write the Cannizzaro products Let R denote the 2-methylphenyl group, $o\text{-CH}_3\text{C}_6\text{H}_4$. With concentrated sodium hydroxide, one molecule is oxidised and another is reduced:



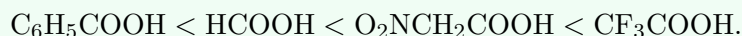
The products in the alkaline reaction mixture are sodium 2-methylbenzoate, $o\text{-CH}_3\text{C}_6\text{H}_4\text{COONa}$, and 2-methylbenzyl alcohol, $o\text{-CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{OH}$. Acidification of the salt subsequently gives 2-methylbenzoic acid; the direct alkaline product is its salt.

Step 5: (iii) Compare the stability of the conjugate bases Benzoic acid is weaker than formic acid. The nitro group in nitroacetic acid withdraws electrons strongly through the sigma bonds and stabilises its

Quick Tip to Solve: Install the meta-directing acetyl group before nitration. For the identification, the 1,2-diacid fixes the relative positions of the two oxidisable side chains.

carboxylate ion, making it stronger than formic acid. The three fluorine atoms in trifluoroacetic acid exert an especially powerful electron-withdrawing inductive effect, making it the strongest of the four. Thus compare conjugate-base stabilisation, rather than simply counting carbon atoms.

Step 6: Conclusion The conversions proceed through phenylmagnesium bromide plus ethanal, and through acetophenone followed by nitration, respectively. The unknown is 2-methylbenzaldehyde; its Cannizzaro products are sodium 2-methylbenzoate and 2-methylbenzyl alcohol. The increasing acid-strength order is



Quick Tip to Solve: Install the meta-directing acetyl group before nitration. For the identification, the 1,2-diacid fixes the relative positions of the two oxidisable side chains.

OR

31(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.

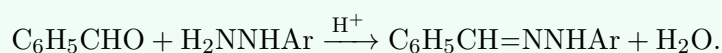
[5 marks]

Solution:

Concept:

- Aldehydes condense with 2,4-DNP reagent. The corresponding hydrazone forms with elimination of water.
- In crossed aldol condensation, the enolate of a carbonyl compound with α -hydrogens adds to an aldehyde. Heating removes water to give an α,β -unsaturated carbonyl compound.
- An electron-withdrawing carboxyl group deactivates a benzene ring towards electrophilic substitution, while intermolecular hydrogen bonding raises the boiling point of carboxylic acids.
- Tollens' reagent oxidises an aliphatic aldehyde to a carboxylate ion while its silver(I) ions are reduced to metallic silver; a simple ketone does not respond.

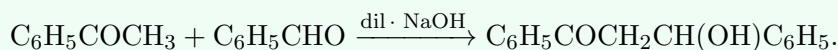
Step 1: (i)(I) Form the 2,4-dinitrophenylhydrazone Benzaldehyde reacts with acidified 2,4-dinitrophenylhydrazine to give benzaldehyde 2,4-dinitrophenylhydrazone, usually seen as an orange precipitate. Let Ar denote the 2,4-dinitrophenyl group, $\text{C}_6\text{H}_3(\text{NO}_2)_2$, with the nitro groups at positions 2 and 4 relative to the hydrazine attachment:



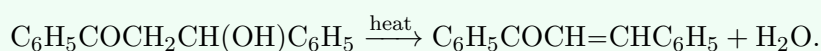
Quick Tip to Solve: In this crossed aldol reaction, acetophenone supplies the enolate and retains its carbonyl; benzaldehyde supplies the carbon that becomes the β -carbon of chalcone.

The terminal amino group of the reagent condenses with the carbonyl group; the carbonyl oxygen is replaced by =NNHAr. This accounts for the hydrazone product and loss of one molecule of water.

Step 2: (i)(II) Carry out crossed aldol condensation Acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$, contains α -hydrogens and forms an enolate in dilute sodium hydroxide. Benzaldehyde has no α -hydrogen and acts as the carbonyl acceptor. Addition first produces the β -hydroxy ketone:



Heating causes dehydration, extending conjugation between the carbonyl and double bond:

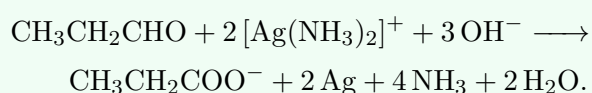


The product is benzalacetophenone (chalcone), also called 1,3-diphenylprop-2-en-1-one, with the trans form predominating.

Step 3: (ii)(I) Explain the failure of Friedel–Crafts reaction In benzoic acid, the $-\text{COOH}$ group withdraws electron density from the ring by both inductive and resonance effects. This makes the ring too strongly deactivated for ordinary Friedel–Crafts alkylation or acylation. The carboxyl group also coordinates with the Lewis-acid catalyst, such as AlCl_3 , which further inhibits the reaction. Thus the required electrophilic substitution does not occur under the usual Friedel–Crafts conditions.

Step 4: (ii)(II) Relate boiling point to hydrogen-bonded association Carboxylic-acid molecules associate into cyclic dimers held together by two intermolecular hydrogen bonds. Each $-\text{COOH}$ group can donate a hydrogen bond through its hydroxyl hydrogen and accept one through its carbonyl oxygen. Although alcohols also hydrogen-bond, this strongly associated acid dimer gives stronger overall intermolecular attraction. More thermal energy is therefore required to separate the molecules, so carboxylic acids have higher boiling points than alcohols of comparable molecular mass.

Step 5: (iii) Distinguish propanal from propanone using Tollens' reagent Warm each compound separately with freshly prepared Tollens' reagent in a clean test tube. Propanal gives a silver mirror because its aldehyde group is oxidised to propanoate; propanone gives no silver mirror because its ketone group does not reduce this reagent. The ionic equation is

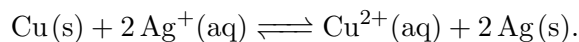


The visible deposition of metallic silver is the distinguishing observation, rather than merely stating that the aldehyde is oxidised.

Step 6: Conclusion Benzaldehyde forms its 2,4-dinitrophenylhydrazone with 2,4-DNP and chalcone, $\text{C}_6\text{H}_5\text{COCH}=\text{CHC}_6\text{H}_5$, with acetophenone followed by heating. Benzoic acid resists Friedel–Crafts reaction because its ring is strongly deactivated; hydrogen-bonded dimers account for the higher boiling points of carboxylic acids. Tollens' reagent gives a silver mirror with propanal and no silver mirror with propanone.

Quick Tip to Solve: In this crossed aldol reaction, acetophenone supplies the enolate and retains its carbonyl; benzaldehyde supplies the carbon that becomes the β -carbon of chalcone.

32(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:

- The standard cell potential and equilibrium constant are related by $E_{\text{cell}}^{\circ} = (2.303RT/nF) \log K_c$, where n is electrons transferred per balanced reaction, R is the gas constant, T is temperature and F is the Faraday constant. At 298 K, the coefficient is $0.0591/n$ volt.
- A discharging lead storage battery is a galvanic cell: oxidation occurs at the lead anode and reduction at the lead dioxide cathode in sulphuric acid.
- Faraday's law gives $Q = n_e F$, where n_e is the amount of electrons in moles and $F = 96500 \text{ C mol}^{-1}$.

Step 1: (i) Relate the equilibrium constant to the standard potential Copper is oxidised from 0 to +2, while each silver ion gains one electron. Thus the balanced cell reaction transfers $n = 2$ electrons. The Nernst equation is

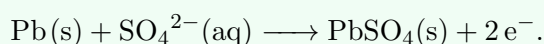
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{2} \log Q_r$$

at the usual standard calculation temperature 298 K, where Q_r is the reaction quotient. At equilibrium $E_{\text{cell}} = 0$ and $Q_r = K_c$. Therefore

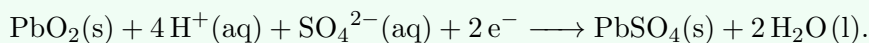
$$E_{\text{cell}}^{\circ} = \frac{0.0591}{2} \log(10^{15}) = \frac{0.0591 \times 15}{2} = 0.44325 \text{ V}.$$

The question asks for the standard potential, which is distinct from the actual potential of the equilibrated cell. Its positive sign agrees with the large equilibrium constant for the forward reaction.

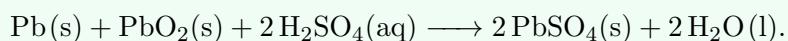
Step 2: (ii) Write the electrode reactions during discharge At the anode, lead loses two electrons and forms lead sulphate:



At the cathode, lead in lead dioxide is reduced from +4 to +2:



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



Both electrodes become coated with lead sulphate and sulphuric acid is consumed as the battery supplies current.

Step 3: (iii) Count the electrons lost by the iron In FeO, iron has oxidation state +2; in Fe_2O_3 , it has

Quick Tip to Solve: Use two electrons for the copper-silver cell, but only one electron per iron atom for FeO oxidation. At equilibrium the actual cell potential is zero, not its standard potential.

oxidation state +3. Each iron atom therefore loses one electron. Since one mole of FeO contains one mole of iron atoms, oxidation requires removal of one mole of electrons:

$$Q = (1 \text{ mol})(96500 \text{ C mol}^{-1}) = 96500 \text{ C}.$$

The two iron atoms in the product formula do not double this charge: one mole of the given reactant produces only half a mole of Fe₂O₃.

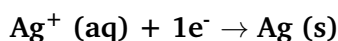
Step 4: Conclusion (i) $E_{\text{cell}}^{\circ} \approx +0.443 \text{ V}$ at 298 K. (ii) The anode and cathode reactions above add to $\text{Pb} + \text{PbO}_2 + 2 \text{H}_2\text{SO}_4 \longrightarrow 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$. (iii) The required charge is $9.65 \times 10^4 \text{ C}$.

Quick Tip to Solve: Use two electrons for the copper-silver cell, but only one electron per iron atom for FeO oxidation. At equilibrium the actual cell potential is zero, not its standard potential.

OR

32(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} . For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^{\circ}$.
- At 25°C, the Nernst equation is $E = E^{\circ} - (0.0591/n) \log Q_r$, where n is the number of electrons in the half reaction and Q_r is its reaction quotient. A pure solid has unit activity.
- An electrolyte conducts through mobile ions. The conventional dry cell uses a moist salt paste, whereas the alkaline hydrogen-oxygen fuel cell uses aqueous potassium hydroxide.

Step 1: (i) Calculate the molar conductivity The given conductivity is $\kappa = 7.2 \times 10^{-5} \text{ S cm}^{-1}$ and the concentration is $c = 0.0024 \text{ mol L}^{-1}$. The factor 1000 converts litres to cubic centimetres so that the units are consistent:

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

Acetic acid is a weak electrolyte. Its conductivity at this concentration is lower than the limiting value because only a fraction of its molecules produce ions.

Step 2: (i) Obtain the fraction dissociated At infinite dilution, the limiting molar conductivity

Quick Tip to Solve: First compute $\Lambda_m = 30.0$ and divide by 390.5. For the silver reduction half cell, remember that the ion is a reactant, so $E = E^{\circ} + 0.0591 \log [\text{Ag}^+]$.

corresponds to complete dissociation. Thus the fraction dissociated at the given concentration is

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{30.0}{390.5} = 0.07682.$$

The conductivity units cancel. Expressing this dimensionless fraction as a percentage gives $100\alpha = 7.682\%$. Do not confuse the fraction 0.0768 with a percentage of 0.0768%.

Step 3: (ii) Apply the Nernst equation to the silver electrode For $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$, one electron is accepted, so $n = 1$. Solid silver has unit activity and the reaction quotient is $Q_r = 1/[\text{Ag}^+]$. Using the concentration relative to the standard concentration,

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

This is the reduction potential of the half cell relative to the standard hydrogen electrode. Diluting silver ions makes reduction less favourable, so the potential is below +0.80 V, consistent with the calculated sign of the change.

Step 4: (iii) Identify the two electrolytes (I) A conventional dry cell contains a moist paste of ammonium chloride, NH_4Cl , and zinc chloride, ZnCl_2 . The paste provides ions while limiting leakage. (II) The hydrogen-oxygen fuel cell uses aqueous potassium hydroxide, KOH , commonly a concentrated solution. Hydroxide ions carry charge through its electrolyte; hydrogen and oxygen are supplied continuously to the electrodes.

Step 5: Conclusion (i) The degree of dissociation is $\alpha \approx 0.0768$, or 7.68%. (ii) The silver half-cell reduction potential is +0.682 V. (iii) Dry cell: moist NH_4Cl - ZnCl_2 paste; hydrogen-oxygen fuel cell: aqueous KOH .

Quick Tip to Solve: First compute $\Lambda_m = 30.0$ and divide by 390.5. For the silver reduction half cell, remember that the ion is a reactant, so $E = E^\circ + 0.0591 \log[\text{Ag}^+]$.

33(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:

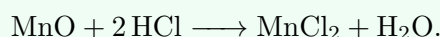
Concept:

- For the same transition metal, an oxide in a low oxidation state is generally basic, while an oxide in a high oxidation state is acidic.

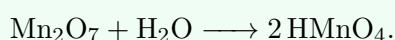
Quick Tip to Solve: For the three comparisons, check oxidation state, metallic bonding and the configuration after reduction, respectively. In dichromate preparation, acidify first and introduce potassium ions second.

- Enthalpy of atomization measures the energy needed to separate a metal into gaseous atoms; stronger metallic bonding gives a larger value.
- An oxidising agent accepts electrons. The stability of the initial and reduced electronic configurations helps explain its tendency to be reduced.
- Acidification converts chromate into dichromate. Potassium dichromate is less soluble than sodium dichromate and can be separated by crystallisation.

Step 1: (i)(I) Compare the oxidation states in the oxides Oxygen has oxidation state -2 . Manganese is therefore in the $+2$ state in MnO , but in the $+7$ state in Mn_2O_7 . The low-oxidation-state oxide MnO is predominantly ionic and reacts with acids, showing basic character:

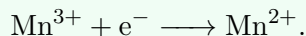


In its high oxidation state, manganese forms the covalent acidic oxide Mn_2O_7 , which is the anhydride of permanganic acid:



Step 2: (i)(II) Relate atomization enthalpy to metallic bonding The atomic electronic configurations are $\text{Fe} : [\text{Ar}] 3d^6 4s^2$ and $\text{Cu} : [\text{Ar}] 3d^{10} 4s^1$. Iron has more unpaired d electrons available to contribute to metallic bonding, whereas copper has a filled $3d$ subshell. The stronger overall metallic bonding in iron requires more energy to separate its atoms. Hence iron has a higher enthalpy of atomization than copper.

Step 3: (i)(III) Compare the stability of the reduced ions Mn^{3+} has configuration $[\text{Ar}] 3d^4$. It readily accepts an electron to form the particularly stable half-filled $3d^5$ configuration of Mn^{2+} :



In contrast, Cr^{3+} has the stable $3d^3$ configuration, with three electrons in the lower-energy t_{2g} orbitals of its octahedral aqua complex. Reduction to Cr^{2+} produces $3d^4$, losing this favourable arrangement. Thus Cr^{3+} is less readily reduced and Mn^{3+} is the stronger oxidising agent.

Step 4: (ii) Acidify sodium chromate to form sodium dichromate Treat an aqueous solution of sodium chromate with sulphuric acid. Acidification shifts the chromate–dichromate equilibrium towards the orange dichromate ion. The balanced molecular equation is



The corresponding ionic change is $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O}$; chromium remains in oxidation state $+6$, so this step is not a redox reaction.

Step 5: (ii) Convert sodium dichromate into potassium dichromate Add potassium chloride to the concentrated sodium dichromate solution:



On cooling, the less soluble potassium dichromate crystallises as orange crystals. Separate the crystals from the mother liquor. The difference in solubility makes this conversion useful for isolating the

Quick Tip to Solve: For the three comparisons, check oxidation state, metallic bonding and the configuration after reduction, respectively. In dichromate preparation, acidify first and introduce potassium ions second.

potassium salt.

Step 6: Conclusion The low and high oxidation states explain basic MnO and acidic Mn_2O_7 ; stronger metallic bonding explains iron's higher atomization enthalpy; formation of stable Mn^{2+} explains the greater oxidising power of Mn^{3+} . Prepare $\text{K}_2\text{Cr}_2\text{O}_7$ by acidifying Na_2CrO_4 , then adding KCl and crystallising the product.

Quick Tip to Solve: For the three comparisons, check oxidation state, metallic bonding and the configuration after reduction, respectively. In dichromate preparation, acidify first and introduce potassium ions second.

OR

33(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:

- Orbitals with similar energies can participate in bonding, leading to several accessible oxidation states. Electronic configurations help explain stable ions.
- The standard reduction potential $E^\circ_{\text{M}^{2+}/\text{M}}$ depends on the combined energetics of atomization, ionization and hydration, rather than on any one contribution alone.
- In the usual aqueous transition-metal ions, visible-light absorption associated with transitions between split d orbitals requires a partially filled d subshell; d^0 and d^{10} ions in the given list are colourless.

Step 1: (i) Explain the greater complexity of actinoid chemistry In actinoids, the $5f$, $6d$ and $7s$ subshells have comparable energies, so different numbers of electrons can participate in bonding. Actinoids consequently exhibit a wider range of oxidation states than lanthanoids, whose chemistry is dominated by the +3 state. Their $5f$ electrons also participate more readily in bonding than the more deeply buried $4f$ electrons of lanthanoids. These factors produce more varied compounds and more complicated chemistry; radioactivity additionally makes their experimental study difficult.

Step 2: (ii) Identify the energetic contributions to reduction potentials Consider the reverse of reduction, namely forming an aqueous divalent ion from the solid metal. This involves atomizing M(s) , removing two electrons from the gaseous atom, and hydrating the resulting gaseous M^{2+} ion. Thus atomization enthalpy, the sum of the first two ionization enthalpies, and hydration enthalpy all contribute to the overall energetics. These quantities vary irregularly across the $3d$ series because of

Quick Tip to Solve: Remove the $4s$ electrons before the $3d$ electrons when finding these ionic configurations. In this list, eliminate the d^0 and d^{10} ions to identify the coloured pair.

differing electronic configurations and the extra stability of half-filled and completely filled subshells. Their combined effect, including the associated entropy changes, determines the free-energy change and hence the electrode potential. Consequently, the $E_{M^{2+}/M}^{\circ}$ values do not follow a regular trend.

Step 3: (iii) Identify the chromium oxoanion and the lanthanoid (I) The oxoanion stable in acidic medium is the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$. Increasing the acid concentration favours its formation:



(II) Cerium, Ce, exhibits the +4 oxidation state. The Ce^{4+} ion has the stable xenon noble-gas configuration, $[\text{Xe}]$, with an empty 4*f* subshell.

Step 4: (iv) Write the thermal decomposition of permanganate Heating potassium permanganate produces potassium manganate, manganese dioxide and oxygen:



The equation conserves two potassium atoms, two manganese atoms and eight oxygen atoms. The solid products contain manganese in the +6 and +4 states, respectively, while oxygen gas is evolved.

Step 5: (v) Check the d-electron configuration of each aqueous ion The configurations and resulting colour predictions are:

Ion	Configuration	Prediction
Cu^+	$3d^{10}$	Colourless
Sc^{3+}	$3d^0$	Colourless
Fe^{2+}	$3d^6$	Coloured
Ti^{3+}	$3d^1$	Coloured
Zn^{2+}	$3d^{10}$	Colourless

In aqueous complexes of Fe^{2+} and Ti^{3+} , partially filled *d* subshells allow electronic transitions between ligand-field-split *d* levels with absorption of visible light. The empty or filled *d* subshells of the other listed ions do not allow such transitions.

Step 6: Conclusion Actinoids show more varied oxidation states, while irregular atomization, ionization and hydration contributions cause irregular reduction potentials. The requested species are $\text{Cr}_2\text{O}_7^{2-}$ and cerium. Heating KMnO_4 gives K_2MnO_4 , MnO_2 and O_2 ; the coloured aqueous ions in the list are Fe^{2+} and Ti^{3+} .

Quick Tip to Solve: Remove the 4*s* electrons before the 3*d* electrons when finding these ionic configurations. In this list, eliminate the d^0 and d^{10} ions to identify the coloured pair.