

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-3-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

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

Section A (16 marks)

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each.

1. The mole fraction of a solute in 2.0 molal aqueous solution is:

[1 mark]

- (A) 1.87
- (B) 0.347
- (C) 0.0347
- (D) 0.00347

Correct Answer: (C) 0.0347

Solution:

Concept:

- Molality is moles of solute per kilogram of solvent; mole fraction is moles of a component divided by total moles.
- For water, molar mass is 18 g mol^{-1} .

Step 1: Choose a solvent basis Take 1 kg of water. A 2.0 molal solution then contains 2.0 mol of solute. Water contains $n_w = 1000/18 = 55.56 \text{ mol}$. Molality uses solvent mass, not solution mass.

Step 2: Calculate the mole fraction

$$x_s = \frac{n_s}{n_s + n_w} = \frac{2.0}{2.0 + 55.56} = 0.03475 \simeq 0.0347.$$

A mole fraction cannot exceed unity, eliminating the first value; the remaining incorrect values differ by powers of ten.

Step 3: Conclusion The mole fraction is 0.0347. Hence, the correct option is (C).

Quick Tip to Solve: Use 1 kg of water: its 55.56 mol must be included in the total moles.

2. On electrolysis of very dilute aqueous solution of NaCl using platinum electrodes:

[1 mark]

- (A) H_2 gas is evolved at anode.
- (B) Na is produced at cathode.
- (C) O_2 gas is evolved at anode.
- (D) H_2 gas is evolved at cathode.

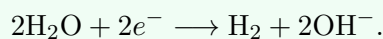
Correct Answer: Both (C) and (D): O_2 at the anode and H_2 at the cathode.

Solution:

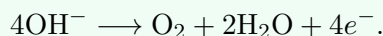
Concept:

- In dilute aqueous sodium chloride, water is preferentially reduced at an inert platinum cathode.
- At very low chloride concentration, water or hydroxide is oxidised at the anode, producing oxygen.

Quick Tip to Solve: For very dilute NaCl with inert electrodes, check both electrodes: oxygen at anode and hydrogen at cathode.

Step 1: Examine the cathode

Hydrogen forms at the cathode. Sodium is not deposited because reduction of water is easier than reduction of sodium ions. Thus the printed statement D is true and B is false.

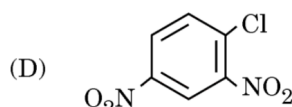
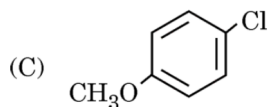
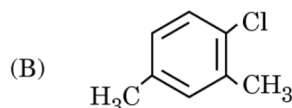
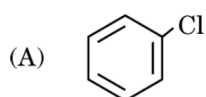
Step 2: Examine the anode

For the specified very dilute solution, oxygen evolves at the anode, making C true. Hydrogen does not evolve at the anode, so A is false. Platinum acts as an inert electrode.

Step 3: Conclusion Both (C) and (D) are correct: oxygen evolves at the anode and hydrogen at the cathode. The printed options do not give a unique single answer.

Quick Tip to Solve: For very dilute NaCl with inert electrodes, check both electrodes: oxygen at anode and hydrogen at cathode.

3. Which of the following compounds is most reactive towards nucleophilic substitution reaction with aqueous NaOH? [1 mark]



- (A) Chlorobenzene
(B) 2,4-dimethylchlorobenzene
(C) 4-methoxychlorobenzene
(D) 2,4-dinitrochlorobenzene

Correct Answer: (D) 2,4-dinitrochlorobenzene

Solution:**Concept:**

- An electron-withdrawing nitro group at an ortho or para position activates an aryl chloride towards nucleophilic aromatic substitution.
- The nitro group stabilises the negatively charged addition intermediate through resonance.

Step 1: Identify the activating groups In option D, the chlorine-bearing ring has nitro groups at both the ortho and para positions. After hydroxide attacks the carbon bearing chlorine, the negative charge of the intermediate can be delocalised onto both nitro groups, strongly lowering the barrier to substitution.

Step 2: Compare the other structures Chlorobenzene lacks this stabilisation. Methyl groups donate

Quick Tip to Solve: Look for nitro groups ortho or para to chlorine; two such groups strongly favour substitution.

electron density, while a para methoxy group is a strong resonance donor; these substituents do not stabilise the anionic intermediate in the manner of ortho and para nitro groups. Therefore none of A, B or C is more reactive than D.

Step 3: Conclusion 2,4-Dinitrochlorobenzene is the most reactive. Hence, the correct option is (D).

Quick Tip to Solve: Look for nitro groups ortho or para to chlorine; two such groups strongly favour substitution.

4. The dehydration of 1°, 2° and 3° alcohols follows the order:

[1 mark]

(A) $2^\circ > 1^\circ > 3^\circ$

(B) $3^\circ > 2^\circ > 1^\circ$

(C) $1^\circ > 2^\circ > 3^\circ$

(D) $1^\circ > 3^\circ > 2^\circ$

Correct Answer: (B) $3^\circ > 2^\circ > 1^\circ$

Solution:

Concept:

- Acid-catalysed dehydration removes water from an alcohol to form an alkene.
- The ease of dehydration usually follows the stability of the carbocation-like intermediate or transition state: tertiary exceeds secondary, which exceeds primary.

Step 1: Relate structure to dehydration Protonation converts the hydroxyl group into a better leaving group, water. Tertiary alcohols undergo loss of water most readily because alkyl groups stabilise developing positive charge through the inductive effect and hyperconjugation.

Step 2: Arrange the classes Secondary alcohols have less stabilisation than tertiary alcohols; primary alcohols have the least and generally require more vigorous conditions. Hence the decreasing ease is $3^\circ > 2^\circ > 1^\circ$. Every other listed order incorrectly places a less substituted class ahead of a more readily dehydrated class.

Step 3: Conclusion The order is $3^\circ > 2^\circ > 1^\circ$. Hence, the correct option is (B).

Quick Tip to Solve: For ordinary acid dehydration, rank alcohols by stabilisation of positive charge: tertiary first.

5. The oxidation number of Co in $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{SO}_4$ is:

[1 mark]

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

Correct Answer: (A) +3

Solution:

Concept:

- The sum of oxidation numbers and ligand charges equals the charge on the complex ion.
- Ammine, NH_3 , is neutral; nitrito, ONO^- , has charge -1 , and sulphate has charge -2 .

Step 1: Find the complex charge The compound $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{SO}_4$ is electrically neutral. Its one sulphate ion carries charge -2 , so the complex ion must carry charge $+2$. The oxygen linkage of nitrito does not change its ionic charge.

Step 2: Balance charges within the brackets Let the cobalt oxidation number be x . Then

$$x + 5(0) + (-1) = +2, \quad x = +3.$$

Values $+2, +4, +6$ would give complex charges $+1, +3, +5$, respectively, and cannot balance the single sulphate ion shown.

Step 3: Conclusion The oxidation number of cobalt is $+3$. Hence, the correct option is (A).

Quick Tip to Solve: First use the outside sulphate to find the complex charge, then subtract the ligand charges.

6. According to Werner's theory, the primary valencies of the central metal atom:

[1 mark]

- (A) are satisfied by neutral molecules or negative ions.
- (B) are equal to its coordination number.
- (C) are satisfied by negative ions.
- (D) are non-ionisable.

Correct Answer: (C) are satisfied by negative ions.

Solution:

Concept:

- Werner primary valency corresponds to the oxidation state of the central metal and is satisfied by negative ions.
- Secondary valency corresponds to coordination number and is satisfied by neutral molecules or negative ions.

Step 1: Identify primary valency Primary valencies are ionisable valencies associated with charge balance. Since neutral molecules supply no negative charge, they cannot satisfy primary valency. Negative ions satisfy it, whether they are present outside the coordination sphere or also coordinated

Quick Tip to Solve: Pair primary valency with oxidation state and anions; pair secondary valency with coordination number.

to the metal.

Step 2: Distinguish the alternatives The description involving neutral molecules or negative ions belongs to secondary valency. Coordination number also describes secondary valency, rather than primary valency. Finally, non-ionisability characterises secondary valencies in Werner theory; primary valencies are ionisable.

Step 3: Conclusion Primary valencies are satisfied by negative ions. Hence, the correct option is (C).

Quick Tip to Solve: Pair primary valency with oxidation state and anions; pair secondary valency with coordination number.

7. Which reagent is used to distinguish between $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$?

[1 mark]

- (A) KMnO_4
- (B) $\text{CHCl}_3 + \text{KOH}$ (ethanolic)
- (C) $\text{NaOH} + \text{I}_2$
- (D) Neutral FeCl_3

Correct Answer: (B) $\text{CHCl}_3 + \text{KOH}$ (ethanolic)

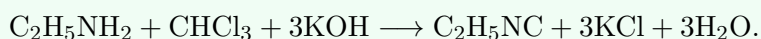
Solution:

Concept:

- The carbylamine test is given by primary amines, both aliphatic and aromatic, with chloroform and alcoholic potassium hydroxide.
- Secondary and tertiary amines do not form isocyanides in this test.

Step 1: Classify the printed amines Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, has one ethyl group bonded to nitrogen and is primary. Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, has two ethyl groups bonded to nitrogen and is secondary.

Step 2: Apply the distinguishing reaction On heating with chloroform and ethanolic KOH, ethylamine forms foul-smelling ethyl isocyanide:



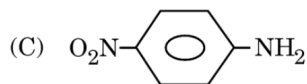
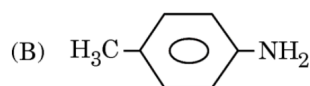
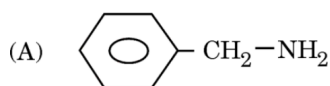
Diethylamine gives no carbylamine reaction. Permanganate is a general oxidant; iodine with alkali is the iodoform reagent, and neutral ferric chloride is used for phenolic groups. These do not provide the stated primary-versus-secondary amine test.

Step 3: Conclusion Use CHCl_3 and ethanolic KOH. Hence, the correct option is (B).

Quick Tip to Solve: Count carbon groups on nitrogen: only the primary amine gives the carbylamine test with alcoholic KOH.

8. Among the following, which one has the lowest value of pK_b ?

[1 mark]



(A) Benzylamine ($C_6H_5CH_2NH_2$)

(B) 4-Methylaniline ($p\text{-}CH_3C_6H_4NH_2$)

(C) 4-Nitroaniline ($p\text{-}O_2NC_6H_4NH_2$)

(D) Aniline ($C_6H_5NH_2$)

Correct Answer: (A) Benzylamine ($C_6H_5CH_2NH_2$)

Solution:

Concept:

- Basic strength increases with the base dissociation constant K_b ; hence $pK_b = -\log K_b$ decreases as basic strength increases.
- A nitrogen lone pair available for accepting a proton gives greater basicity than one delocalised into an aromatic ring.

Step 1: Identify the strongest base In benzylamine, $C_6H_5CH_2NH_2$, the intervening CH_2 group prevents conjugation of the nitrogen lone pair with the benzene ring. Its lone pair is therefore readily available for protonation.

Step 2: Compare all the alternatives In aniline and both substituted anilines, the nitrogen lone pair is delocalised into the aromatic ring. The methyl group increases basicity relative to aniline, whereas the nitro group strongly decreases it. Nevertheless, none is as basic as benzylamine, which behaves as an aliphatic amine.

Step 3: Conclusion Benzylamine has the lowest pK_b . Hence, the correct option is (A).

Quick Tip to Solve: For aryl versus benzyl amines, check whether nitrogen is directly bonded to the ring before comparing substituent effects.

9. In aqueous acidified solution, CrO_4^{2-} ion converts to which of the following?

[1 mark]

- (A) CrO_3
- (B) Cr^{3+}
- (C) $\text{Cr}_2\text{O}_7^{2-}$
- (D) CrO

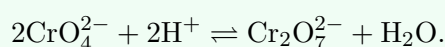
Correct Answer: (C) $\text{Cr}_2\text{O}_7^{2-}$

Solution:

Concept:

- Chromate and dichromate interconvert through an acid-base equilibrium without changing the oxidation state of chromium.
- Adding acid increases $[\text{H}^+]$, shifting an equilibrium toward the side that consumes hydrogen ions.

Step 1: Write the balanced equilibrium



Both sides contain two chromium atoms, eight oxygen atoms including water, and total charge -2 .

Step 2: Apply acidification and reject the other products Added acid drives this equilibrium to the right, converting yellow chromate into orange dichromate. Chromium remains in oxidation state $+6$. Formation of Cr^{3+} or CrO would require reduction; acidification alone supplies no reducing agent. CrO_3 is not the aqueous interconversion product asked here.

Step 3: Conclusion The product is $\text{Cr}_2\text{O}_7^{2-}$. Hence, the correct option is (C).

Quick Tip to Solve: Remember: acid turns yellow chromate into orange dichromate; alkali reverses this change.

10. The boiling point of an azeotropic mixture of water and nitric acid is more than that of pure water and nitric acid. The mixture shows:

[1 mark]

- (A) no deviation from Raoult's law
- (B) that solution is an ideal solution
- (C) positive deviation from Raoult's law
- (D) negative deviation from Raoult's law

Correct Answer: (D) negative deviation from Raoult's law

Solution:

Concept:

- A liquid boils when its vapour pressure becomes equal to the external pressure.
- Negative deviation from Raoult's law means the total vapour pressure is lower than the ideal-solution prediction at the same temperature.

Step 1: Relate boiling temperature to vapour pressure The mixture boils above both pure components.

Quick Tip to Solve: Match maximum boiling point with minimum escaping tendency and negative deviation from Raoult's law.

It therefore needs a higher temperature to attain the external pressure. This is characteristic of a maximum-boiling azeotrope, associated with reduced escaping tendency of the molecules.

Step 2: Identify the deviation Stronger attraction between unlike components lowers their partial vapour pressures relative to Raoult's law, producing negative deviation. Positive deviation instead favours a minimum-boiling azeotrope. No deviation and an ideal solution describe Raoult-law behaviour and do not explain this maximum in boiling temperature.

Step 3: Conclusion The mixture shows negative deviation from Raoult's law. Hence, the correct option is (D).

Quick Tip to Solve: Match maximum boiling point with minimum escaping tendency and negative deviation from Raoult's law.

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

[1 mark]

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

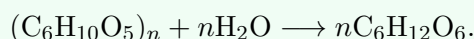
Correct Answer: (A) Starch

Solution:

Concept:

- Hydrolysis cleaves glycosidic bonds with water to release the constituent monosaccharides.
- A homopolysaccharide containing only glucose units yields only glucose on complete hydrolysis.

Step 1: Identify the glucose polymer Starch consists of amylose and amylopectin, both built entirely from α -D-glucose units. Complete hydrolysis therefore gives only glucose:



Step 2: Check the remaining carbohydrates Sucrose gives glucose and fructose, while lactose gives glucose and galactose, so neither yields glucose alone. Galactose is already a monosaccharide; it cannot be hydrolysed into glucose by cleavage of glycosidic bonds. Thus it does not meet the condition either.

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

Quick Tip to Solve: List the monomer units: starch contains glucose only, while sucrose and lactose each contain two different sugars.

12. For the reaction $2A \rightarrow 3B$, the rate of reaction $+d[B]/dt$ is equal to:

[1 mark]

- (A) $-(3/2) d[A]/dt$
- (B) $-(2/3) d[A]/dt$
- (C) $-(1/2) d[A]/dt$
- (D) $+3 d[A]/dt$

Correct Answer: (A) $-(3/2) d[A]/dt$

Solution:

Concept:

- For $aA \rightarrow bB$, the reaction rate is $r = -\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt}$.
- Reactant concentration decreases and product concentration increases, so their concentration derivatives have opposite signs.

Step 1: Apply the stoichiometric coefficients For $2A \rightarrow 3B$,

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{3} \frac{d[B]}{dt}.$$

This normalises the disappearance and appearance rates to the same rate of reaction.

Step 2: Obtain the requested appearance rate Multiplying by 3 gives

$$\frac{d[B]}{dt} = -\frac{3}{2} \frac{d[A]}{dt}.$$

Three moles of B appear for every two moles of A consumed, which confirms the factor $3/2$. The reciprocal factor and $1/2$ do not express this ratio; the positive factor 3 gives the wrong sign for a reactant derivative.

Step 3: Conclusion $+d[B]/dt = -(3/2)d[A]/dt$. Hence, the correct option is (A).

Quick Tip to Solve: Distinguish the normalised reaction rate from a species rate: multiply the normalised rate by that species coefficient.

13. Assertion (A): Separation of Zr and Hf is difficult.

Reason (R): Zr and Hf have almost identical atomic and ionic radii due to lanthanoid contraction.

[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:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series due to poor shielding by $4f$ electrons.
- Elements with similar ionic sizes, charges and valence configurations exhibit closely similar chemical behaviour.

Step 1: Judge Assertion (A) The assertion is true. Zirconium and hafnium show very similar chemical properties and commonly form compounds in the +4 oxidation state. Their close similarity makes ordinary chemical separation difficult.

Step 2: Judge Reason (R) The reason is true. Hafnium follows the lanthanoid series. The contraction caused by ineffective shielding of increasing nuclear charge by $4f$ electrons nearly compensates for the expected size increase from Zr to Hf, leaving their atomic and ionic radii almost identical.

Step 3: Connect the reason to the assertion The almost identical sizes, together with their common oxidation state and group, lead to similar compound formation and chemical reactions. Thus the radius similarity caused by lanthanoid contraction directly explains the difficulty of separating Zr and Hf.

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

Quick Tip to Solve: For Zr-Hf similarity, link poor $4f$ shielding to nearly equal radii and then to similar chemistry.

14. Assertion (A): Phenol is more acidic than 4-methylphenol.

Reason (R): The presence of an electron releasing group in phenol makes it more acidic. [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:

- Acidity depends on the stability of the conjugate base: stabilising phenoxide increases acidity.
- An electron-releasing substituent increases electron density and destabilises the negatively charged phenoxide ion relative to phenoxide without that substituent.

Step 1: Judge Assertion (A) The assertion is true. Phenol loses a proton to form phenoxide. In 4-methylphenol, the para methyl group releases electron density through its inductive effect and hyperconjugation, making its conjugate base less stable. Therefore 4-methylphenol is less acidic than phenol.

Step 2: Judge Reason (R) The reason is false. An electron-releasing group generally decreases phenol acidity, rather than increasing it, because it disfavors the negatively charged conjugate base. Electron-withdrawing groups have the opposite effect when they stabilise phenoxide.

Step 3: Select the appropriate truth combination Since the assertion is true but the reason states the opposite of the correct substituent effect, the choices in which both statements are true must be rejected. The assertion-false choice is also inconsistent with the acidity comparison.

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

Quick Tip to Solve: Check phenol acidity through phenoxide stability: electron donation destabilises its negative charge and reduces acidity.

15. Assertion (A): Aromatic primary amines can easily be prepared by Gabriel phthalimide synthesis.

Reason (R): Gabriel phthalimide synthesis is used to prepare only aliphatic primary amines. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Gabriel synthesis forms a primary amine by alkylation of the phthalimide anion followed by hydrolysis.
- Aryl halides resist the nucleophilic substitution needed in this synthesis.

Step 1: Judge the assertion The assertion is false. Aromatic primary amines such as aniline cannot readily be obtained by Gabriel phthalimide synthesis. The required substitution of an aryl halide by the phthalimide anion does not occur under the usual conditions.

Step 2: Judge the reason The reason is true: this method is used to prepare aliphatic primary amines. An alkyl halide undergoes nucleophilic substitution with potassium phthalimide, and hydrolysis then releases the primary amine.

Step 3: Relate the statements Since A is false and R is true, neither option (A) nor (B), which requires both statements to be true, is possible. Option (C) also reverses the correct truth values.

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

Quick Tip to Solve: In Gabriel synthesis, first check whether the halide is alkyl or aryl: the usual alkylation works for alkyl halides.

16. Assertion (A): Order of reaction is not applicable for elementary reaction but applicable for complex reaction.

Reason (R): Order of reaction is an experimental quantity.

[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:

- For a rate law $r = k[A]^m[B]^n$, the reaction order is $m + n$.
- Order is determined experimentally; molecularity describes an elementary step.

Step 1: Judge the assertion The assertion is false. Order is applicable to both elementary and complex reactions. For an elementary reaction, the rate-law exponents follow the reactant stoichiometry of that single step, so its order equals its molecularity.

Step 2: Judge the reason The reason is true. Reaction order is an experimental quantity obtained from the observed rate law. For a complex reaction it need not equal the sum of the stoichiometric coefficients in the overall balanced equation.

Step 3: Relate the statements The experimental nature of order does not restrict it to complex reactions. Options (A) and (B) incorrectly treat A as true, while option (C) incorrectly treats R as false.

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

Quick Tip to Solve: Distinguish order from molecularity: order applies to the rate law, whereas molecularity belongs to an elementary step.

Section B (10 marks)

17. Explain why, on addition of 1 mol of KCl to 1 litre of water, the boiling point of water increases, while the addition of 1 mol of methyl alcohol to 1 litre of water decreases the boiling point. [2 marks]

Solution:

Concept:

- A liquid boils when its total vapour pressure equals the external atmospheric pressure.
- A non-volatile solute lowers solvent vapour pressure; a volatile component also contributes its own partial vapour pressure.

Step 1: Addition of potassium chloride KCl is a non-volatile electrolyte. On dissolving, it gives K^+

Quick Tip to Solve: Before using $\Delta T_b = iK_b m$, check whether the added substance is non-volatile; methanol contributes vapour itself.

and Cl^- ions, lowering the escaping tendency and vapour pressure of water. At the boiling point of pure water the solution therefore has a vapour pressure below atmospheric pressure. It must be heated to a higher temperature to boil. This is boiling-point elevation, described for a dilute solution by $\Delta T_b = iK_b m > 0$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality.

Step 2: Addition of methyl alcohol Methyl alcohol (methanol) is volatile and has a lower boiling point than water. Its vapour contributes to the total vapour pressure of the mixture. For the stated dilute aqueous mixture, the total vapour pressure is greater than that of pure water at the same temperature, so it reaches atmospheric pressure at a lower temperature. The non-volatile-solute boiling-point-elevation formula cannot be applied to methanol as though it contributed no vapour.

Step 3: Conclusion KCl lowers the vapour pressure and raises the boiling point; volatile methanol increases the total vapour pressure and lowers the boiling point.

Quick Tip to Solve: Before using $\Delta T_b = iK_b m$, check whether the added substance is non-volatile; methanol contributes vapour itself.

18(a). Write IUPAC names of the following compounds:

(i) $[PtCl_2(en)_2]SO_4$

(ii) $(NH_4)_2[CoF_4]$

[2 marks]

Solution:

Concept:

- Find the metal oxidation state from the overall complex charge and the charges on its ligands.
- Name ligands alphabetically; use bis for a repeated polydentate ligand and the ending -ate for an anionic coordination entity.

Step 1: Name the platinum compound In $[PtCl_2(en)_2]SO_4$, sulphate is SO_4^{2-} , so the complex cation has charge +2. Each chlorido ligand has charge -1 and each ethane-1,2-diamine ligand (en) is neutral. Hence $x - 2 = +2$, giving platinum oxidation state +4. Chlorido precedes ethane-1,2-diamine alphabetically; two en ligands require bis. The name is dichloridobis(ethane-1,2-diamine)platinum(IV) sulphate.

Step 2: Name the cobalt compound In $(NH_4)_2[CoF_4]$, the two ammonium cations give a total charge of +2, so $[CoF_4]^{2-}$ is the anion. With four fluoro ligands, $x + 4(-1) = -2$, yielding cobalt oxidation state +2. The negative coordination entity is named cobaltate, and four fluoro ligands give tetrafluorido. The name is ammonium tetrafluoridocobaltate(II).

Step 3: Conclusion (i) Dichloridobis(ethane-1,2-diamine)platinum(IV) sulphate.

(ii) Ammonium tetrafluoridocobaltate(II).

Quick Tip to Solve: Use the counter-ion to find the complex charge before assigning the metal oxidation state and its Roman numeral.

18(b). Define the following terms with a suitable example in each case:

(i) Ambidentate ligand

(ii) Double salt

[2 marks]

Solution:

Concept:

- Ambidentate ligands possess two different potential donor atoms but bind through only one of them at a time.
- A double salt is a crystalline combination of simple salts that dissociates completely into its constituent ions in water.

Step 1: Ambidentate ligand and example An ambidentate ligand is a ligand capable of coordinating to a metal ion through either of two different donor atoms, using only one in a given coordination bond. For example, NO_2^- can bind through nitrogen (nitrito-N) or through oxygen (nitrito-O). These alternative attachment modes give linkage isomerism. It is not a bidentate ligand: a bidentate ligand attaches through two donor atoms simultaneously to form two coordinate bonds.

Step 2: Double salt and example A double salt is formed by crystallising two simple salts together in a definite proportion. It loses its individual crystal identity on dissolution and gives all the constituent ions in solution. For example, Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, gives 2NH_4^+ , Fe^{2+} and 2SO_4^{2-} ions in aqueous solution. Unlike a coordination compound, it does not retain a complex ion containing these constituents.

Step 3: Conclusion (i) Ambidentate ligand: one ligand with two alternative donor atoms, for example NO_2^- .

(ii) Double salt: a crystalline combination that dissociates into constituent ions, for example Mohr's salt.

Quick Tip to Solve: For ambidentate, emphasise alternative donor atoms; for a double salt, emphasise complete dissociation into constituent ions.

19. For the compound having molecular formula $\text{C}_4\text{H}_9\text{Br}$, write:

(a) the isomer which is most reactive towards $\text{S}_{\text{N}}1$ displacement.

(b) the isomer which, on reacting with Na metal in the presence of dry ether, gives 2,5-Dimethylhexane.

[2 marks]

Solution:

Concept:

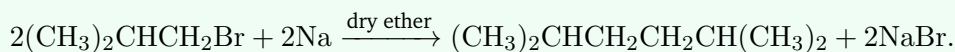
- In an $\text{S}_{\text{N}}1$ reaction, slow ionisation produces a carbocation; the more stable the carbocation, the faster the reaction.
- The Wurtz reaction couples two identical alkyl groups: $2\text{RBr} + 2\text{Na} \rightarrow \text{R-R} + 2\text{NaBr}$, in dry ether.

Step 1: (a) Identify the fastest $\text{S}_{\text{N}}1$ isomer The required isomer is 2-bromo-2-methylpropane (tert-

Quick Tip to Solve: For a symmetrical Wurtz product, split its central bond and replace each broken bond by Br.

butyl bromide), $(\text{CH}_3)_3\text{CBr}$. Its ionisation gives the tertiary tert-butyl carbocation, stabilised by the electron-releasing effect and hyperconjugation of three methyl groups. The other isomers form secondary or primary carbocations and therefore react more slowly by this mechanism.

Step 2: (b) Identify the Wurtz starting compound Cut the central carbon-carbon bond of 2,5-dimethylhexane into two identical fragments. Each fragment is $(\text{CH}_3)_2\text{CHCH}_2-$, so bromine must be attached to its terminal carbon. The isomer is 1-bromo-2-methylpropane (isobutyl bromide):



Step 3: Conclusion (a) 2-Bromo-2-methylpropane; (b) 1-bromo-2-methylpropane.

Quick Tip to Solve: For a symmetrical Wurtz product, split its central bond and replace each broken bond by Br.

20. For a reaction $\text{A} + \text{B} \rightarrow \text{Products}$, the rate law is:

$$\text{Rate} = k[\text{A}][\text{B}]^{3/2}$$

Write the overall order of the reaction. Can this reaction be an elementary reaction? Give reason in support of your answer. [2 marks]

Solution:

Concept:

- Overall order is the sum of the experimentally determined concentration exponents in the rate law.
- An elementary step follows the law of mass action: its rate-law exponents are the numbers of reacting particles and are non-negative integers.

Step 1: Calculate the overall order The given law is $r = k[\text{A}][\text{B}]^{3/2}$, where k is the rate constant. Thus the reaction is first order with respect to A and order $3/2$ with respect to B. Adding these exponents,

$$n = 1 + \frac{3}{2} = \frac{5}{2} = 2.5.$$

The coefficients in the overall chemical equation do not determine the experimental order.

Step 2: Decide whether the reaction is elementary The fractional exponent $3/2$ cannot represent a number of B particles taking part in one elementary collision. Moreover, an elementary step with the written reactants $\text{A} + \text{B}$ would have rate $k[\text{A}][\text{B}]$, of overall order 2. Therefore the given reaction is complex, involving a sequence of elementary steps; its observed fractional order arises from the mechanism rather than a fractional molecularity.

Step 3: Conclusion The overall order is $5/2$. The reaction cannot be elementary because its rate law has a fractional order.

Quick Tip to Solve: Add rate-law exponents for order; use integer reacting-particle counts only for molecularity.

21. How do you explain the following?

(a) Presence of a carbonyl group in glucose.

(b) Presence of five –OH groups in glucose.

[2 marks]

Solution:

Concept:

- Carbonyl compounds react with hydroxylamine to form oximes and can add hydrogen cyanide to form cyanohydrins.
- Acetylation replaces the hydrogen of each alcoholic hydroxyl group by an acetyl group; the number of acetate groups counts the hydroxyl groups.

Step 1: (a) Evidence for the carbonyl group Glucose reacts with hydroxylamine, NH_2OH , to give glucose oxime. It also adds HCN to give a cyanohydrin. Both are characteristic reactions of a carbonyl group, establishing that the open-chain form of glucose contains $>\text{C}=\text{O}$. In the oxime reaction, the carbonyl oxygen is replaced by $=\text{N}-\text{OH}$, with elimination of water. These reactions establish a carbonyl group; mild oxidation provides the further evidence that it is aldehydic.

Step 2: (b) Evidence for five hydroxyl groups On treatment with excess acetic anhydride, glucose forms glucose pentaacetate. Each alcoholic –OH group supplies one hydrogen for replacement by $-\text{COCH}_3$, producing an $-\text{OCOCH}_3$ ester group. Formation of the pentaacetate therefore shows that glucose contains five acetylatable hydroxyl groups. This experimental observation, rather than merely counting oxygens in the molecular formula, establishes their number.

Step 3: Conclusion Oxime and cyanohydrin formation establish a carbonyl group; formation of glucose pentaacetate establishes five –OH groups.

Quick Tip to Solve: Link each structural feature to its diagnostic derivative: oxime for carbonyl, pentaacetate for five OH groups.

Section C (21 marks)

22. Give reasons for the following:

(a) Alkyl halides, though polar, yet their solubility in water is very low.

(b) p-Dichlorobenzene has higher melting point than those of o- and m-isomers.

(c) $\text{CH}_3\text{-I}$ is more reactive than $\text{CH}_3\text{-Br}$ towards $\text{S}_\text{N}2$ reactions.

[3 marks]

Solution:

Concept:

- Dissolution depends on the balance between energy needed to separate solute and solvent particles and energy released by new solute-solvent attractions.
- Crystal packing affects melting point; bond strength and leaving-group ability affect nucleophilic substitution.

Step 1: (a) Low solubility of alkyl halides in water Although the carbon-halogen bond is polar, alkyl halides cannot form strong hydrogen bonds with water. Dissolution requires breaking some hydrogen

Quick Tip to Solve: For these comparisons, match the property to its cause: hydration, crystal symmetry, and leaving-group ability.

bonds between water molecules and separating alkyl halide molecules. The new water-alkyl halide attractions are insufficient to compensate for the energy required to disrupt the strong water-water hydrogen bonds. Consequently, only a small amount dissolves; polarity alone does not ensure high water solubility.

Step 2: (b) Higher melting point of the para isomer The para isomer of dichlorobenzene is more symmetrical than the ortho and meta isomers. Its molecules consequently pack more closely and regularly in the crystal lattice. This efficient packing gives stronger overall intermolecular cohesion in the solid, so more thermal energy is needed to disrupt the lattice. Thus *p*-dichlorobenzene has the higher melting point; the explanation concerns solid-state packing.

Step 3: (c) Greater S_N2 reactivity of methyl iodide Both methyl halides have the same small methyl group, so their steric hindrance to backside attack is comparable. The C–I bond is longer and weaker than the C–Br bond and is broken more readily during substitution. Also, I^- is a better leaving group than Br^- . Hence methyl iodide reacts faster in S_N2 reactions despite the greater polarity of the carbon-bromine bond.

Step 4: Conclusion Low aqueous solubility follows from inadequate hydration; the para isomer melts higher because of efficient crystal packing; CH_3I reacts faster because its C–I bond is weaker and iodide leaves more readily.

Quick Tip to Solve: For these comparisons, match the property to its cause: hydration, crystal symmetry, and leaving-group ability.

23. How will you obtain the following from benzene diazonium chloride? Write chemical equations involved:

(a) Phenol

(b) Iodobenzene

(c) *p*-Aminoazobenzene

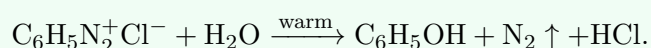
[3 marks]

Solution:

Concept:

- Arenediazonium salts undergo replacement of the diazonium group, $-N_2^+$, by suitable nucleophiles; loss of stable nitrogen gas favours these reactions.
- Azo coupling retains both nitrogen atoms as an $-N=N-$ linkage. Aniline activates its aromatic ring and directs coupling mainly to its free para position.

Step 1: Obtain phenol by hydrolysis Warm an aqueous solution of benzene diazonium chloride. Water replaces the diazonium group by a hydroxyl group, with nitrogen gas evolving:

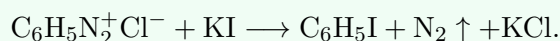


The product is phenol; warming is used because the diazonium salt is otherwise preserved in the cold.

Step 2: Obtain iodobenzene using potassium iodide Treat benzene diazonium chloride with aqueous potassium iodide. The iodide ion replaces the diazonium group directly; a copper(I) catalyst is

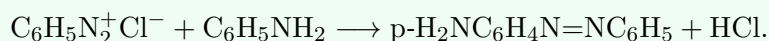
Quick Tip to Solve: For the aminoazo product, couple with aniline at its para carbon; do not replace the diazonium group with an amino group.

unnecessary for this conversion:



This substitution gives iodobenzene and liberates nitrogen.

Step 3: Obtain p-aminoazobenzene by coupling Add cold benzene diazonium chloride solution to aniline in a mildly acidic medium, keeping the temperature at 273–278 K. The electrophilic diazonium ion couples at the para position of aniline:



This is an azo-coupling reaction: the azo linkage remains in the coloured product, unlike the preceding substitutions that expel nitrogen gas.

Step 4: Conclusion Thus warming with water gives phenol, treatment with KI gives iodobenzene, and cold coupling with aniline in mildly acidic medium gives p-aminoazobenzene.

Quick Tip to Solve: For the aminoazo product, couple with aniline at its para carbon; do not replace the diazonium group with an amino group.

24. An organic compound (A) with molecular formula $\text{C}_3\text{H}_5\text{N}$ on reaction with $\text{C}_6\text{H}_5\text{MgBr}$ followed by hydrolysis, gives a compound (B). Compound (B) forms an orange-red precipitate with 2,4-DNP reagent and does not give iodoform test. It neither reduces Tollens' or Fehling's reagent nor does it decolourise bromine water. On drastic oxidation with chromic acid it gives a carboxylic acid (C) having molecular formula $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds (A), (B) and (C). Write the reactions of compound (A) with $\text{C}_6\text{H}_5\text{MgBr}$ followed by hydrolysis to give compound (B). [3 marks]

Solution:

Concept:

- A nitrile $\text{R}-\text{C}\equiv\text{N}$ reacts with a Grignard reagent to form an imine magnesium salt; acid hydrolysis converts its nitrile carbon into the carbonyl carbon of a ketone.
- 2,4-DNP detects aldehydes and ketones. A negative Tollens' test supports a ketone, while a negative iodoform test excludes the methyl-ketone group $-\text{COCH}_3$.

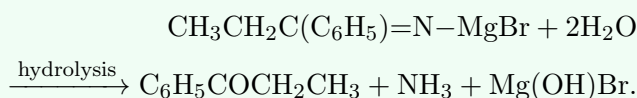
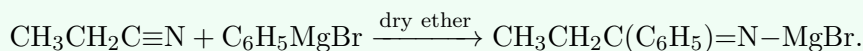
Step 1: Identify the nitrile and carbonyl compound The molecular formula $\text{C}_3\text{H}_5\text{N}$ fits propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$. Addition of the phenyl group from $\text{C}_6\text{H}_5\text{MgBr}$, followed by hydrolysis, gives $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$, propiophenone (1-phenylpropan-1-one). Thus A is propanenitrile and B is propiophenone. The carbonyl carbon comes from the nitrile group, so the ethyl group remains attached to it.

Step 2: Check all the observations and identify the acid Propiophenone contains a ketonic carbonyl group and therefore forms an orange-red 2,4-dinitrophenylhydrazone precipitate. Being a ketone, it does not reduce Tollens' or Fehling's reagent. Its carbonyl is attached to an ethyl group, not a methyl group, explaining the negative iodoform test. It has no non-aromatic carbon-carbon double bond and hence does not decolourise bromine water under the stated test conditions. Drastic oxidation cleaves

Quick Tip to Solve: In a nitrile-Grignard conversion, keep the nitrile carbon: it becomes the ketone carbonyl carbon after hydrolysis.

the ketone side chain to yield benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$; its formula is $\text{C}_7\text{H}_6\text{O}_2$, as required for C .

Step 3: Write addition and hydrolysis reactions The two stages of ketone formation are:



Acidic aqueous work-up is normally used; the ammonia is then present as ammonium ions. Hydrolysis releases the ketone only after the Grignard addition is complete.

Step 4: Conclusion $A = \text{CH}_3\text{CH}_2\text{CN}$, $B = \text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$, $C = \text{C}_6\text{H}_5\text{COOH}$. These are propanenitrile, propiophenone and benzoic acid, respectively.

Quick Tip to Solve: In a nitrile-Grignard conversion, keep the nitrile carbon: it becomes the ketone carbonyl carbon after hydrolysis.

25. An antifreeze solution is prepared by dissolving 31 g of ethylene glycol (Molar mass = 62 g mol^{-1}) in 600 g of water. Calculate the freezing point of the solution. (K_f for water = $1.86 \text{ K kg mol}^{-1}$) [3 marks]

Solution:

Concept:

- For a dilute solution, the depression in freezing point is $\Delta T_f = iK_fm$, where K_f is the cryoscopic constant of the solvent and m is the molality of the solute.
- Molality is the number of moles of solute per kilogram of solvent. Ethylene glycol is a non-electrolyte in water, so its van't Hoff factor is $i = 1$.
- The freezing point depression is positive: $\Delta T_f = T_f^0 - T_f$, where T_f^0 and T_f are the freezing points of pure solvent and solution.

Step 1: Calculate the amount of ethylene glycol The mass of ethylene glycol is 31 g, and its molar mass is 62 g mol^{-1} . Therefore,

$$n = \frac{\text{mass}}{\text{molar mass}} = \frac{31 \text{ g}}{62 \text{ g mol}^{-1}} = 0.500 \text{ mol}.$$

No dissociation correction is needed because the dissolved molecules remain neutral solute particles.

Step 2: Calculate molality using the solvent mass The mass of water, rather than the total solution mass, enters the denominator:

$$\begin{aligned} m_{\text{water}} &= 600 \text{ g} = 0.600 \text{ kg}. \\ m &= \frac{0.500 \text{ mol}}{0.600 \text{ kg}} = 0.8333 \text{ mol kg}^{-1}. \end{aligned}$$

Using 631 g, the total solution mass, would not give molality and would underestimate the depression.

Quick Tip to Solve: Convert only the water mass to kilograms, calculate the positive depression, and subtract it from water's normal freezing point.

Step 3: Find depression and the solution freezing point Substituting the given cryoscopic constant,

$$\begin{aligned}\Delta T_f &= 1 \times 1.86 \text{ K kg mol}^{-1} \times 0.8333 \text{ mol kg}^{-1} \\ &= 1.55 \text{ K}.\end{aligned}$$

Pure water freezes at 0°C . A temperature difference of 1.55 K equals a difference of 1.55°C , so

$$T_f = 0 - 1.55 = -1.55^\circ\text{C}.$$

The negative sign expresses the lowering of freezing point caused by the dissolved antifreeze.

Step 4: Conclusion The freezing point of the antifreeze solution is -1.55°C , approximately 271.60 K.

Quick Tip to Solve: Convert only the water mass to kilograms, calculate the positive depression, and subtract it from water's normal freezing point.

26(a). Answer the following questions about the complexes $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$:

- Write the hybridization involved in each case.
- Which of them is the inner orbital complex and which one is the outer orbital complex?
- Compare their magnetic behaviour.

[Atomic number: Ni = 28]

[3 marks]

Solution:

Concept:

- The oxidation state of nickel in both complexes is +2. Neutral Ni is $[\text{Ar}]3d^84s^2$, so Ni^{2+} is $[\text{Ar}]3d^8$.
- Ligand field strength determines pairing: Cl^- is weak field, whereas CN^- is strong field. Unpaired electrons cause paramagnetism; fully paired electrons give diamagnetism.

Step 1: Find the hybridization in each complex In $[\text{NiCl}_4]^{2-}$, the weak-field chloride ligands do not pair the two unpaired 3d electrons. One 4s and three 4p orbitals mix to give sp^3 hybridization and tetrahedral geometry. In $[\text{Ni}(\text{CN})_4]^{2-}$, cyanide causes pairing of the eight 3d electrons into four orbitals, leaving one 3d orbital vacant. This orbital combines with 4s and two 4p orbitals, giving dsp^2 hybridization and square-planar geometry.

Step 2: Identify inner and outer orbital complexes The cyanide complex uses an inner 3d orbital and is therefore an inner orbital complex. The chloride complex uses the outer 4s and 4p orbitals and is an outer orbital complex.

Step 3: Compare magnetic behaviour The chloride complex contains two unpaired electrons and is paramagnetic. Its spin-only moment is $\mu = \sqrt{n(n+2)} = \sqrt{8} \simeq 2.83$ Bohr magnetons, with $n = 2$. The cyanide complex has no unpaired electrons and is diamagnetic, with a spin-only moment of zero.

Step 4: Conclusion $[\text{NiCl}_4]^{2-}$: sp^3 , outer orbital, paramagnetic (two unpaired electrons). $[\text{Ni}(\text{CN})_4]^{2-}$: dsp^2 , inner orbital, diamagnetic.

Quick Tip to Solve: For four-coordinate nickel(II), use ligand strength: chloride gives tetrahedral sp^3 , while cyanide gives square-planar dsp^2 .

26(b). (i) Name two coordination compounds which are important in biological systems.

(ii) What is meant by chelate effect? Give an example.

(iii) Why are low spin tetrahedral complexes rarely formed?

[3 marks]

Solution:

Concept:

- Coordination compounds contain a central metal atom or ion bonded to donor ligands; many biological molecules contain such metal centres.
- A chelating ligand binds the same metal through two or more donor atoms and forms rings. In a tetrahedral field the splitting Δ_t is small compared with the electron-pairing energy P .

Step 1: Name biological coordination compounds Haemoglobin and chlorophyll are two important examples. Haemoglobin contains iron coordinated within a porphyrin unit and is involved in oxygen transport in blood. Chlorophyll contains magnesium coordinated by a porphyrin-like ring and participates in the absorption of light during photosynthesis.

Step 2: Explain the chelate effect with an example The chelate effect is the enhanced stability of a complex containing a multidentate ligand, compared with a similar complex formed by corresponding monodentate ligands. For example, ethane-1,2-diamine (en) coordinates through both nitrogen atoms and forms five-membered chelate rings in $[\text{Ni}(\text{en})_3]^{2+}$. This complex is more stable than the corresponding ammonia complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$; replacing several separate ligands by chelating ligands generally gives a favourable entropy contribution.

Step 3: Explain the rarity of low-spin tetrahedral complexes Tetrahedral crystal-field splitting is small: for comparable metal and ligand combinations, $\Delta_t \approx \frac{4}{9}\Delta_o$, where Δ_o is the octahedral splitting. Usually $\Delta_t < P$, so electrons occupy the higher tetrahedral orbitals singly rather than pairing in lower orbitals. Thus tetrahedral complexes normally adopt high-spin configurations; low-spin tetrahedral complexes are rarely formed.

Step 4: Conclusion Examples are haemoglobin and chlorophyll. Chelation enhances complex stability through multidentate ring formation. Small tetrahedral splitting normally favours unpaired electrons and hence high spin.

Quick Tip to Solve: For tetrahedral spin questions compare splitting with pairing energy: small tetrahedral splitting makes promotion preferable to pairing.

27. State Kohlrausch's law of independent migration of ions. With the help of a curve, explain why it is not easy to determine Λ_m^0 for weak electrolytes by extrapolating the concentration - molar conductivity curve, as it is for strong electrolytes. [3 marks]

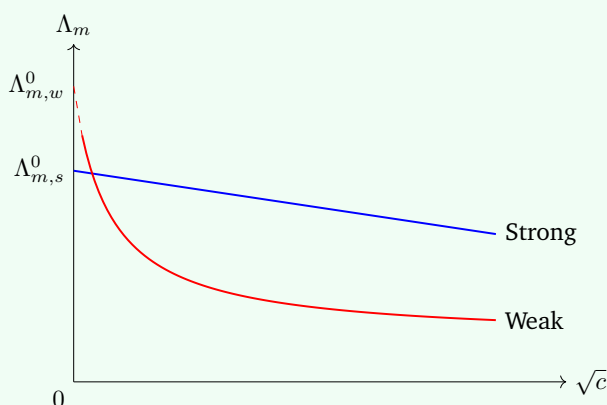
Solution:

Concept:

- Kohlrausch's law: at infinite dilution each ion contributes independently to the limiting molar conductivity of an electrolyte, irrespective of the other ion present.
- For an electrolyte with ν_+ cations and ν_- anions per formula unit, $\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where λ_i^0 is the limiting ionic molar conductivity.

Step 1: State the law quantitatively At infinite dilution, interionic interactions become negligible, so the ionic contributions are additive. For example, $\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0$. The ionic coefficients must be included for other stoichiometries, such as $\Lambda_m^0(\text{CaCl}_2) = \lambda_{\text{Ca}^{2+}}^0 + 2\lambda_{\text{Cl}^-}^0$.

Step 2: Compare the concentration curves For a strong electrolyte in dilute solution, $\Lambda_m = \Lambda_m^0 - A\sqrt{c}$, where c is concentration and A is a constant for the electrolyte under the given conditions. Thus a plot of Λ_m against $\sqrt{c}$ is approximately linear; extrapolation to $\sqrt{c} = 0$ gives the intercept Λ_m^0 . A weak electrolyte is only partially ionised at finite concentration. Dilution increases its degree of ionisation strongly, producing a sharply rising, nonlinear curve as concentration approaches zero.



Schematic variation of molar conductivity with square root of concentration; the weak-electrolyte limiting intercept is indicated.

Step 3: Explain why direct extrapolation is unreliable The weak-electrolyte curve has no convenient straight portion that can be reliably extended to zero concentration. At extremely low concentrations, accurate conductivity measurement is also difficult. Hence its limiting value is obtained using Kohlrausch's law and strong-electrolyte data, rather than direct extrapolation. For acetic acid,

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}).$$

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

Step 4: Conclusion Strong electrolytes give an approximately straight Λ_m -versus- $\sqrt{c}$ plot at low concentration. Weak electrolytes give a steep nonlinear curve because ionisation increases on dilution, making direct extrapolation unreliable.

Quick Tip to Solve: Always plot conductivity against square root of concentration when using the straight-line strong-electrolyte extrapolation.

28. The half-life period of a radioactive element is 1.5×10^{10} years. Calculate the time in which the activity of the element is reduced to 75% of its original value.

[Given: $\log 2 = 0.30$, $\log 3 = 0.48$, $\log 4 = 0.60$]

[3 marks]

Solution:

Concept:

- Radioactive decay follows first-order kinetics: $A = A_0 e^{-kt}$, where A_0 and A are the initial and remaining activities, k is the decay constant and t is elapsed time.
- The half-life is $t_{1/2} = \ln 2/k$. Activity is proportional to the number of undecayed radioactive nuclei.

Step 1: Interpret the remaining activity The activity is reduced to 75% of its original value, so $A = 0.75A_0$. Hence $A_0/A = 1/0.75 = 4/3$. This is a loss of only 25% of the original activity; it is not a loss of 75%. The required time must therefore be smaller than one half-life.

Step 2: Eliminate the decay constant For first-order decay,

$$t = \frac{2.303}{k} \log \frac{A_0}{A}, \quad t_{1/2} = \frac{2.303}{k} \log 2.$$

Dividing these equations avoids unnecessary rounding of k :

$$\frac{t}{t_{1/2}} = \frac{\log(4/3)}{\log 2}.$$

The logarithms here are common logarithms, as supplied in the question.

Step 3: Substitute the given logarithms Using the printed values,

$$\log(4/3) = \log 4 - \log 3 = 0.60 - 0.48 = 0.12.$$

Therefore

$$t = (1.5 \times 10^{10}) \frac{0.12}{0.30} = 0.60 \times 10^{10} \text{ years}.$$

The ratio 0.40 is less than unity, consistent with the remaining activity being greater than half the original activity.

Step 4: Conclusion The required time is 6.0×10^9 years, using the logarithms given in the question.

Quick Tip to Solve: For a stated remaining percentage, use initial activity divided by remaining activity inside the logarithm.

Section D (8 marks)

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

29(a). Case study (Alcohols, Phenols and Ethers): Alcohols have higher boiling points than other compounds, namely hydrocarbons, ethers and haloalkanes of comparable molecular masses. On oxidation, primary alcohols yield aldehydes with mild oxidizing agents and carboxylic acids with strong oxidizing agents. Secondary alcohols yield ketones on oxidation while tertiary alcohols are resistant to oxidation. Ethers may be prepared by dehydration of alcohols and Williamson synthesis. The C-O bond in ethers can be cleaved by hydrogen halides. 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. In presence of NaOH, phenol generates phenoxide ion which is even more reactive than phenol. Thus, in alkaline medium, phenol undergoes Kolbe's reaction.

(a) Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to aldehyde

(ii) Oxidation of a primary alcohol to carboxylic acid

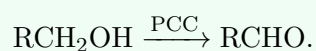
[2 marks]

Solution:

Concept:

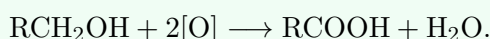
- A primary alcohol RCH_2OH first oxidises to an aldehyde RCHO ; further oxidation gives RCOOH .
- A mild, controlled oxidant stops at the aldehyde stage, whereas a strong oxidant under suitable conditions carries oxidation through to the carboxylic acid.

Step 1: (i) Obtain the aldehyde Use pyridinium chlorochromate (PCC) in an anhydrous organic medium such as dichloromethane. PCC is a mild oxidising reagent and converts the primary alcohol to the corresponding aldehyde:



Anhydrous conditions help avoid further oxidation to the acid.

Step 2: (ii) Obtain the carboxylic acid Use acidified potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$, with heating under reflux. The aldehyde initially formed is oxidised further:



Acidified potassium permanganate is another suitable strong oxidising reagent. Here $[\text{O}]$ denotes an oxidising equivalent.

Step 3: Conclusion (i) PCC; (ii) acidified $\text{K}_2\text{Cr}_2\text{O}_7$ with heating (or acidified KMnO_4).

Quick Tip to Solve: Choose PCC to stop at the aldehyde; choose a strong acidified oxidant to reach the carboxylic acid.

29(b). Write the reaction involved in Kolbe's reaction.

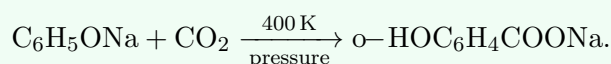
[1 mark]

Solution:

Concept:

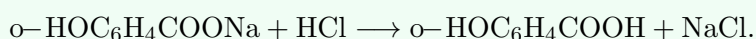
- In Kolbe's reaction, sodium phenoxide reacts with carbon dioxide under pressure and subsequent acidification gives salicylic acid.
- The phenoxide group activates the aromatic ring; carboxylation occurs predominantly at an ortho position.

Step 1: Carboxylate sodium phenoxide Heat sodium phenoxide with CO_2 at about 400 K under pressure:



The intermediate is sodium salicylate.

Step 2: Acidify the salt Treatment with dilute acid protonates the carboxylate group:



The product has adjacent hydroxyl and carboxyl groups on the benzene ring.

Step 3: Conclusion Kolbe's reaction gives salicylic acid (2-hydroxybenzoic acid) from sodium phenoxide and CO_2 , followed by acidification.

Quick Tip to Solve: Include both carbon dioxide treatment of sodium phenoxide and the final acidification step.

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

[1 mark]

Solution:

Concept:

- Ordinary oxidation of an alcohol to a carbonyl compound removes hydrogen from the O-H group and from the carbon bearing the hydroxyl group.
- A tertiary alcohol has the structure R_3COH ; its hydroxyl-bearing carbon has no hydrogen atom.

Step 1: Inspect the hydroxyl-bearing carbon In a tertiary alcohol, this carbon is bonded to three carbon groups and the oxygen of the hydroxyl group. It therefore lacks the hydrogen required for the usual conversion of an alcohol into a carbonyl compound.

Step 2: Explain the resistance Oxidation would require cleavage of a carbon-carbon bond, which does not occur readily with ordinary mild oxidising agents. Under vigorous conditions oxidation can occur with carbon-skeleton cleavage, so the resistance refers to normal alcohol-oxidation conditions.

Step 3: Conclusion Tertiary alcohols resist oxidation because no hydrogen is attached to the carbon bearing -OH; oxidation requires carbon-carbon bond cleavage.

Quick Tip to Solve: Look for a hydrogen on the carbon bonded to OH, rather than the hydrogen of the OH group itself.

29(c). Write the products of the following reaction:



[1 mark]

Solution:

Concept:

- Hydrogen iodide protonates the ether oxygen, making the carbon–oxygen bond easier to cleave.
- For an ether containing a tertiary alkyl group, cleavage occurs at the tertiary carbon through a relatively stable tertiary carbocation.

Step 1: Choose the bond that cleaves In tert-butyl ethyl ether, the tert-butyl carbon is tertiary. After oxygen protonation, cleavage of its bond to oxygen produces a tert-butyl carbocation and ethanol. Thus the usual attack at the less hindered ethyl group is not the controlling pathway here.

Step 2: Capture the carbocation Iodide ion combines with the tertiary carbocation to form tert-butyl iodide:



The products are the tertiary alkyl iodide and the alcohol from the ethyl fragment.

Step 3: Conclusion The products are $(\text{CH}_3)_3\text{CI}$ (2-iodo-2-methylpropane) and $\text{C}_2\text{H}_5\text{OH}$ (ethanol).

Quick Tip to Solve: For tertiary alkyl ethers with HI, check for tertiary carbocation formation before applying the less hindered carbon rule.

30(a). Case study (Biomolecules): Living systems are made up of various complex biomolecules like carbohydrates, proteins, nucleic acids, lipids, etc. Proteins and carbohydrates are essential constituents of our food. In addition, some simple molecules like vitamins and mineral salts also play an important role in the functions of organisms. All proteins are polymers of α -amino acids. Proteins can be classified into two types on the basis of their molecular shape - Fibrous and Globular proteins. Vitamins are accessory food factors required in the diet. They are classified as fat-soluble and water-soluble. Deficiency of vitamins leads to many diseases. Nucleic acids are the polymers of nucleotides which in turn consist of a base, a pentose sugar and phosphate moiety. There are two types of nucleic acids - DNA and RNA. Nucleic acids are responsible for the transfer of characters from parents to offsprings.

(a) Write the name of basic building units of proteins and nucleic acids. How can you differentiate between Fibrous and Globular proteins on the basis of their structures?

[2 marks]

Solution:

Concept:

- A polymer is formed by joining repeating building units called monomers. Proteins and nucleic acids have different monomers and different linking bonds.
- The classification of proteins as fibrous or globular depends on the overall arrangement and shape of their polypeptide chains.

Quick Tip to Solve: Pair proteins with amino acids and nucleic acids with nucleotides; then contrast long fibres with compact folds.

Step 1: Identify the basic building units Proteins are polymers of α -amino acids, joined through peptide bonds. Nucleic acids are polymers of nucleotides, joined through phosphodiester linkages. Each nucleotide consists of a nitrogenous base, a pentose sugar and a phosphate group; a base or sugar alone is therefore not the complete building unit of a nucleic acid.

Step 2: Compare the structures of the two protein classes In fibrous proteins, polypeptide chains run parallel and are held together by hydrogen bonds and disulphide bonds, producing long, fibre-like structures. Keratin is an example. In globular proteins, polypeptide chains coil and fold into compact, approximately spherical structures; insulin is an example. Thus the required structural distinction is an elongated, fibre-like arrangement versus a compact, folded arrangement.

Step 3: Conclusion Proteins have α -amino acids as their basic units; nucleic acids have nucleotides. Fibrous proteins have long, parallel, fibre-like chains, whereas globular proteins have chains folded into compact spherical shapes.

Quick Tip to Solve: Pair proteins with amino acids and nucleic acids with nucleotides; then contrast long fibres with compact folds.

30(b). What products would be formed when a nucleotide from DNA containing thymine is hydrolyzed?

[1 mark]

Solution:

Concept:

- A nucleotide contains three components: a nitrogenous base, a pentose sugar and a phosphate group.
- Complete hydrolysis of a nucleotide releases these constituent components; the sugar in DNA is 2-deoxyribose.

Step 1: Identify the base and sugar The question specifies thymine as the nitrogenous base. Since the nucleotide belongs to DNA, its pentose sugar is 2-deoxyribose, rather than the ribose present in RNA.

Step 2: Account for the phosphate component Hydrolysis also liberates the phosphate component as phosphoric acid. Listing only thymine and sugar would describe the components of a nucleoside and would omit the additional group that makes it a nucleotide.

Step 3: Conclusion The products are thymine, 2-deoxyribose and phosphoric acid.

Quick Tip to Solve: For nucleotide hydrolysis, always list base, sugar and phosphate; DNA fixes the sugar as deoxyribose.

30(b). Write one structural difference between DNA and RNA.

[1 mark]

Solution:

Concept:

- DNA and RNA are nucleic acids whose nucleotides contain a nitrogenous base, a pentose sugar and phosphate.
- Their pentose sugars differ structurally at the carbon atom numbered 2'.

Step 1: Identify the sugar in DNA DNA contains 2-deoxyribose. Its 2' carbon carries a hydrogen atom where ribose has a hydroxyl group; this is the structural meaning of the prefix deoxy.

Step 2: Compare it with the sugar in RNA RNA contains ribose, with an –OH group at the 2' carbon. Comparing the same position in the two sugars gives one precise structural difference without relying on their different biological functions.

Step 3: Conclusion DNA contains 2-deoxyribose sugar, whereas RNA contains ribose sugar: DNA has 2'-H in place of the 2'-OH present in RNA.

Quick Tip to Solve: Use the sugar difference: deoxyribose in DNA has one less oxygen atom than ribose in RNA.

30(c). Give one example each of a fat-soluble vitamin and a water-soluble vitamin.

[1 mark]

Solution:

Concept:

- Vitamins are classified according to their solubility in fats or in water.
- Vitamins A, D, E and K are fat-soluble; vitamin C and the B-group vitamins are water-soluble.

Step 1: Select a fat-soluble vitamin Vitamin A is a valid example of the fat-soluble class. It belongs to the group of vitamins that dissolve in fats and oils and are stored in the body.

Step 2: Select a water-soluble vitamin Vitamin C, also called ascorbic acid, is a valid water-soluble example. It belongs to a different solubility class from vitamin A, so the pair supplies one example of each type requested.

Step 3: Conclusion Fat-soluble vitamin: vitamin A. Water-soluble vitamin: vitamin C.

Quick Tip to Solve: Remember A, D, E and K as fat-soluble; choose vitamin C for a simple water-soluble example.

Section E (15 marks)

31(a). (i) Calculate the electrode potential of a half-cell for zinc electrode dipping in 0.01 M ZnSO_4 solution at 25°C .

Given: $E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$; $[\log 10 = 1]$

(ii) Write anode, cathode and overall reaction involved in dry cell.

(iii) Equilibrium constant (K_c) is related to E°_{cell} , but not to E_{cell} . Why?

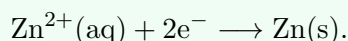
[5 marks]

Solution:

Concept:

- The Nernst equation connects an electrode's reduction potential with the activity of the ions taking part. At 298 K, $E = E^\circ - (0.0591/n) \log Q$, where n is the number of electrons and Q the reaction quotient.
- A dry cell converts the oxidation of zinc and reduction of manganese dioxide into electrical energy. Its zinc container is the anode; the graphite rod collects current from the cathode mixture.
- Standard Gibbs energy obeys $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -RT \ln K_c$, where F is the Faraday constant and R the gas constant.

Step 1: (i) Write the zinc reduction half-reaction The quoted standard potential is a reduction potential, so use



Here $n = 2$. The activity of solid zinc is unity, and approximating the zinc-ion activity by its molar concentration gives $Q = 1/[\text{Zn}^{2+}]$. Hence

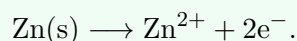
$$E = E^\circ + \frac{0.0591}{2} \log[\text{Zn}^{2+}].$$

Step 2: (i) Substitute the concentration Zinc sulphate supplies $[\text{Zn}^{2+}] = 0.01 = 10^{-2} \text{ M}$. Therefore,

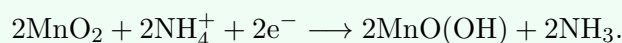
$$\begin{aligned} E &= -0.76 + \frac{0.0591}{2} \log(10^{-2}) \\ &= -0.76 - 0.0591 = -0.8191 \text{ V}. \end{aligned}$$

Dilution decreases the reduction potential, consistent with zinc ions being less readily reduced at lower concentration.

Step 3: (ii) Give the dry-cell reactions At the zinc anode, oxidation releases electrons:

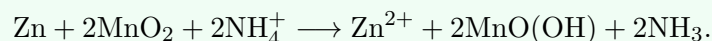


At the cathode, manganese dioxide is reduced in the presence of ammonium ions:



Quick Tip to Solve: For a metal-ion reduction to a pure metal, use a plus sign before the logarithm of the metal-ion concentration; dilution then makes the reduction potential smaller.

Adding the two half-reactions cancels the electrons and gives



The graphite rod serves as a conductor; it is not consumed in this reaction. The ammonia formed can complex with zinc ions in the paste.

Step 4: (iii) Distinguish standard potential from operating potential Combining the two expressions for standard Gibbs energy gives

$$\ln K_c = \frac{nF E_{\text{cell}}^\circ}{RT}.$$

At a fixed temperature the equilibrium constant is fixed, as is the standard cell potential. In contrast, the actual cell potential depends on the instantaneous concentrations through $E_{\text{cell}} = E_{\text{cell}}^\circ - (RT/nF) \ln Q$. At equilibrium $Q = K_c$ and $E_{\text{cell}} = 0$, regardless of the value of K_c . Thus the actual potential cannot determine the equilibrium constant without knowledge of Q .

Step 5: Conclusion (i) The zinc reduction potential is -0.8191 V , approximately -0.82 V . (ii) Zinc is oxidised and MnO_2 is reduced in the dry-cell reactions above. (iii) K_c is related to E_{cell}° through standard Gibbs energy, whereas E_{cell} varies with composition and vanishes at equilibrium.

Quick Tip to Solve: For a metal-ion reduction to a pure metal, use a plus sign before the logarithm of the metal-ion concentration; dilution then makes the reduction potential smaller.

OR

31(b). (i) The conductivity of 0.001 M solution of acetic acid is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given: $\lambda^\circ_{\text{CH}_3\text{COO}^-} = 40.9 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda^\circ_{\text{H}^+} = 349.6 \text{ S cm}^2 \text{ mol}^{-1}$.

(ii) Give reasons for the following:

(I) Why does a mercury cell deliver a constant voltage for its entire life?

(II) Why is it necessary to use salt bridge in a galvanic cell?

[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} .
- By Kohlrausch's law, the limiting molar conductivity of acetic acid is the sum of the limiting ionic molar conductivities of H^+ and CH_3COO^- . Its degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.
- A constant cell potential requires an essentially constant reaction quotient. A salt bridge completes the internal ionic circuit and maintains electrical neutrality in both half-cells.

Step 1: (i) Calculate the molar conductivity The given values are $\kappa = 3.905 \times 10^{-5} \text{ S cm}^{-1}$ and

Quick Tip to Solve: Add the two limiting ionic conductivities before dividing: here 39.05 is exactly one-tenth of 390.5, so the dissociation is 10 percent.

$c = 0.001 \text{ mol L}^{-1}$. The factor 1000 converts litres to cubic centimetres, so that the units match:

$$\begin{aligned}\Lambda_m &= \frac{1000 \times 3.905 \times 10^{-5}}{0.001} \\ &= 39.05 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

This value is the conductivity contribution per mole at the stated concentration, not the conductivity of the solution itself.

Step 2: (i) Find the limiting value and degree of dissociation Acetic acid dissociates as $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$. Its limiting molar conductivity is

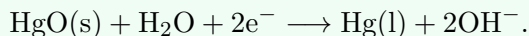
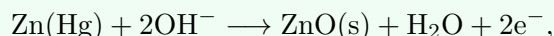
$$\begin{aligned}\Lambda_m^\circ &= \lambda_{\text{H}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ \\ &= 349.6 + 40.9 = 390.5 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

At infinite dilution the weak electrolyte is effectively completely dissociated. Comparing the measured value with this limit gives

$$\alpha = \frac{39.05}{390.5} = 0.100, \quad 100\alpha = 10.0\%.$$

Thus only one-tenth of the acid molecules are dissociated under the stated conditions, consistent with acetic acid being a weak electrolyte.

Step 3: (ii)(I) Explain the constant voltage of a mercury cell The alkaline mercury cell has the following electrode reactions:



Adding gives $\text{Zn(Hg)} + \text{HgO(s)} \longrightarrow \text{ZnO(s)} + \text{Hg(l)}$. The hydroxide ions and water cancel, so the overall reaction produces no net change in the electrolyte's ionic concentration. The activities of the solid and liquid phases remain essentially constant during useful operation. The reaction quotient and therefore the cell potential remain practically constant throughout its working life.

Step 4: (ii)(II) Explain the need for a salt bridge As oxidation occurs, positive charge tends to accumulate in the anode compartment; reduction tends to leave excess negative charge in the cathode compartment. Without ionic migration these charge imbalances oppose further electron transfer, and the current soon stops. The salt bridge supplies mobile, non-reacting ions: anions migrate towards the anode and cations towards the cathode to maintain electroneutrality. It completes the internal electrical circuit while limiting direct bulk mixing of the two solutions, and it reduces the liquid-junction potential.

Step 5: Conclusion (i) $\Lambda_m = 39.05 \text{ S cm}^2 \text{ mol}^{-1}$ and $\alpha = 0.100 = 10.0\%$. (ii)(I) The mercury-cell reaction leaves electrolyte concentration essentially unchanged, giving constant voltage. (ii)(II) The salt bridge maintains electrical neutrality and completes the ionic circuit, allowing sustained current.

Quick Tip to Solve: Add the two limiting ionic conductivities before dividing: here 39.05 is exactly one-tenth of 390.5, so the dissociation is 10 percent.

32(a). (i) Describe giving reason which one of the following pairs has the property indicated:

(I) Fe or Cu - higher melting point

(II) Ti^{3+} or Sc^{3+} - coloured in aqueous solution

(III) Cr or Zn - higher third ionisation enthalpy

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

(I) Fe^{2+} ion

(II) I^- ion

[5 marks]

Solution:

Concept:

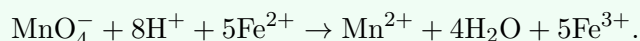
- Strong metallic bonding, involving available valence electrons, generally gives a higher melting point in transition metals.
- A partially filled d subshell permits d-d electronic transitions; an ion with a d^0 configuration cannot show this source of colour.
- Third ionisation enthalpy is the energy required for $M^{2+}(g) \rightarrow M^{3+}(g) + e^-$. Removing an electron from a stable half-filled subshell is especially difficult.
- In acidic medium, permanganate is reduced according to $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$.

Step 1: (a)(i)(I) Compare metallic bonding Fe has the higher melting point. Iron has more unpaired d electrons available for participation in strong metallic bonding than copper, whose atomic configuration is $[\text{Ar}]3d^{10}4s^1$. Consequently the metallic bonds in iron are stronger, and more energy is required to break up its metallic lattice on melting.

Step 2: (a)(i)(II) Compare the aqueous ions Ti^{3+} is coloured in aqueous solution. Titanium loses its two 4s electrons and one 3d electron to form $\text{Ti}^{3+} : [\text{Ar}]3d^1$. In its hydrated ion, visible light can promote this d electron between split d levels. In contrast, $\text{Sc}^{3+} : [\text{Ar}]3d^0$ has no d electron for a d-d transition and is colourless.

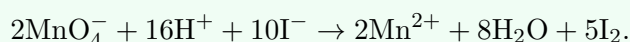
Step 3: (a)(i)(III) Compare the third ionisation enthalpies Zn has the higher third ionisation enthalpy. Chromium has $\text{Cr}^{2+} : [\text{Ar}]3d^4$, whereas zinc has $\text{Zn}^{2+} : [\text{Ar}]3d^{10}$. The third electron of zinc must be removed from its particularly stable, completely filled $3d^{10}$ subshell. Hence zinc requires more energy for this removal because its completely filled d subshell is disrupted.

Step 4: (a)(ii)(I) Oxidation of iron(II) Each Fe^{2+} ion loses one electron to give Fe^{3+} . Multiplying this oxidation half-reaction by five and adding the permanganate reduction gives



The charge on each side is +17, so both charge and atoms balance.

Step 5: (a)(ii)(II) Oxidation of iodide Iodide forms iodine by $2\text{I}^- \rightarrow \text{I}_2 + 2e^-$. The least common multiple of the electron counts is ten. Thus the balanced ionic equation is



Both sides have charge +4, and manganese, oxygen, hydrogen and iodine atoms are conserved.

Step 6: Conclusion The required choices are Fe , Ti^{3+} , Zn , respectively. Acidic permanganate

Quick Tip to Solve: For the third ionisation enthalpy, write the configuration of the doubly charged ion first; zinc must lose an electron from a full d subshell.

oxidises Fe^{2+} to Fe^{3+} and I^- to I_2 , itself forming Mn^{2+} .

Quick Tip to Solve: For the third ionisation enthalpy, write the configuration of the doubly charged ion first; zinc must lose an electron from a full d subshell.

OR

32(b). (i) A black-brown coloured solid (A) when fused with KOH in the presence of air, produces a dark green coloured compound (B) which on electrolytic oxidation in alkaline medium gives a dark purple coloured compound (C). Identify (A), (B) and (C). Write the reactions involved.

(ii) What happens when an acidic solution of the green compound (B) is allowed to stand for some time? Also write the equation involved. What is this type of reaction called? [5 marks]

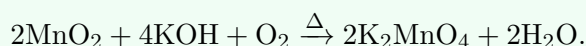
Solution:

Concept:

- Manganese forms several coloured compounds because it can exhibit different oxidation states: +4 in MnO_2 , +6 in manganate, and +7 in permanganate.
- Fusion with alkali in the presence of oxygen oxidises manganese dioxide to potassium manganate. Electrolytic oxidation then removes one electron from each manganate ion.
- Disproportionation is a redox reaction in which the same species is simultaneously oxidised and reduced to products with higher and lower oxidation states.

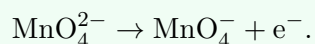
Step 1: (b)(i) Identify the three compounds The black-brown solid is manganese dioxide, $A = \text{MnO}_2$. Its manganese oxidation state is +4. The dark green product is potassium manganate, $B = \text{K}_2\text{MnO}_4$, containing manganese in the +6 state. The dark purple product is potassium permanganate, $C = \text{KMnO}_4$, containing manganese in the +7 state. Thus the colour changes accompany successive oxidation of manganese.

Step 2: Write the alkaline fusion reaction Heating manganese dioxide with potassium hydroxide in air gives potassium manganate. Oxygen from air acts as the oxidising agent:

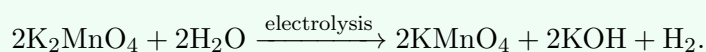


Each of the two manganese atoms loses two electrons, while oxygen accepts four electrons overall. Potassium hydroxide supplies the alkaline medium and the potassium ions of the green salt.

Step 3: Write the electrolytic oxidation During electrolysis in alkaline solution the manganate ion loses one electron at the anode:



The resulting permanganate ion forms the dark purple potassium salt. Combining the anodic change with hydrogen evolution at the cathode gives the overall equation



The ionic half-equation directly shows the required conversion of manganese from +6 to +7.

Quick Tip to Solve: Track manganese as +4 to +6 to +7 during preparation; in acidic manganate, +6 splits into +7 and +4, identifying disproportionation.

Step 4: (b)(ii) Describe the change on standing in acid The green manganate solution is unstable in acidic medium. On standing, it forms purple permanganate ions and a brown precipitate of manganese dioxide:



The total charge is -2 on each side, and all atoms balance. Of three manganese atoms initially in oxidation state $+6$, two are oxidised to $+7$, losing two electrons altogether, and one is reduced to $+4$, gaining those two electrons. Because manganate itself undergoes both oxidation and reduction, this is a **disproportionation reaction**.

Step 5: Conclusion $A = \text{MnO}_2$, $B = \text{K}_2\text{MnO}_4$, $C = \text{KMnO}_4$. Acidic manganate disproportionates into purple permanganate and brown manganese dioxide.

Quick Tip to Solve: Track manganese as $+4$ to $+6$ to $+7$ during preparation; in acidic manganate, $+6$ splits into $+7$ and $+4$, identifying disproportionation.

33(a). (i) Write the product(s) when:

(I) One mol of ethanal is treated with 1 mol of CH_3OH in the presence of dry HCl gas.

(II) Benzaldehyde is treated with conc. NaOH .

(III) Ethanoic acid is heated in the presence of P_2O_5 .

(ii) Write a simple chemical test to distinguish between Ethanal and Propanal.

(iii) Write the name of the reagent to transform Allyl alcohol to Propanal.

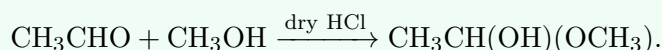
[5 marks]

Solution:

Concept:

- Acid-catalysed addition of one molecule of an alcohol to an aldehyde gives a hemiacetal, containing both an $-\text{OH}$ group and an $-\text{OR}$ group on the former carbonyl carbon.
- Aldehydes without an α -hydrogen undergo the Cannizzaro reaction with concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.
- P_2O_5 is a dehydrating agent. The iodoform test detects ethanal and compounds that contain, or can form, the $\text{CH}_3\text{CO}-$ group. Mild oxidation converts a primary allylic alcohol to its aldehyde while preserving its carbon-carbon double bond.

Step 1: (i)(I) Add one equivalent of methanol to ethanal In the presence of dry hydrogen chloride, methanol adds across the carbonyl group of ethanal:



The product is the hemiacetal, $\text{CH}_3\text{CH}(\text{OH})(\text{OCH}_3)$, named 1-methoxyethan-1-ol. One methoxy group and one hydroxyl group are attached to the same carbon. The stated one mole of methanol corresponds to this addition product; formation of the full acetal involves a second molecule of methanol and elimination of water.

Step 2: (i)(II) Carry out the Cannizzaro reaction Benzaldehyde has no α -hydrogen and therefore

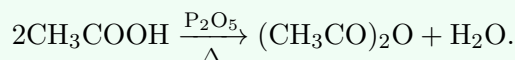
Quick Tip to Solve: Count the alcohol equivalents: one gives a hemiacetal. For two aldehydes, use iodoform rather than Tollens' reagent when only ethanal has the required methyl carbonyl arrangement.

undergoes disproportionation in concentrated sodium hydroxide:



The products are benzyl alcohol and sodium benzoate. The salt, rather than benzoic acid, is obtained in the alkaline reaction mixture; acidification would subsequently give the acid.

Step 3: (i)(III) Dehydrate ethanoic acid On heating, phosphorus pentoxide removes water from two molecules of ethanoic acid, forming ethanoic anhydride:



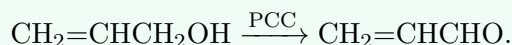
The water shown is the net water eliminated in anhydride formation and is taken up by the dehydrating agent.

Step 4: (ii) Distinguish ethanal from propanal by the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3 , whereas propanal gives no yellow precipitate:



Ethanal has the required $\text{CH}_3\text{CO}-$ arrangement with hydrogen as the other substituent on the carbonyl carbon; propanal does not. Tollens' reagent would not distinguish this pair because both are aldehydes and give a positive silver-mirror test.

Step 5: (iii) Oxidise allyl alcohol selectively Use pyridinium chlorochromate (PCC), a mild oxidising agent, typically in an anhydrous organic solvent:



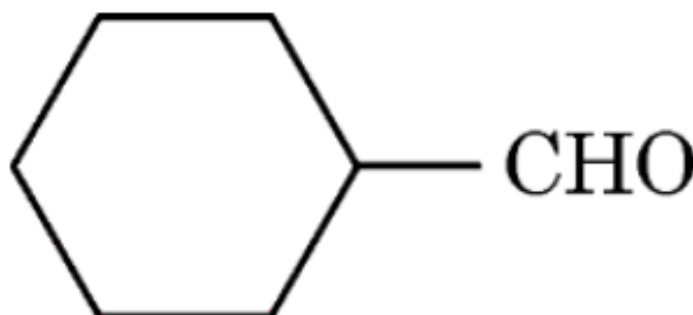
The primary alcohol group is oxidised to an aldehyde, giving propenal (acrolein). The carbon-carbon double bond is retained; a mild reagent avoids further oxidation of the aldehyde to the corresponding acid.

Step 6: Conclusion (i) The products are (I) $\text{CH}_3\text{CH}(\text{OH})(\text{OCH}_3)$, (II) benzyl alcohol and sodium benzoate, and (III) ethanoic anhydride. (ii) Ethanal gives a yellow iodoform precipitate with I_2/NaOH ; propanal does not. (iii) The reagent is pyridinium chlorochromate (PCC).

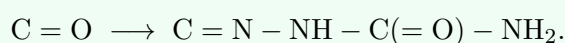
Quick Tip to Solve: Count the alcohol equivalents: one gives a hemiacetal. For two aldehydes, use iodoform rather than Tollens' reagent when only ethanal has the required methyl carbonyl arrangement.

- 33(b). (i) Draw the structure of the semicarbazone of acetone.
 (ii) Why are α -hydrogen atoms of aldehydes and ketones acidic in nature?
 (iii) Arrange the following compounds in increasing order of their reactivity towards HCN:
 CH_3COCH_3 , CH_3CHO , $(\text{CH}_3)_3\text{C-CO-CH}_3$
 (iv) Write the reaction involved in Etard reaction.
 (v) Write the product when reacts with Zn(Hg)/conc. HCl .

[5 marks]

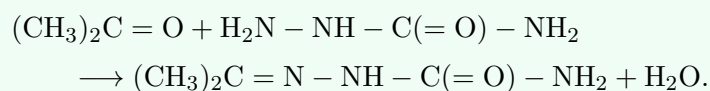
**Solution:****Concept:**

- A carbonyl compound condenses with the terminal amino group of semicarbazide. Its carbonyl oxygen is replaced by the semicarbazone linkage:



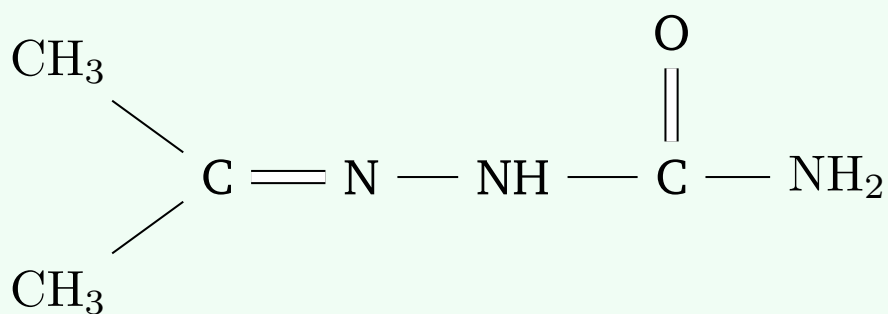
- Removal of an α -hydrogen gives a resonance-stabilised enolate ion. Nucleophilic addition is favoured by a more electrophilic and less crowded carbonyl carbon.
- Etard oxidation converts the side-chain methyl group of toluene into an aldehyde. Clemmensen reduction, using Zn(Hg) and concentrated HCl , converts aldehyde $-\text{CHO}$ into $-\text{CH}_3$.

Step 1: (i) Structure of acetone semicarbazone Acetone reacts with semicarbazide by condensation, with loss of water:



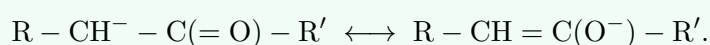
The two methyl groups remain attached to the original carbonyl carbon. The terminal amino nitrogen of semicarbazide forms the new double bond; its amide group remains unchanged. The displayed structure is shown below.

Quick Tip to Solve: In Clemmensen reduction, keep every carbon: a ring bearing $-\text{CHO}$ becomes the same ring bearing $-\text{CH}_3$, not the unsubstituted ring.



Displayed structure of acetone semicarbazone

Step 2: (ii) Acidity of alpha-hydrogen atoms The carbonyl group withdraws electron density, and loss of a proton from the adjacent carbon produces an enolate ion. Its negative charge is delocalised between carbon and oxygen:

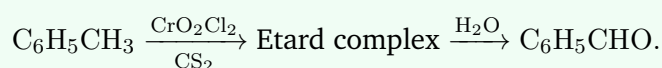


Resonance stabilises this conjugate base, making removal of an α -hydrogen easier than removal of a hydrogen from an ordinary alkane. Thus aldehydes and ketones containing α -hydrogen atoms show acidic character at that position.

Step 3: (iii) Increasing reactivity towards HCN Cyanide ion attacks the electrophilic carbonyl carbon. Alkyl groups reduce its positive character through their electron-releasing effect and also obstruct the approaching nucleophile. Ethanal has only one alkyl group and one small hydrogen attached to the carbonyl carbon; acetone has two methyl groups. The tert-butyl group in the third ketone creates especially strong steric hindrance. Hence the increasing order is

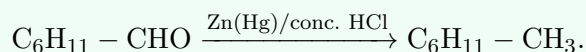


Step 4: (iv) Etard reaction Toluene is oxidised with chromyl chloride in an inert solvent such as carbon disulphide. The resulting Etard complex gives benzaldehyde on hydrolysis:



This controlled side-chain oxidation stops at the aldehyde stage.

Step 5: (v) Product of Clemmensen reduction The printed substrate is a cyclohexane ring bearing a formyl group, $\text{C}_6\text{H}_{11} - \text{CHO}$. Zinc amalgam and concentrated hydrochloric acid reduce this exocyclic aldehyde group to a methyl group:



The carbon of the formyl group is retained; only its oxygen is removed during reduction. The saturated ring remains intact, giving methylcyclohexane.

Step 6: Conclusion (i) $(\text{CH}_3)_2\text{C} = \text{N} - \text{NH} - \text{C}(=\text{O}) - \text{NH}_2$; (ii) the enolate conjugate base is

Quick Tip to Solve: In Clemmensen reduction, keep every carbon: a ring bearing $-\text{CHO}$ becomes the same ring bearing $-\text{CH}_3$, not the unsubstituted ring.

resonance stabilised; (iii) $(\text{CH}_3)_3\text{C} - \text{CO} - \text{CH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO}$; (iv) toluene gives benzaldehyde by chromyl chloride oxidation followed by hydrolysis; (v) methylcyclohexane.

Quick Tip to Solve: In Clemmensen reduction, keep every carbon: a ring bearing $-\text{CHO}$ becomes the same ring bearing $-\text{CH}_3$, not the unsubstituted ring.