CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-7-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **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. Which of the following transition metal ion is not coloured? [1 mark]

(A) Cu^{+}

(B) Ni^{2+}

(C) Co^{2+}

(D) V^{3+}

Correct Answer: (A) Cu^{+}

Solution:

Concept:

- Colour in many transition-metal ions arises when electrons absorb visible light and undergo transitions between split d orbitals.
- A d^{10} ion has a completely filled d subshell and cannot show the usual d-d transitions.

Step 1: Determine the electronic configurations Copper has configuration $[Ar]3d^{10}4s^{1}$. Removing its outer $4s$ electron gives Cu^{+} the configuration $[Ar]3d^{10}$. Thus its d subshell is completely filled.

Step 2: Compare the remaining ions Ni^{2+}, Co^{2+} and V^{3+} have configurations $3d^{8}$, $3d^{7}$ and $3d^{2}$, respectively. Their partially filled d subshells permit transitions responsible for colour; hence options (B), (C) and (D) do not satisfy the question.

Step 3: Conclusion Cu^{+} is not coloured because it has a $3d^{10}$ configuration. Hence, the correct option is (A).

Quick Tip to Solve: Remove the outer s electrons before counting d electrons; a full d^{10} subshell rules out ordinary d-d colour.

2. Which of the following solutions will have the highest boiling point in water? [1 mark]

(A) 1% KCl

(B) 1% glucose

(C) 1% urea

(D) 1% $CaCl_2$

Correct Answer: (D) 1% $CaCl_2$

Solution:

Concept:

- Elevation in boiling point is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the solvent's boiling-point constant and m the molality.
- Equal percentage concentrations give equal solute masses for the same amount of solution. Compare i/M, where M is the solute's molar mass, rather than i alone.

Quick Tip to Solve: For equal percentage solutions, compare i/M; for equal molality solutions, compare i alone.

Step 1: Count particles produced by each solute Glucose and urea are non-electrolytes, so $i = 1$. For dilute aqueous solutions, $\mathrm{KCl} \longrightarrow \mathrm{K^+} + \mathrm{Cl^-}$ gives $i = 2$, while $\mathrm{CaCl_2} \longrightarrow \mathrm{Ca^{2+}} + 2\,\mathrm{Cl^-}$ gives $i = 3$, taking complete dissociation as the standard comparison.

Step 2: Compare particle amounts for equal masses For the same solute mass and solvent mass, boiling-point elevation is proportional to i/M. Using molar masses in g mol^{-1}:

$$\begin{aligned} \mathrm{KCl}: &\quad 2/74.5 = 0.02685, \\ \text{glucose}: &\quad 1/180 = 0.00556, \\ \text{urea}: &\quad 1/60 = 0.01667, \\ \mathrm{CaCl_2}: &\quad 3/111 = 0.02703. \end{aligned}$$

The calcium chloride value is slightly greater than the potassium chloride value; the non-electrolytes give smaller values. Thus comparing only the number of ions would miss the close competition between (A) and (D).

Step 3: Conclusion The 1% $\mathrm{CaCl_2}$ solution gives the greatest boiling-point elevation and hence the highest boiling point. Hence, the correct option is (D).

Quick Tip to Solve: For equal percentage solutions, compare i/M; for equal molality solutions, compare i alone.

3. During electrolysis of dilute H_2SO_4, using platinum electrodes, the gas evolved at the anode is: [1 mark]

(A) H_2 gas

(B) O_2 gas

(C) SO_2 gas

(D) SO_3 gas

Correct Answer: (B) O_2 gas

Solution:

Concept:

- Oxidation occurs at the anode and reduction occurs at the cathode during electrolysis.
- Platinum is an inert electrode. In dilute aqueous sulphuric acid, water is oxidised to oxygen at the anode, while hydrogen ions are reduced at the cathode.

Step 1: Write the anode reaction Water loses electrons at the positive platinum anode. The balanced oxidation half-reaction in acidic medium is

$$2\,\mathrm{H_2O} \longrightarrow \mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-}.$$

Both atoms and charge are conserved. The gaseous product of this oxidation is oxygen.

Step 2: Distinguish the alternative gases Hydrogen is produced by $2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}$, but this is reduction at the cathode, so (A) names the wrong electrode's product. Sulphate ions remain

Quick Tip to Solve: In electrolysis of acidified water with inert electrodes, remember anode oxidation gives oxygen and cathode reduction gives hydrogen.

in solution under these conditions: neither SO_2 nor SO_3 is the gas liberated at the inert anode, eliminating (C) and (D).

Step 3: Conclusion O_2 gas is evolved at the anode. Hence, the correct option is (B).

Quick Tip to Solve: In electrolysis of acidified water with inert electrodes, remember anode oxidation gives oxygen and cathode reduction gives hydrogen.

4. The activation energy (E_a) of a reaction can be determined from the slope of which of the following plots? [1 mark]

(A) $\ln k$ vs. T
(B) $\frac{\ln k}{T}$ vs. T
(C) $\ln k$ vs. $\frac{1}{T}$
(D) $\frac{T}{\ln k}$ vs. $\frac{1}{T}$

Correct Answer: (C) $\ln k$ vs. $\frac{1}{T}$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the pre-exponential factor, E_a the activation energy and R the gas constant.
- Taking natural logarithms gives a straight-line relationship between $\ln k$ and reciprocal absolute temperature $1/T$.

Step 1: Put the equation into straight-line form Take the natural logarithm of the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{R}\left(\frac{1}{T}\right).$$

Comparing with $y = c + sx$, use $y = \ln k$, $x = 1/T$, intercept $c = \ln A$ and slope $s = -E_a/R$.

Step 2: Identify the required axes A plot of $\ln k$ vertically against $1/T$ horizontally therefore has a negative slope from which $E_a = -Rs$. Plotting against T directly in (A), or using $(\ln k)/T$ in (B), does not produce this linear form. The transformed ordinate $T/\ln k$ in (D) also does not give the required Arrhenius slope.

Step 3: Conclusion Use the plot of $\ln k$ versus $1/T$, whose slope is $-E_a/R$. Hence, the correct option is (C).

Quick Tip to Solve: First rewrite Arrhenius as $\ln k = \ln A - (E_a/R)(1/T)$; the coefficient of the horizontal variable gives the slope.

5. Which of the following represents the fraction of molecules with energies equal to or greater than E_a? [1 mark]

(A) $\frac{-E_a}{RT}$

(B) $e^{-E_a/(RT)}$

(C) $e^{+E_a/(RT)}$

(D) $\frac{+E_a}{RT}$

Correct Answer: (B) $e^{-E_a/(RT)}$

Solution:

Concept:

- In the Arrhenius treatment, the exponential factor $e^{-E_a/(RT)}$ represents the fraction of molecules with energy sufficient to cross the activation barrier.
- E_a is the molar activation energy, R the gas constant and T the absolute temperature. The ratio $E_a/(RT)$ is dimensionless.

Step 1: Apply the energy-distribution factor For positive activation energy and temperature, put $x = E_a/(RT) > 0$. The required factor is e^{-x}, which lies between zero and one. As temperature rises, x decreases and this factor increases, agreeing with the increased number of molecules able to react.

Step 2: Check all printed alternatives Option (B) is exactly $e^{-E_a/(RT)}$. Option (A), $-E_a/(RT)$, is negative and cannot be a fraction of molecules. Option (C), $e^{+E_a/(RT)}$, exceeds one for positive E_a. Option (D), $+E_a/(RT)$, is a plain ratio, not the exponential distribution factor, and decreases rather than increases on raising temperature.

Step 3: Conclusion The required fraction is $e^{-E_a/(RT)}$. Hence, the correct option is (B).

Quick Tip to Solve: Check that a proposed fraction lies between zero and one and increases with temperature; the negative exponential passes both tests.

6. The number of moles of AgCl precipitated when excess $AgNO_3$ solution is mixed with one mole of $[Co(NH_3)_3Cl_3]$ is: [1 mark]

(A) 0

(B) 1

(C) 2

(D) 3

Correct Answer: (A) 0

Solution:

Concept:

- Only free chloride ions outside the coordination sphere readily precipitate with aqueous silver nitrate as $AgCl$.
- Ligands inside square brackets are bonded to the central metal; coordinated chloride must not be counted as free counter-ions.

Quick Tip to Solve: For silver nitrate tests on coordination compounds, count chloride ions outside the brackets, not chlorido ligands inside them.

Step 1: Locate the chloride ligands In $[Co(NH_3)_3Cl_3]$, all three chlorides occur inside the square brackets, along with the three neutral ammonia ligands. They are therefore coordinated to cobalt. The complex is neutral: cobalt's $+3$ oxidation state balances three chlorido ligands, each carrying -1 charge.

Step 2: Count precipitable chloride ions There are no chloride counter-ions outside the brackets. Thus one mole of this compound supplies zero moles of free Cl^- for $Ag^+ + Cl^- \longrightarrow AgCl\downarrow$. Excess silver nitrate does not make the three coordinated chlorides into freely ionising counter-ions. Options (B), (C) and (D) incorrectly count one, two or all three coordinated ligands as free chloride.

Step 3: Conclusion The amount of $AgCl$ precipitated is 0 mol. Hence, the correct option is (A).

Quick Tip to Solve: For silver nitrate tests on coordination compounds, count chloride ions outside the brackets, not chlorido ligands inside them.

7. Which of the following haloalkanes react with aqueous KOH most rapidly by S_N1 reaction? [1 mark]

(A) 2-Chlorobutane

(B) 1-Bromobutane

(C) 2-Bromo-2-Methylpropane

(D) 2,2-Dimethyl-1-Chloropropane

Correct Answer: (C) 2-Bromo-2-Methylpropane

Solution:

Concept:

- An S_N1 reaction proceeds by slow ionisation of a carbon-halogen bond to form a carbocation, followed by nucleophilic attack.
- The rate depends strongly on carbocation stability: tertiary carbocations are generally more stable than secondary, which are more stable than primary ones.

Step 1: Compare the carbocations formed 2-Bromo-2-methylpropane, $(CH_3)_3CBr$, forms a tertiary tert-butyl carbocation on loss of bromide. Three alkyl groups stabilise its positive charge by the electron-releasing inductive effect and hyperconjugation. This favours the slow ionisation step in aqueous medium.

Step 2: Eliminate the less reactive substrates 2-Chlorobutane forms a secondary carbocation. 1-Bromobutane and 2,2-dimethyl-1-chloropropane would initially form primary carbocations, so their ionisation is less favourable. The highly branched appearance of the last compound does not make its carbon bearing chlorine tertiary. Bromide is also a better leaving group than chloride, further supporting the tertiary bromide over the secondary chloride.

Step 3: Conclusion 2-Bromo-2-methylpropane reacts most rapidly with aqueous KOH by the S_N1 mechanism. Hence, the correct option is (C).

Quick Tip to Solve: Classify the carbon directly bonded to the halogen; remote branching does not change a primary halide into a tertiary halide.

8. The reaction

$R - OH + Na \longrightarrow RO^{-}Na^{+} + \frac{1}{2}H_2(g)$

suggests that alcohols are: [1 mark]

(A) Acidic

(B) Basic

(C) Neutral

(D) Amphoteric

Correct Answer: (A) Acidic

Solution:

Concept:

- An acid can donate a proton. The hydrogen of the hydroxyl group, $-OH$, is the acidic hydrogen in an alcohol.
- Sodium displaces this hydroxyl hydrogen, producing sodium alkoxide, $RO^{-}Na^{+}$, and hydrogen gas.

Step 1: Identify the hydrogen that is removed In the printed reaction, $R - OH$ becomes RO^{-}. The oxygen retains the organic group R, while the hydroxyl hydrogen is removed. Two such hydrogen atoms combine to give H_2, so one mole of alcohol yields half a mole of hydrogen gas.

Step 2: Interpret the reaction and test the options The formation of an alkoxide by displacement of the hydroxyl hydrogen demonstrates the weak acidic nature of the alcohol. Hence acidic is appropriate. A basic reaction would establish proton acceptance, which this equation does not show; neutral does not account for the acidic hydrogen. Amphoteric would require evidence of both acidic and basic behaviour, whereas the printed reaction demonstrates only acidity.

Step 3: Conclusion The reaction suggests that alcohols are **acidic**. Hence, the correct option is **(A)**.

Quick Tip to Solve: For an alcohol reacting with sodium, follow the lost hydroxyl hydrogen: alkoxide plus hydrogen gas signals acidity.

9. At low temperature, phenol reacts with Br_2 in CS_2 to form: [1 mark]

(A) 2,4,6-tribromophenol

(B) p-bromophenol

(C) o- and p-bromophenol

(D) 2,4-dibromophenol

Correct Answer: (C) o- and p-bromophenol

Solution:

Concept:

- The $-OH$ group activates the benzene ring towards electrophilic substitution and directs incoming substituents to the ortho and para positions.
- Bromination in a non-polar solvent such as CS_2 at low temperature gives predominantly mono-

Quick Tip to Solve: Check the solvent before choosing a bromination product: cold non-polar solvent gives ortho/para monobromination; bromine water gives tribromination.

bromination rather than exhaustive substitution.

Step 1: Use the directing effect of the hydroxyl group Electron donation from oxygen increases electron density especially at the ortho and para positions relative to $-\mathrm{OH}$. Therefore, replacement of a ring hydrogen by bromine produces both o-bromophenol and p-bromophenol. The para product is the major component because its formation involves less steric hindrance.

Step 2: Apply the stated reaction conditions The question specifies low temperature and $\mathrm{CS_2}$, so the reaction is controlled to monobromination. Option (B) names only the major para product and omits the ortho product. The tribromo product in (A) is characteristic of treatment with bromine water; the dibromo product in (D) is not the standard product mixture under these conditions.

Step 3: Conclusion The products are o- and p-bromophenol. Hence, the correct option is **(C)**.

Quick Tip to Solve: Check the solvent before choosing a bromination product: cold non-polar solvent gives ortho/para monobromination; bromine water gives tribromination.

10. When alkyl iodide is treated with large excess of ammonia, the major product obtained is: [1 mark]

(A) Tertiary amine

(B) Quaternary ammonium salt

(C) Secondary amine

(D) Primary amine

Correct Answer: (D) Primary amine

Solution:

Concept:

- Ammonia acts as a nucleophile and replaces iodide in an alkyl iodide, forming an alkylammonium salt that gives a primary amine on deprotonation.
- A large excess of ammonia favours its reaction with the alkyl halide and suppresses further alkylation of the amine product.

Step 1: Identify the first amine formed The initial substitution introduces one alkyl group on nitrogen. The overall reaction may be written as

$$\mathrm{RI} + 2\mathrm{NH_3} \longrightarrow \mathrm{RNH_2} + \mathrm{NH_4I}.$$

Thus, the first amine formed is $\mathrm{RNH_2}$, which is a primary amine because nitrogen is attached to one organic group.

Step 2: Use the excess-ammonia condition The primary amine can itself react with additional alkyl iodide, giving secondary and then tertiary amines; further alkylation can give a quaternary ammonium salt. However, when ammonia is present in large excess, an alkyl iodide molecule is much more likely to encounter ammonia than the amine product. Further alkylation is consequently suppressed, so options (A), (B) and (C) are not the major product.

Step 3: Conclusion The major product is a **primary amine**. Hence, the correct option is **(D)**.

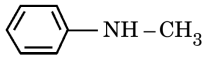
Quick Tip to Solve: In ammonolysis, underline large excess of ammonia: it favours the first substitution and therefore the primary amine.

11. An amine 'X' reacts with Hinsberg reagent and the product obtained is soluble in alkali. The amine 'X' is: [1 mark]

(A) CH_3-NH_2

(B) $(CH_3)_2NH$

(C) $(CH_3)_3N$

(D) 

Correct Answer: (A) CH_3-NH_2

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$, used to distinguish primary, secondary and tertiary amines.
- A primary amine gives a sulphonamide retaining one $N-H$ bond. This hydrogen is acidic because of the electron-withdrawing sulphonyl group, allowing salt formation in alkali.

Step 1: Identify the alkali-soluble product Methylamine is a primary amine and reacts to form $C_6H_5SO_2NHCH_3$. The product retains an acidic nitrogen-bound hydrogen and reacts with alkali to form a soluble salt:

$$C_6H_5SO_2NHCH_3 + OH^- \longrightarrow C_6H_5SO_2N^-CH_3 + H_2O.$$

Hence, its Hinsberg product satisfies the stated solubility condition.

Step 2: Eliminate the other amines Dimethylamine in (B) and N-methylaniline in (D) are secondary amines. Their sulphonamides have no $N-H$ bond, so they do not form these alkali-soluble salts. Trimethylamine in (C) is tertiary and has no nitrogen-bound hydrogen; it does not form a sulphonamide with Hinsberg reagent under the test conditions.

Step 3: Conclusion The amine X is CH_3NH_2, methylamine. Hence, the correct option is **(A)**.

Quick Tip to Solve: For an alkali-soluble Hinsberg product, check for the remaining N-H bond: a primary amine leaves one after sulphonylation.

12. α-helix structure refers to: [1 mark]

(A) primary structure of protein

(B) secondary structure of protein

(C) tertiary structure of protein

(D) quaternary structure of protein

Correct Answer: (B) secondary structure of protein

Solution:

Concept:

- Primary structure is the amino-acid sequence of a protein; secondary structure describes regular local folding of its polypeptide backbone.
- The α-helix is stabilised by hydrogen bonds between peptide carbonyl and peptide $N-H$ groups

Quick Tip to Solve: Associate alpha-helix and beta-pleated sheet with secondary structure; reserve tertiary for the complete folding of one chain.

within the same chain.

Step 1: Identify what the helix describes An α-helix is a regular coiled arrangement of the polypeptide backbone. Hydrogen bonding holds this repeating arrangement in place. Since it specifies the local spatial arrangement rather than the sequence of amino acids, it belongs to the secondary level of protein structure.

Step 2: Distinguish the other structural levels Primary structure in (A) states the order of amino acids linked by peptide bonds and does not describe coiling. Tertiary structure in (C) describes the overall three-dimensional folding of an entire polypeptide chain. Quaternary structure in (D) describes the arrangement of multiple polypeptide subunits. Neither of these overall arrangements is the specific local helix asked about.

Step 3: Conclusion The α-helix refers to the **secondary structure of a protein**. Hence, the correct option is **(B)**.

Quick Tip to Solve: Associate alpha-helix and beta-pleated sheet with secondary structure; reserve tertiary for the complete folding of one chain.

13. Assertion (A): A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation.
Reason (R): o-nitrophenol is steam volatile due to intermolecular hydrogen bonding. [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:

- Intramolecular hydrogen bonding takes place within a molecule, whereas intermolecular hydrogen bonding associates separate molecules.
- o-Nitrophenol is steam volatile because of intramolecular hydrogen bonding; intermolecular association makes p-nitrophenol less volatile.

Step 1: Judge the assertion The assertion is true. A mixture of o-nitrophenol and p-nitrophenol can be separated by steam distillation because the ortho isomer distils with steam much more readily, leaving the para isomer behind.

Step 2: Judge the reason The reason is false. In the ortho isomer the hydroxyl group and nitro group are adjacent, permitting hydrogen bonding within the same molecule. This is intramolecular hydrogen bonding, not the intermolecular hydrogen bonding stated in the reason. The para isomer forms intermolecular hydrogen bonds and consequently exhibits greater molecular association.

Step 3: Check the explanatory connection The actual explanation for the separation is the difference

Quick Tip to Solve: In nitrophenols, remember ortho means an internal hydrogen bond and steam volatility; para means intermolecular association.

in intermolecular association and hence steam volatility. Intramolecular hydrogen bonding in the ortho isomer reduces association between its molecules. The printed reason attributes its volatility to the wrong kind of hydrogen bonding, so it cannot explain the true assertion.

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

Quick Tip to Solve: In nitrophenols, remember ortho means an internal hydrogen bond and steam volatility; para means intermolecular association.

14. Assertion (A): Cooking time is reduced in pressure cooker.

Reason (R): Boiling point of water inside the pressure cooker is elevated. [1 mark]

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

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

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

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

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

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure acting on its surface.
- Increasing external pressure raises the boiling temperature of water, allowing food to cook at a higher temperature.

Step 1: Judge the assertion The assertion is true. Cooking time is reduced in a pressure cooker because the cooking water and steam can reach temperatures above the normal boiling point of water at atmospheric pressure. Food therefore cooks faster.

Step 2: Judge the reason The reason is also true. Steam is retained in the cooker, raising the pressure inside it. Water must reach a higher temperature before its vapour pressure equals this increased pressure, so the boiling point of water inside the cooker is elevated.

Step 3: Check whether the reason explains the assertion The elevated boiling temperature is precisely the cause of the reduced cooking time: a higher cooking temperature speeds the processes by which food becomes cooked. Thus, the reason directly explains the assertion. Options (C) and (D) incorrectly reject a true statement, and option (B) incorrectly denies this causal connection.

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

Quick Tip to Solve: For a pressure cooker, follow the causal chain: higher pressure raises the boiling point, raising cooking temperature and reducing time.

15. Assertion (A): Actinoids show irregularities in their electronic configurations.

Reason (R): Actinoids are radioactive in nature. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Actinoids have closely spaced $5f$, $6d$ and $7s$ energy levels; their relative energies can change across the series.
- Radioactivity results from instability of the atomic nucleus, whereas electronic configuration describes the distribution of electrons outside it.

Step 1: Judge the assertion Assertion (A) is true. The small differences between the energies of the $5f$, $6d$ and $7s$ orbitals lead to irregular electron distributions among these orbitals in actinoids.

Step 2: Judge the reason Reason (R) is also true. All actinoid elements are radioactive: their unstable nuclei undergo radioactive decay.

Step 3: Test the explanatory link Nuclear instability does not explain the irregular occupation of electronic orbitals. The assertion is explained by the small energy separations of the orbitals, not by radioactivity. Thus (A) is excluded because the explanatory link is absent; (C) and (D) are excluded because neither statement is false.

Step 4: Conclusion Both statements are true, but the reason does not explain the assertion. Hence, the correct option is (B).

Quick Tip to Solve: For actinoids, link configuration irregularities to close orbital energies; link radioactivity to the nucleus.

16. Assertion (A): Vitamin K can be stored in our body.

Reason (R): Vitamin K is a water soluble vitamin. [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:

- Vitamins A, D, E and K are fat soluble and can be stored in the body's liver and fatty tissues.
- Vitamins of the B group and vitamin C are water soluble; they are generally not stored to the same extent and require regular dietary intake.

Step 1: Judge the assertion Assertion (A) is true. Vitamin K belongs to the fat-soluble group of vitamins and can be stored in the body, including the liver and fatty tissues.

Step 2: Judge the reason Reason (R) is false. Vitamin K is fat soluble, not water soluble. Its association with fats allows storage in tissues; the reason gives the wrong solubility classification.

Step 3: Select the statement combination Since the assertion is true and the reason is false, neither combination in which both statements are true is valid. The alternative in which the assertion is false and the reason true reverses both judgements and must also be rejected.

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

Quick Tip to Solve: Remember the fat-soluble set as A, D, E and K before judging vitamin storage and solubility statements.

Section B (10 marks)

17. What is meant by positive deviation from Raoult's law? Give an example. What type of azeotrope is formed by positive deviation? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary liquid mixture is $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$, where x denotes liquid mole fraction and p° the vapour pressure of the pure liquid.
- Weaker unlike-molecule attractions make escape into the vapour phase easier and raise the vapour pressure above the ideal value.

Step 1: Define positive deviation and give an example A solution shows positive deviation when its component partial vapour pressures, and hence its total vapour pressure, are greater than the values

Quick Tip to Solve: Connect higher vapour pressure with easier boiling: positive deviation leads to the minimum-boiling azeotrope type.

predicted by Raoult's law:

$$p_A > x_A p_A^\circ, \qquad p_B > x_B p_B^\circ.$$

An example is an ethanol-acetone mixture. Acetone disrupts some of the hydrogen bonding between ethanol molecules, so the unlike interactions are weaker than the interactions present in the pure liquids. More molecules can therefore escape into the vapour.

Step 2: Identify the azeotrope type A sufficiently large positive deviation produces a maximum in total vapour pressure and consequently a minimum in boiling temperature at a particular composition. At this composition the liquid and vapour have the same composition, so the mixture boils at constant composition and forms a minimum-boiling azeotrope. Small positive deviations need not produce an azeotrope.

Step 3: Conclusion Positive deviation means vapour pressure greater than Raoult's-law predictions; ethanol-acetone is an example. When an azeotrope forms because of positive deviation, it is a minimum-boiling azeotrope.

Quick Tip to Solve: Connect higher vapour pressure with easier boiling: positive deviation leads to the minimum-boiling azeotrope type.

18. State a condition under which a bimolecular reaction is kinetically first order reaction. Give an example. For which type of reactions, do order and molecularity have the same value? [2 marks]

Solution:

Concept:

- A bimolecular elementary reaction involving two different reactants has a rate proportional to the product of their concentrations.
- If one reactant is in large excess, its concentration is effectively constant; its contribution can be absorbed into an observed rate constant.
- Order is obtained from the rate law, whereas molecularity counts the reacting species in a single elementary step.

Step 1: State the condition for apparent first-order kinetics For a reaction with rate $r = k[A][B]$, take B in such large excess that its concentration changes negligibly during the reaction. Then

$$r = k'[A], \qquad k' = k[B]_{\text{approximately constant}}.$$

The reaction is kinetically first order with respect to the changing reactant concentration and is called a pseudo-first-order reaction. The observed first-order rate law does not change the underlying molecularity.

Step 2: Give an example and relate order to molecularity Hydrolysis of ethyl acetate in excess water is an example:

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH.$$

With water effectively constant (and any acid catalyst concentration held fixed), the observed rate is proportional to the ester concentration. Order and molecularity have the same value for simple

Quick Tip to Solve: Look for a reactant in large excess: treat its concentration as constant and absorb it into the observed rate constant.

elementary reactions, for which the rate law follows the reactants participating in the single step. For a complex reaction, overall stoichiometric coefficients do not in general determine its order.

Step 3: Conclusion A bimolecular reaction is pseudo-first order when one reactant is in large excess, as in ethyl acetate hydrolysis in excess water. Order and molecularity agree for simple elementary reactions.

Quick Tip to Solve: Look for a reactant in large excess: treat its concentration as constant and absorb it into the observed rate constant.

19(a). Write the IUPAC name of the complex $[Pt(en)_2Cl_2]^{2+}$. Draw the structure of geometrical isomer of this complex which is optically inactive. [2 marks]

Solution:

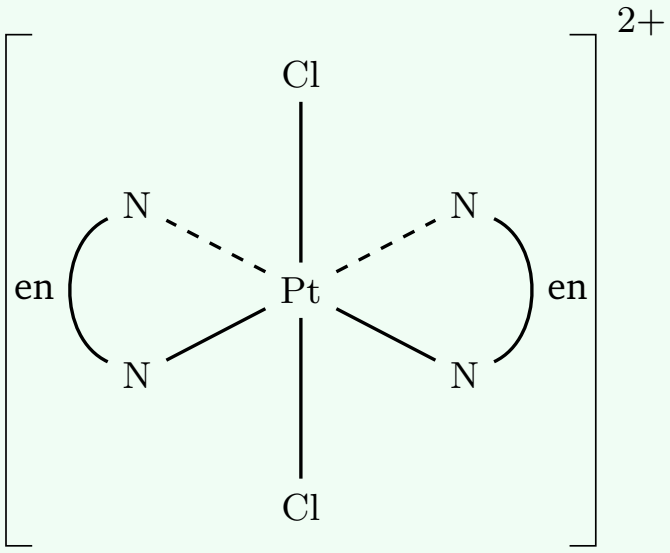
Concept:

- Ethane-1,2-diamine (en), $H_2NCH_2CH_2NH_2$, is a neutral bidentate ligand: each molecule supplies two nitrogen donor atoms.
- In an octahedral complex of the type $[M(en)_2Cl_2]$, the chlorido ligands may be adjacent (cis) or opposite (trans). A plane of symmetry makes the trans form optically inactive.

Step 1: Determine the oxidation state and name the complex Let the oxidation state of platinum be x. Each en ligand has zero charge and each chlorido ligand has charge -1. Thus $x + 2(0) + 2(-1) = +2$, giving $x = +4$. List chlorido before ethane-1,2-diamine alphabetically; use bis for the two ligands whose name already contains numerical locants. As the coordination entity is cationic, the metal retains the name platinum. The IUPAC name is **dichloridobis(ethane-1,2-diamine)platinum(IV) ion**.

Step 2: Draw the optically inactive trans isomer The two en molecules occupy four coordination sites, while the two chlorido ligands occupy the remaining two sites. Put the chlorido ligands on opposite axial positions, so the $Cl-Pt-Cl$ angle is $180°$. Each curved link in the sketch joins the two nitrogen donors of one en chelate. Solid and dashed bonds distinguish front and rear equatorial donors. The equatorial plane is a symmetry plane: reflection exchanges the identical upper and lower chlorido ligands and leaves the equatorial chelates unchanged. Thus the trans form is achiral; the cis form can instead form an optically active enantiomeric pair.

Quick Tip to Solve: Count each en twice when checking coordination number, but give it zero charge when calculating the metal oxidation state; opposite chlorido ligands identify the inactive trans form.



trans: opposite chlorido ligands

Trans octahedral isomer; each paired nitrogen donor set belongs to one en ligand.

Step 3: Conclusion The complex is **dichloridobis(ethane-1,2-diamine)platinum(IV) ion**. Its **trans geometrical isomer**, drawn below the structural step, is optically inactive.

Quick Tip to Solve: Count each en twice when checking coordination number, but give it zero charge when calculating the metal oxidation state; opposite chlorido ligands identify the inactive trans form.

OR

19(b). (i) Write the formula of the following coordination compound:
Pentaamminecarbonatocobalt(III)chloride
(ii) Write the IUPAC name of the linkage isomer of the complex $[Co(NH_3)_5(NO_2)]Cl_2$. [2 marks]

Solution:

Concept:

- The charge on a coordination entity is the sum of the metal oxidation state and the charges on all its ligands. Ammine, NH_3, is neutral, whereas carbonato, CO_3^{2-}, has charge -2.
- Linkage isomerism occurs when an ambidentate ligand attaches through different donor atoms. The nitrite ion, NO_2^-, can bind through nitrogen or oxygen.

Step 1: Write the formula of pentaamminecarbonatocobalt(III) chloride Cobalt(III) supplies charge $+3$. The five ammine ligands contribute no charge, while the carbonato ligand contributes -2. Therefore the coordination entity has charge $+3-2=+1$, and one chloride ion is required outside the coordination sphere to give an electrically neutral compound. The requested formula is

$$[Co(NH_3)_5(CO_3)]Cl.$$

Quick Tip to Solve: First balance the charge to place chloride outside the brackets; for a linkage isomer, change the donor atom from N to O while retaining the same ligand composition.

Keep carbonato inside the brackets because it is a ligand, and chloride outside because it is the counter-ion.

Step 2: Identify and name the linkage isomer In the given nitro complex, the nitrite ligand is attached through nitrogen. Its linkage isomer has the same ligand composition but attaches through oxygen, giving $[Co(NH_3)_5(ONO)]Cl_2$. The two chloride counter-ions mean that the complex ion is $+2$. Since nitrite contributes -1, cobalt is in oxidation state $+3$. The IUPAC name of this oxygen-bonded isomer is **pentaammine(nitrito-O)cobalt(III) chloride**. The nitrito-O designation identifies the coordinating atom and distinguishes it from the nitrogen-bonded nitro isomer.

Step 3: Conclusion (i) $[Co(NH_3)_5(CO_3)]Cl$.

(ii) **Pentaammine(nitrito-O)cobalt(III) chloride**, $[Co(NH_3)_5(ONO)]Cl_2$.

Quick Tip to Solve: First balance the charge to place chloride outside the brackets; for a linkage isomer, change the donor atom from N to O while retaining the same ligand composition.

20. Why are haloarenes less reactive towards nucleophilic substitution reaction? How does the presence of nitro (-NO_2) group at ortho- and para-positions in haloarenes increase the reactivity towards nucleophilic substitution reaction? [2 marks]

Solution:

Concept:

- Nucleophilic substitution requires cleavage of the carbon-halogen bond. In haloarenes, resonance between a halogen lone pair and the aromatic ring gives the $C-X$ bond partial double-bond character, where X is a halogen.
- An electron-withdrawing nitro group at an ortho or para position stabilises the negatively charged intermediate formed during nucleophilic aromatic substitution.

Step 1: Explain the low reactivity of haloarenes Delocalisation of a halogen lone pair into the benzene ring gives the carbon-halogen bond partial double-bond character. This bond is consequently shorter and stronger than the corresponding bond in a haloalkane and is harder to break. The bonded ring carbon is also sp^2-hybridised, which further strengthens its bond to halogen compared with an sp^3 carbon. Ordinary substitution routes are unfavourable: bond ionisation would produce an unstable phenyl cation, and the aromatic framework makes the usual backside attack at the halogen-bearing carbon difficult. Thus haloarenes resist ordinary nucleophilic substitution.

Step 2: Explain activation by an ortho or para nitro group A nitro group, $-NO_2$, withdraws electron density by its inductive and resonance effects. It makes the halogen-bearing carbon more susceptible to nucleophilic attack. More decisively, when the nucleophile adds to this carbon, the resulting anionic intermediate delocalises its negative charge to the ortho and para positions. A nitro group at either position can accept this charge through resonance, spreading it onto its oxygen atoms and stabilising the intermediate. Halide elimination then restores aromaticity. This lowers the barrier for the addition-elimination pathway and increases the substitution rate. A meta nitro group cannot provide this direct resonance stabilisation of the intermediate.

Step 3: Conclusion Haloarenes are less reactive because their carbon-halogen bond has partial double-

Quick Tip to Solve: For nitro activation, track where the intermediate's negative charge can resonate: ortho and para nitro groups accept it, but a meta nitro group cannot do so directly.

bond character and is strong. An ortho or para $-NO_2$ group increases reactivity by withdrawing electron density and, especially, stabilising the anionic substitution intermediate by resonance.

Quick Tip to Solve: For nitro activation, track where the intermediate's negative charge can resonate: ortho and para nitro groups accept it, but a meta nitro group cannot do so directly.

21. The two strands in DNA are not identical but complementary. Explain. What products would be formed when DNA is hydrolysed? [2 marks]

Solution:

Concept:

- DNA is made of two polynucleotide strands held together by specific hydrogen bonding between their nitrogenous bases: adenine pairs with thymine, and guanine pairs with cytosine.
- Each DNA nucleotide contains a nitrogenous base, 2-deoxy-D-ribose and phosphate. Complete hydrolysis breaks DNA down into these constituent units.

Step 1: Explain complementary base pairing In the DNA double helix, adenine (A) on one strand pairs with thymine (T) on the other through two hydrogen bonds. Guanine (G) pairs with cytosine (C) through three hydrogen bonds. Thus the bases opposite one another are complementary partners, rather than identical bases. Once the base sequence on one strand is known, the sequence of the other strand is fixed by the rules A–T and G–C. For example, the sequence $5'$-ATGC-$3'$ corresponds to $3'$-TACG-$5'$ on its partner. The strands run in opposite directions, so they are antiparallel as well as complementary.

Step 2: List the products of complete DNA hydrolysis Complete hydrolysis releases the pentose sugar **2-deoxy-D-ribose**, **phosphoric acid**, H_3PO_4, and the nitrogenous bases **adenine, guanine, cytosine and thymine**. Hydrolysis of the sugar-phosphate backbone releases the phosphate component, while cleavage of the sugar-base bonds releases the bases. The sugar is deoxyribose rather than ribose, and the pyrimidine base characteristic of DNA here is thymine rather than uracil. These distinctions identify the hydrolysis products specifically as those of DNA.

Step 3: Conclusion The DNA strands are complementary because A pairs specifically with T and G with C; therefore one strand determines the other. Complete hydrolysis gives **2-deoxy-D-ribose, phosphoric acid, adenine, guanine, cytosine and thymine**.

Quick Tip to Solve: Replace A with T and G with C when finding the partner strand; for complete hydrolysis, list sugar, phosphate and all four bases, remembering deoxyribose and thymine for DNA.

Section C (21 marks)

22. 0.3 g of acetic acid (Molar mass = 60 g mol^{-1}) dissolved in 30 g of benzene shows a depression in freezing point equal to 0.45°C. Calculate the percentage association of acid if it forms a dimer in the solution.

(Given: K_f for benzene = 5.12 K kg mol^{-1}) [3 marks]

Solution:

Concept:

- Freezing-point depression is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f is the solvent's molal depression constant and m is the molality calculated before association.
- Association reduces the number of solute particles. For dimer formation, $2\mathrm{CH_3COOH} \rightleftharpoons (\mathrm{CH_3COOH})_2$, the fraction associated α obeys $i = 1 - \alpha/2$.

Step 1: Calculate the molality before association The amount of acetic acid is $n = 0.3/60 = 0.005$ mol, and the mass of benzene is $30\text{ g} = 0.030$ kg. Hence,

$$m = \frac{0.005}{0.030} = \frac{1}{6}\text{ mol kg}^{-1}.$$

If the acid remained entirely monomeric, its freezing-point depression would be

$$(\Delta T_f)_{\text{normal}} = K_f m = 5.12 \times \frac{1}{6} = 0.8533\text{ K}.$$

A temperature interval of $0.45\,^\circ$C equals 0.45 K.

Step 2: Find the particle-number reduction The observed depression is smaller because some acid molecules form dimers. Thus,

$$i = \frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{normal}}} = \frac{0.45}{5.12/6} = 0.52734.$$

Starting with one mole of acid, association of a fraction α leaves $1 - \alpha$ mole of monomers and creates $\alpha/2$ mole of dimers. The total number of solute particles therefore becomes $1 - \alpha/2$ times the initial number.

Step 3: Calculate the percentage association Substituting the calculated factor into the dimer relation gives

$$0.52734 = 1 - \frac{\alpha}{2},$$

$$\alpha = 2(1 - 0.52734) = 0.94531,$$

$$\text{Percentage association} = 0.94531 \times 100 = 94.531\%.$$

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

Step 4: Conclusion Approximately $\boxed{94.5\%}$ of the acetic acid is associated into dimers in benzene.

Quick Tip to Solve: For dimers, calculate $i = \Delta T_f/(K_f m)$ first and use percentage association $= 200(1 - i)$; convert solvent grams to kilograms.

23(a). Write the name of the cell which is generally used in inverters. Write the reactions taking place at anode and cathode of this cell, when it is in use. [3 marks]

Solution:

Concept:

- A lead storage battery is a rechargeable secondary cell commonly used in inverters. During discharge it acts as a galvanic cell: oxidation occurs at the anode and reduction occurs at the cathode.
- Its active electrode materials are lead Pb and lead dioxide $\mathrm{PbO_2}$, with aqueous sulphuric acid as electrolyte. Both electrodes form lead sulphate $\mathrm{PbSO_4}$ on discharge.

Step 1: Identify the cell and its operating mode The cell generally used in inverters is the lead storage cell, also called the lead-acid cell. A battery consists of several such cells connected together. The phrase "when it is in use" refers to discharge: stored chemical energy supplies electrical energy to the inverter. Lead is the negative electrode (anode), while lead dioxide is the positive electrode (cathode).

Step 2: Write oxidation at the anode Lead changes from oxidation state 0 to $+2$, releasing two electrons. Sulphate ions combine with the oxidised lead to form lead sulphate:

$$\mathrm{Pb(s) + SO_4^{2-}(aq) \longrightarrow PbSO_4(s) + 2e^-}.$$

The charge on each side is -2, and one lead atom and one sulphate group occur on each side. Electrons flow from this electrode through the external circuit.

Step 3: Write reduction at the cathode Lead in $\mathrm{PbO_2}$ changes from $+4$ to $+2$, accepting two electrons. In the acidic electrolyte,

$$\mathrm{PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(l)}.$$

Adding the two half-reactions cancels the electrons and gives

$$\mathrm{Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)}.$$

Sulphuric acid is consumed during discharge, so the electrolyte concentration decreases. Charging reverses the net reaction.

Step 4: Conclusion The cell is the $\boxed{\text{lead storage (lead-acid) cell}}$. On discharge, Pb is oxidised at the anode and $\mathrm{PbO_2}$ is reduced at the cathode, producing $\mathrm{PbSO_4}$ at both electrodes as shown above.

Quick Tip to Solve: For a lead storage cell in use, remember that both electrodes become $\mathrm{PbSO_4}$; write oxidation of Pb first and balance the cathode in acid.

OR

23(b). Explain why electrolysis of an aqueous solution of NaCl gives H_2 gas at cathode and Cl_2 gas at anode? Write overall reaction.

(Given: $E^\circ_{Na^+/Na}$ = -2.71 V, $E^\circ_{H_2O/H_2}$ = -0.83 V, $E^\circ_{Cl_2/2Cl^-}$ = +1.36 V, $E^\circ_{H^+/O_2/H_2O}$ = +1.23 V) [3 marks]

Solution:

Concept:

- At the cathode, reduction occurs; the species with the more favourable reduction potential is preferentially discharged. Water can supply hydrogen in an aqueous electrolyte.
- At the anode, oxidation occurs. Actual discharge depends on the electrode potential and the overpotential, the extra potential needed for an electrode reaction to proceed at an appreciable rate.

Step 1: Compare the competing cathode reactions The possible reductions are

$$\begin{aligned} \mathrm{Na^+ + e^- \longrightarrow Na}, &\qquad E^\circ = -2.71\,\mathrm{V}, \\ \mathrm{2H_2O + 2e^- \longrightarrow H_2 + 2OH^-}, &\qquad E^\circ = -0.83\,\mathrm{V}. \end{aligned}$$

Reduction of water has the higher (less negative) reduction potential and is easier than reduction of sodium ions. Hence water is reduced at the cathode, liberating hydrogen gas and leaving hydroxide ions in solution; sodium metal is not deposited.

Step 2: Explain chlorine formation at the anode Chloride ions and water can both undergo oxidation:

$$\begin{aligned} \mathrm{2Cl^- \longrightarrow Cl_2 + 2e^-}, \\ \mathrm{2H_2O \longrightarrow O_2 + 4H^+ + 4e^-}. \end{aligned}$$

The given standard reduction potentials are $+1.36\,\mathrm{V}$ for $\mathrm{Cl_2/2Cl^-}$ and $+1.23\,\mathrm{V}$ for the oxygen/water couple. These values alone suggest that water oxidation should occur more readily. However, oxygen evolution has a substantial overpotential. Consequently, chloride oxidation occurs preferentially and chlorine gas is released.

Step 3: Add the half-reactions Combining the water-reduction equation with chloride oxidation cancels two electrons:

$$\mathrm{2H_2O(l) + 2Cl^-(aq) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)}.$$

Sodium ions remain in solution and accompany the hydroxide ions. Including them gives the overall molecular equation

$$\mathrm{2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g) + Cl_2(g)}.$$

Step 4: Conclusion Water reduction produces H_2 at the cathode; oxygen overpotential favours Cl_2 at the anode. Overall: $\mathrm{2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2}$.

Quick Tip to Solve: Compare reduction potentials at the cathode, but include oxygen overpotential at the anode; add half-reactions only after cancelling electrons.

24. The following data were obtained during the first order thermal decomposition of $N_2O_5(g)$ at constant volume:

$$2\,N_2O_5(g) \longrightarrow 2\,N_2O_4(g) + O_2(g)$$

Calculate rate constant.

[Given: $\log 2 = 0.3010,\ \log 10 = 1$**]** [3 marks]

S.No.	Time/s	Total Pressure/atm
1	0	0·5
2	100	0·625

Solution:

Concept:

- At constant volume and temperature, each gas's partial pressure is proportional to its amount. The total pressure is the sum of all partial pressures.
- For $2\,N_2O_5 \longrightarrow 2\,N_2O_4 + O_2$, consumption of reactant pressure x produces product pressures x and $x/2$.
- A first order reaction obeys $k = (2.303/t)\log(P_0/P_A)$, where P_0 and P_A are initial and remaining reactant pressures, and t is elapsed time.

Step 1: Express the total pressure using stoichiometry Initially only N_2O_5 is present, so its initial pressure is $P_0 = 0.500$ atm. Let x atm of this reactant have decomposed by $t = 100$ s. The remaining reactant pressure is $P_0 - x$, while the pressures of N_2O_4 and O_2 are x and $x/2$, respectively. Hence,

$$P_t = (P_0 - x) + x + \frac{x}{2} = P_0 + \frac{x}{2}.$$

The increase in total pressure therefore measures half the reactant pressure consumed, rather than the remaining reactant pressure.

Step 2: Calculate the remaining reactant pressure At 100 s, $P_t = 0.625$ atm. Thus,

$$x = 2(P_t - P_0) = 2(0.625 - 0.500) = 0.250\,\text{atm}.$$

$$P_A = P_0 - x = 0.500 - 0.250 = 0.250\,\text{atm}.$$

The reactant pressure has fallen to exactly half its initial value. Using the measured total pressure directly in the rate equation would be incorrect because it includes both gaseous products.

Step 3: Apply the integrated first order rate equation Substitute the reactant pressures and the supplied logarithm:

$$k = \frac{2.303}{100}\log\frac{0.500}{0.250} = \frac{2.303 \times 0.3010}{100} = 6.93203 \times 10^{-3}\,\text{s}^{-1}.$$

As a check, half the reactant decomposes in 100 s, so $k = 0.693/t_{1/2}$ gives the same value. The time is in seconds, which fixes the unit of the first order rate constant.

Quick Tip to Solve: For this decomposition, first find $P_A = 3P_0 - 2P_t$; use reactant partial pressure, not total pressure, in the first order formula.

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

Quick Tip to Solve: For this decomposition, first find $P_A = 3P_0 - 2P_t$; use reactant partial pressure, not total pressure, in the first order formula.

25. A compound (A) with molecular formula C_4H_9I which is a primary alkyl halide, reacts with alcoholic KOH to give compound (B). Compound (B) reacts with HI to give (C) which is an isomer of (A). When (A) reacts with Na metal in the presence of dry ether, it gives a compound (D), C_8H_{18}, which is different from the compound formed when n-butyl iodide reacts with sodium. Write the structures of (A), (B), (C) and (D). Write the chemical equation when compound (A) is reacted with alcoholic KOH. [3 marks]

Solution:

Concept:

- Alcoholic KOH removes a beta hydrogen and the halogen from adjacent carbon atoms of an alkyl halide, forming an alkene by dehydrohalogenation.
- Addition of HI to an unsymmetrical alkene follows Markovnikov's rule: hydrogen goes to the double-bond carbon having more hydrogens.
- In the Wurtz reaction, $2\,\text{RI} + 2\,\text{Na} \longrightarrow \text{R}{-}\text{R} + 2\,\text{NaI}$ in dry ether couples two identical alkyl groups without changing each group's carbon skeleton.

Step 1: Identify the primary alkyl iodide A The primary iodides with formula C_4H_9I are n-butyl iodide, $CH_3CH_2CH_2CH_2I$, and isobutyl iodide, $(CH_3)_2CHCH_2I$. The Wurtz product is stated to differ from the product obtained from n-butyl iodide, which is n-octane. Thus A must be the branched primary iodide:

$$\text{A}: \quad CH_3{-}CH(CH_3){-}CH_2I.$$

Its name is 1-iodo-2-methylpropane. The carbon bonded to iodine is a CH_2 carbon joined to just one other carbon, confirming that A is primary.

Step 2: Eliminate HI to obtain B and then add HI to obtain C The beta hydrogen on the adjacent CH group is removed with iodine from the CH_2I group. The required balanced equation is

$$(CH_3)_2CHCH_2I + KOH \xrightarrow[\text{heat}]{\text{alcohol}} (CH_3)_2C{=}CH_2 + KI + H_2O.$$

Therefore B is 2-methylpropene, $CH_2{=}C(CH_3)_2$. In its reaction with HI, hydrogen adds to the terminal CH_2 carbon and iodine to the more substituted carbon:

$$CH_2{=}C(CH_3)_2 + HI \longrightarrow (CH_3)_3CI.$$

Hence C is 2-iodo-2-methylpropane, a tertiary iodide with the same molecular formula as A, as required.

Step 3: Couple two molecules of A to obtain D Sodium removes the iodines and couples the two

Quick Tip to Solve: Use the Wurtz clue first: excluding n-octane selects isobutyl iodide; connect its two CH_2I carbons to get D.

carbons that originally carried iodine:

$$2\,(CH_3)_2CHCH_2I + 2\,Na \xrightarrow{\text{dry ether}} (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2\,NaI.$$

Thus D has the condensed structure $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$, named 2,5-dimethylhexane. It contains eight carbon atoms and has formula C_8H_{18}, but is branched and therefore differs from n-octane.

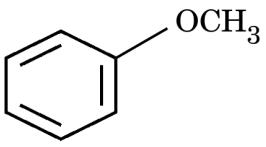
Step 4: Conclusion The required structures are

$$\begin{aligned} &\text{A}: \quad (CH_3)_2CHCH_2I, \\ &\text{B}: \quad CH_2{=}C(CH_3)_2, \\ &\text{C}: \quad (CH_3)_3CI, \\ &\text{D}: \quad CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3. \end{aligned}$$

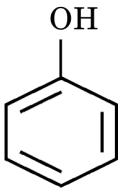
The alcoholic-KOH elimination equation for A is given in Step 2.

Quick Tip to Solve: Use the Wurtz clue first: excluding n-octane selects isobutyl iodide; connect its two CH_2I carbons to get D.

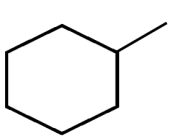
26. Write structure of the products of the following reactions: [3 marks]

(a) 

$+\,HI \longrightarrow$

(b) 

$+$ conc. $HNO_3 \longrightarrow$

(c) 

$+\,HCHO \xrightarrow{H^+/H_2O}$

Solution:

Concept:

- In cleavage of an aryl methyl ether by HI, iodide attacks the methyl carbon. The aryl–oxygen bond is retained, producing a phenol and methyl iodide.
- The $-OH$ group activates the benzene ring towards electrophilic substitution at the ortho and para positions; concentrated nitric acid gives extensive nitration.

Quick Tip to Solve: Break anisole at its methyl–oxygen bond; for formaldehyde plus a Grignard reagent, append $-CH_2OH$ to the reagent's alkyl group.

- A Grignard reagent RMgBr adds its R group to formaldehyde. Acidic hydrolysis of the resulting alkoxide gives the primary alcohol $\mathrm{RCH_2OH}$, with one additional carbon.

Step 1: Cleave anisole in reaction (a) The ether is $\mathrm{C_6H_5{-}O{-}CH_3}$. Protonation of oxygen allows iodide to attack the methyl group by an S_N2 mechanism. The carbon attached to oxygen in the benzene ring is sp^2-hybridised and does not undergo this displacement. Hence the products have structures

$$\mathrm{C_6H_5{-}OH} \quad \text{and} \quad \mathrm{CH_3{-}I}.$$

The balanced reaction is

$$\mathrm{C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I}.$$

These products are phenol and iodomethane, respectively; iodobenzene and methanol are not the products of this cleavage.

Step 2: Nitrate phenol in reaction (b) With concentrated $\mathrm{HNO_3}$, nitro groups replace the ring hydrogens at both ortho positions and the para position relative to $-\mathrm{OH}$. Taking the carbon bearing $-\mathrm{OH}$ as position 1, the product structure is a benzene ring bearing $-\mathrm{NO_2}$ at positions 2, 4 and 6:

$$\mathrm{HO{-}C_6H_2(NO_2)_3} \quad (\text{nitro groups at } 2, 4, 6).$$

This is 2,4,6-trinitrophenol, commonly called picric acid.

$$\mathrm{C_6H_5OH + 3\,HNO_3 \longrightarrow C_6H_2(NO_2)_3OH + 3\,H_2O}.$$

Concentrated acid gives the trinitro product, rather than just the mononitrophenol mixture associated with dilute nitric acid.

Step 3: Add the cyclohexyl group to formaldehyde in reaction (c) The reagent is cyclohexylmagnesium bromide, $\mathrm{C_6H_{11}MgBr}$. Its cyclohexyl group forms a carbon–carbon bond with the carbonyl carbon of HCHO:

$$\mathrm{C_6H_{11}MgBr + HCHO \longrightarrow C_6H_{11}CH_2OMgBr}.$$

Acidic hydrolysis protonates the oxygen:

$$\mathrm{C_6H_{11}CH_2OMgBr + H_2O \longrightarrow C_6H_{11}CH_2OH + Mg(OH)Br}.$$

The organic product is cyclohexylmethanol: a saturated six-membered carbon ring carrying a $-\mathrm{CH_2{-}OH}$ substituent, condensed as $\mathrm{C_6H_{11}{-}CH_2{-}OH}$. The hydroxyl group is on the added carbon, so the product is a primary alcohol, rather than cyclohexanol.

Step 4: Conclusion (a) $\mathrm{C_6H_5OH + CH_3I}$; (b) $\mathrm{HO{-}C_6H_2(NO_2)_3}$, with $\mathrm{NO_2}$ at positions 2, 4 and 6; (c) $\mathrm{C_6H_{11}{-}CH_2{-}OH}$, cyclohexylmethanol.

Quick Tip to Solve: Break anisole at its methyl–oxygen bond; for formaldehyde plus a Grignard reagent, append $-\mathrm{CH_2OH}$ to the reagent's alkyl group.

27. Give reasons for the following:

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

(b) HCHO is more reactive than CH_3CHO towards addition of HCN.

(c) Vinyl group directly attached with carboxylic acid should decrease the acidity of corresponding carboxylic acid due to resonance, but on the contrary it increases the acidity. [3 marks]

Solution:

Concept:

- Electrophilic aromatic substitution is favoured by an electron-rich benzene ring; an electron-withdrawing substituent deactivates it.
- Nucleophilic addition to a carbonyl depends on the positive character of the carbonyl carbon and on steric hindrance around it.
- A carboxylic acid is stronger when its conjugate carboxylate ion is stabilised. Inductive and resonance effects must be considered together.

Step 1: (a) Examine the effect of the carboxyl group The $-\mathrm{COOH}$ group withdraws electrons from the benzene ring through both its negative inductive ($-I$) and negative resonance ($-R$) effects. Consequently, the ring of benzoic acid is strongly deactivated towards electrophilic substitution and does not undergo Friedel–Crafts alkylation or acylation. In addition, the carboxyl group can interact with the Lewis acid catalyst, $\mathrm{AlCl_3}$, further hindering the reaction.

Step 2: (b) Compare the two carbonyl compounds In $\mathrm{CH_3CHO}$, the methyl group donates electron density by its $+I$ effect, reducing the positive character of the carbonyl carbon. It also provides greater steric hindrance than hydrogen. In HCHO, there is no electron-donating alkyl group and the carbonyl carbon is less crowded. Thus, attack by the nucleophile $\mathrm{CN^-}$, followed by protonation to form a cyanohydrin, is easier for formaldehyde.

Step 3: (c) Compare the opposing effects of a vinyl group A vinyl group contains sp^2-hybridised carbon, which is more electronegative than sp^3-hybridised carbon. Its electron-withdrawing $-I$ effect stabilises the corresponding carboxylate ion. Although conjugation can donate electron density towards the carboxyl group and would oppose acidity, the withdrawing inductive effect predominates here. Hence, the net effect of the directly attached vinyl group is to increase acidity, as in acrylic acid relative to the corresponding saturated acid.

Step 4: Conclusion Benzoic acid fails to undergo Friedel–Crafts reaction because its ring is strongly deactivated; HCHO adds HCN more readily because it has greater electrophilicity and less steric hindrance; the vinyl group increases acidity because its $-I$ effect predominates over the opposing resonance effect.

Quick Tip to Solve: For these comparisons, check ring electron density, carbonyl crowding, and conjugate-base stability separately.

28. Write the reaction of D-Glucose with the following:

(a) HCN

(b) Br_2 water

(c) $(CH_3CO)_2O$ [3 marks]

Solution:

Concept:

- The open-chain form of D-glucose is $CHO - (CHOH)_4 - CH_2OH$; it contains an aldehyde group and five hydroxyl groups.
- HCN adds across a carbonyl group to form a cyanohydrin. Bromine water is a mild oxidising agent that converts an aldehyde to a carboxylic acid.
- Acetic anhydride acetylates each hydroxyl group, replacing its hydrogen by $COCH_3$, to form an acetate ester.

Step 1: (a) Reaction with HCN The aldehyde group undergoes nucleophilic addition: cyanide attacks its carbonyl carbon and the oxygen is then protonated. D-glucose forms glucose cyanohydrin:

$$\begin{aligned} &CHO - (CHOH)_4 - CH_2OH + HCN \\ &\quad \longrightarrow HO - CH(CN) - (CHOH)_4 - CH_2OH. \end{aligned}$$

The carbonyl carbon acquires both $-OH$ and $-CN$. This reaction demonstrates the presence of the carbonyl group in the open-chain form.

Step 2: (b) Reaction with bromine water Bromine water oxidises the terminal aldehyde group to a carboxylic acid, yielding D-gluconic acid. The primary alcohol group at the other end remains unchanged under these mild conditions:

$$\begin{aligned} &CHO - (CHOH)_4 - CH_2OH + Br_2 + H_2O \\ &\quad \longrightarrow COOH - (CHOH)_4 - CH_2OH + 2HBr. \end{aligned}$$

Only the aldehyde end is oxidised; this is not the oxidation of both terminal groups by a stronger oxidising agent.

Step 3: (c) Reaction with acetic anhydride All five hydroxyl groups are acetylated to produce glucose pentaacetate. Writing cyclic glucose as $C_6H_7O(OH)_5$, where the oxygen outside the parentheses is the ring oxygen, the balanced reaction is

$$\begin{aligned} &C_6H_7O(OH)_5 + 5(CH_3CO)_2O \\ &\quad \longrightarrow C_6H_7O(OCOCH_3)_5 + 5CH_3COOH. \end{aligned}$$

Each $-OH$ becomes $-OCOCH_3$; formation of the pentaacetate establishes the presence of five hydroxyl groups in glucose.

Step 4: Conclusion D-glucose forms glucose cyanohydrin with HCN, D-gluconic acid with bromine water, and glucose pentaacetate with acetic anhydride. The corresponding balanced reactions are given above.

Quick Tip to Solve: Track the functional group: HCN adds to CHO, bromine water oxidises CHO, and acetic anhydride acetylates all five OH groups.

Section D (8 marks)

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

29(a). The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields. In tetrahedral coordination entity formation, the d-orbital splitting is smaller as compared to the octahedral entity.

Answer the following questions:

On the basis of CFT, explain why $[Ti(H_2O)_6]Cl_3$ complex is coloured? What happens on heating the complex $[Ti(H_2O)_6]Cl_3$? Give reason.

[Atomic no.: Ti = 22] [2 marks]

Solution:

Concept:

- In an octahedral ligand field, the five degenerate d orbitals split into a lower-energy t_{2g} set and a higher-energy e_g set, separated by Δ_o.
- A d–d transition absorbs light whose photon energy is $h\nu = \Delta_o$; the observed colour is complementary to the absorbed light.

Step 1: Explain the colour using the electronic configuration Water is a neutral ligand and the three chloride counterions each have charge -1, so titanium is in the $+3$ oxidation state. For atomic number 22,

$$\mathrm{Ti} : [\mathrm{Ar}]\,3d^2 4s^2, \qquad \mathrm{Ti}^{3+} : [\mathrm{Ar}]\,3d^1.$$

The six water ligands create an octahedral crystal field. The single d electron occupies a t_{2g} orbital and can absorb visible light to move into an e_g orbital. This selective absorption causes the complex to appear violet; it does not require a change in the oxidation state of titanium.

Step 2: Explain the effect of heating On heating, the coordinated water molecules are removed and the complex becomes colourless. In the CFT explanation, removal of these water ligands removes their octahedral crystal field and hence the splitting responsible for the visible d–d absorption. Thus, the transition that gave the hydrated complex its violet colour is no longer available in that ligand field.

Step 3: Conclusion $[Ti(H_2O)_6]Cl_3$ is violet because Ti^{3+} has a d^1 configuration and undergoes a visible-light $t_{2g} \rightarrow e_g$ transition. Heating removes coordinated water, so the complex becomes colourless.

Quick Tip to Solve: First obtain Ti(III) from the three chloride counterions; then use its single d electron to explain the absorption.

29(b). What is crystal field splitting energy? [1 mark]

Solution:

Concept:

- For an isolated metal ion, the five d orbitals are degenerate: they have the same energy.
- Ligand approach produces unequal electrostatic repulsions and separates the d orbitals into sets of different energies.

Step 1: Identify the separation of orbital energies In an octahedral coordination entity, the ligand field splits the d orbitals into lower-energy t_{2g} orbitals and higher-energy e_g orbitals. Their energy difference is denoted by Δ_o.

Step 2: State what the splitting energy measures Crystal field splitting energy is the energy difference between the sets of d orbitals produced by the ligand field. For the octahedral case,

$$\Delta_o = E(e_g) - E(t_{2g}).$$

It measures the gap between the two sets, rather than the energy required to pair two electrons in one orbital.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the two sets of d orbitals formed on splitting in a ligand field; in an octahedral complex it is Δ_o.

Quick Tip to Solve: Define the gap between the split orbital sets; do not confuse splitting energy with pairing energy P.

OR

29(b). On the basis of Δ_o and P (pairing energy), how can you differentiate between a strong field ligand and a weak field ligand? [1 mark]

Solution:

Concept:

- Δ_o is the energy difference between the lower t_{2g} and upper e_g orbitals in an octahedral field.
- P is the pairing energy required to put two electrons in the same orbital.

Step 1: Compare the two energy costs A strong field ligand produces a large splitting such that $\Delta_o > P$. Pairing in the lower-energy orbitals is then energetically preferred to occupying the upper set.

Step 2: Apply the opposite inequality A weak field ligand produces a small splitting such that $\Delta_o < P$. Occupation of the higher-energy orbitals is then preferred before additional pairing, giving a high-spin arrangement where a spin-state choice exists.

Step 3: Conclusion Strong field: $\boxed{\Delta_o > P}$; weak field: $\boxed{\Delta_o < P}$. Strong fields favour pairing and low spin; weak fields favour unpaired electrons and high spin.

Quick Tip to Solve: Compare the energy of promotion with the energy of pairing: choose the cheaper process.

29(c). Why are low spin tetrahedral complexes rarely observed? [1 mark]

Solution:

Concept:

- In a tetrahedral field, the e orbitals are lower in energy and the t_2 orbitals are higher.
- For comparable metal ions and ligands, $\Delta_t \approx \frac{4}{9}\Delta_o$, so tetrahedral splitting is relatively small.

Step 1: Compare splitting with pairing energy The tetrahedral splitting energy Δ_t is usually less than the electron-pairing energy P. It therefore costs less energy to occupy an available higher-energy orbital than to pair electrons in a lower-energy orbital.

Step 2: Deduce the spin arrangement Electrons consequently occupy the orbitals singly as far as possible before pairing. Tetrahedral complexes therefore normally have a high-spin configuration; the large splitting needed to stabilise a low-spin configuration is seldom attained.

Step 3: Conclusion Low-spin tetrahedral complexes are rarely observed because $\boxed{\Delta_t < P}$ in almost all cases, making promotion more favourable than pairing.

Quick Tip to Solve: For tetrahedral complexes, start with the small splitting, then compare it with pairing energy.

30(a). Amines are usually formed from amides, imides, halides, nitro compounds, etc. They exhibit hydrogen bonding which influences their physical properties. In alkyl amines, a combination of electron releasing, steric and H-bonding factors influence the stability of the substituted ammonium cations in protic polar solvents and thus affect the basic nature of amines. Alkyl amines are found to be stronger bases than ammonia. Amines being basic in nature, react with acids to form salts. Aryldiazonium salts, undergo replacement of the diazonium group with a variety of nucleophiles to produce aryl halides, cyanides, phenols and arenes.

Answer the following questions:

How can you convert the following?

(i) Ethanoic acid to methanamine

(ii) Propanenitrile to 1-aminopropane [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine containing one carbon atom fewer.
- Reduction of a nitrile converts $-\mathrm{C} \equiv \mathrm{N}$ into $-\mathrm{CH_2NH_2}$, retaining its carbon atom.

Step 1: (i) Prepare ethanamide from ethanoic acid Treat ethanoic acid with ammonia to form ammonium ethanoate and heat the salt to obtain ethanamide:

$$\mathrm{CH_3COOH + NH_3 \longrightarrow CH_3COO^-NH_4^+}$$

$$\mathrm{CH_3COO^-NH_4^+ \xrightarrow{\Delta} CH_3CONH_2 + H_2O.}$$

Quick Tip to Solve: Count carbons first: Hofmann degradation removes one carbon, whereas nitrile reduction retains all carbons.

Step 2: (i) Carry out Hofmann bromamide degradation Heat ethanamide with bromine and aqueous sodium hydroxide:

$$CH_3CONH_2 + Br_2 + 4NaOH$$

$$\longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is removed, giving methanamine with one carbon atom.

Step 3: (ii) Reduce propanenitrile Use $LiAlH_4$ in dry ether, followed by hydrolysis:

$$CH_3CH_2C \equiv N \xrightarrow[2.\ H_2O]{1.\ LiAlH_4/\text{ether}} CH_3CH_2CH_2NH_2.$$

The nitrile carbon becomes the terminal CH_2 carbon, so the product is 1-aminopropane with the original three-carbon chain retained.

Step 4: Conclusion (i) Ethanoic acid $\rightarrow$ ethanamide $\xrightarrow{Br_2/NaOH}$ methanamine. (ii) Propanenitrile $\xrightarrow{LiAlH_4,\ H_2O}$ 1-aminopropane.

Quick Tip to Solve: Count carbons first: Hofmann degradation removes one carbon, whereas nitrile reduction retains all carbons.

30(b). Why is pK_b value of aniline more than that of methylamine? [1 mark]

Solution:

Concept:

- $pK_b = -\log_{10} K_b$: a smaller base-dissociation constant means a larger pK_b.
- Basic strength depends on the availability of the nitrogen lone pair for bonding to a proton.

Step 1: Compare the nitrogen lone pairs In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available to accept H^+. In methylamine, the lone pair remains localised on nitrogen.

Step 2: Relate electron donation to base strength The methyl group has a positive inductive effect, increasing electron density on nitrogen and favouring proton acceptance. Methylamine is thus more basic than aniline and has a larger K_b. The negative logarithm reverses this comparison for pK_b.

Step 3: Conclusion $\boxed{pK_b(\text{aniline}) > pK_b(\text{methylamine})}$, because resonance lowers the basicity of aniline while the methyl group increases the basicity of methylamine.

Quick Tip to Solve: First compare lone-pair availability; then reverse the basicity order when writing the pKb order.

30(c). Arrange the following in increasing order of their basic strength in aqueous solution:
CH_3-NH_2, $(CH_3)_2NH$, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- In water, amine basicity depends on both electron donation by alkyl groups and hydration of the conjugate ammonium ion.
- For methylamines, hydration and steric effects modify the order expected from the positive inductive effect alone.

Step 1: Compare primary and secondary methylamines Two methyl groups donate more electron density to nitrogen than one, and the dimethylammonium ion still undergoes effective hydration. Dimethylamine is therefore more basic than methylamine in aqueous solution.

Step 2: Account for the tertiary amine Although three methyl groups increase electron donation, they hinder hydration of the trimethylammonium ion. Its poorer stabilisation by water outweighs that advantage, making trimethylamine less basic than methylamine. Considering electron donation alone would give the wrong aqueous order.

Step 3: Conclusion The increasing order is

$$\boxed{(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH}.$$

Quick Tip to Solve: For methylamines in water, remember tertiary < primary < secondary because hydration changes the inductive order.

OR

30(c). Give the structures of A and B in the following reaction:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{HNO_2} B.$$

[1 mark]

Solution:

Concept:

- Iron and hydrochloric acid reduce an aromatic nitro group to an amino group without changing the benzene ring.
- Aniline undergoes diazotisation with nitrous acid in hydrochloric acid at 273–278 K, forming benzenediazonium chloride.

Step 1: Identify A by nitro-group reduction The starting compound is nitrobenzene. Reduction with Fe/HCl changes $-NO_2$ into $-NH_2$, so A is aniline, structurally $C_6H_5 - NH_2$. The phenyl group remains unchanged.

Step 2: Identify B by diazotisation At 273 K, nitrous acid reacts with the primary aromatic amino

Quick Tip to Solve: Fe/HCl reduces NO2 to NH2; cold nitrous acid converts an aromatic NH2 group into a diazonium salt.

group in the acidic chloride medium:

$$C_6H_5NH_2 + HNO_2 + HCl$$

$$\longrightarrow [C_6H_5 - N \equiv N]^+Cl^- + 2H_2O.$$

Thus B contains a phenyl group bonded to the positively charged diazonium group, with chloride as counterion.

Step 3: Conclusion $\boxed{A = C_6H_5 - NH_2}$ (aniline); $\boxed{B = [C_6H_5 - N \equiv N]^+Cl^-}$ (benzenediazonium chloride).

Quick Tip to Solve: Fe/HCl reduces NO2 to NH2; cold nitrous acid converts an aromatic NH2 group into a diazonium salt.

Section E (15 marks)

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

(I) The $E^\circ_{Mn^{2+}/Mn}$ value for manganese is highly negative, whereas $E^\circ_{Mn^{3+}/Mn^{2+}}$ is highly positive.

(II) Actinoids show wide range of oxidation states.

(III) Transition metals have high melting points.

(ii) Complete the following ionic equations:

(I) $5SO_3^{2-} + 2MnO_4^- + 6H^+ \rightarrow$

(II) $2MnO_4^- + H_2O + I^- \rightarrow$ [5 marks]

Solution:

Concept:

- A half-filled d^5 subshell has extra stability. Electrode potentials reflect the relative stability of the species involved in reduction.
- Similar energies of the $5f$, $6d$ and $7s$ orbitals allow actinoids to use different numbers of electrons in bonding.
- Strong metallic bonding involving ns and $(n-1)d$ electrons accounts for the generally high melting points of transition metals.
- Balance redox equations by equating electrons lost and gained. Permanganate gives Mn^{2+} in acidic medium and MnO_2 in neutral or weakly alkaline medium.

Step 1: (i)(I) Relate manganese potentials to the stable configuration Manganese has configuration $[Ar]\,3d^5 4s^2$, while Mn^{2+} has $[Ar]\,3d^5$. This half-filled subshell is especially stable. The reduction $Mn^{2+} + 2\,e^- \longrightarrow Mn$ is therefore relatively unfavourable: it converts a particularly stable ion into the metal. Thus $E^\circ_{Mn^{2+}/Mn}$ is highly negative.

In contrast, Mn^{3+} has configuration $[Ar]\,3d^4$. Reduction by one electron gives the stable half-filled $3d^5$ configuration:

$$Mn^{3+} + e^- \longrightarrow Mn^{2+}.$$

Quick Tip to Solve: For permanganate equations, first identify the medium: acid gives Mn^{2+}, while water without added acid here gives MnO_2. Then match electron changes before balancing hydrogen, oxygen and charge.

This reduction is favourable, so $E^{\circ}_{Mn^{3+}/Mn^{2+}}$ is highly positive.

Step 2: (i)(II) Explain the oxidation states of actinoids In actinoids, the $5f$, $6d$ and $7s$ subshells have comparable energies. Hence electrons from these subshells can participate in bonding or be removed, in varying numbers. This produces a wide range of oxidation states, especially among the earlier actinoids, where more of the $5f$ electrons are available for bonding.

Step 3: (i)(III) Explain the melting points of transition metals Transition metals generally contribute both ns and $(n-1)d$ electrons to metallic bonding. Participation of several valence electrons gives strong interatomic attraction and high enthalpies of atomisation. Considerable energy is consequently needed to disrupt the metallic lattice, leading to high melting points. The strength varies across a series with the number of electrons available for bonding.

Step 4: (ii)(I) Complete the acidic sulfite reaction Sulfur in SO_3^{2-} is oxidised from $+4$ to $+6$ in SO_4^{2-}, losing two electrons per sulfur atom. Manganese in MnO_4^- is reduced from $+7$ to $+2$, gaining five electrons per manganese atom. Thus five sulfite ions supply the ten electrons required by two permanganate ions. Balance oxygen and hydrogen using water and H^+:

$$5\,SO_3^{2-} + 2\,MnO_4^- + 6\,H^+ \longrightarrow 5\,SO_4^{2-} + 2\,Mn^{2+} + 3\,H_2O.$$

Both sides contain five sulfur atoms, two manganese atoms, twenty-three oxygen atoms and six hydrogen atoms. Each side has net charge -6.

Step 5: (ii)(II) Complete the iodide reaction in neutral medium With water present and no acid specified, permanganate is reduced to MnO_2. Iodide is oxidised from -1 to $+5$ in iodate, IO_3^-, releasing six electrons. Each permanganate ion gains three electrons, so two are required for each iodide ion. The half-reactions are

$$I^- + 6\,OH^- \longrightarrow IO_3^- + 3\,H_2O + 6\,e^-,$$
$$2\,MnO_4^- + 4\,H_2O + 6\,e^- \longrightarrow 2\,MnO_2 + 8\,OH^-.$$

Adding and cancelling gives

$$2\,MnO_4^- + H_2O + I^- \longrightarrow 2\,MnO_2 + IO_3^- + 2\,OH^-.$$

Oxygen, hydrogen and charge balance: each side has nine oxygen atoms, two hydrogen atoms and net charge -3.

Step 6: Conclusion (i) The stable half-filled $3d^5$ configuration of Mn^{2+} explains the two manganese potentials; comparable $5f$, $6d$ and $7s$ energies explain the actinoid oxidation states; strong metallic bonding explains the high melting points.

(ii) The completed products are (I) $5\,SO_4^{2-} + 2\,Mn^{2+} + 3\,H_2O$ and (II) $2\,MnO_2 + IO_3^- + 2\,OH^-$, with the printed reactant coefficients unchanged.

Quick Tip to Solve: For permanganate equations, first identify the medium: acid gives Mn^{2+}, while water without added acid here gives MnO_2. Then match electron changes before balancing hydrogen, oxygen and charge.

OR

31(b). Answer the following questions:

(i) Name two elements of 3d series for which the third ionisation enthalpies are quite high.

(ii) Out of $KMnO_4$ and K_2MnO_4, which one is paramagnetic and why?

(iii) Write any one consequence of lanthanoid contraction.

(iv) How do you prepare potassium manganate from pyrolusite ore?

(v) Why is the ability of oxygen more than fluorine to stabilise higher oxidation states of transition metals? [5 marks]

Solution:

Concept:

- The third ionisation enthalpy is the energy required for $M^{2+}(g) \rightarrow M^{3+}(g) + e^-$. Removing an electron from a stable half-filled or completely filled d subshell requires comparatively high energy.
- Unpaired electrons cause paramagnetism. The oxidation state of manganese determines the number of $3d$ electrons in its oxoanions.
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids because $4f$ electrons shield the nuclear charge poorly.
- An oxidising alkaline fusion converts MnO_2 to manganate. Oxygen can form multiple bonds with transition metals, helping stabilise their higher oxidation states.

Step 1: (i) Identify the elements with high third ionisation enthalpies Manganese and zinc have comparatively high third ionisation enthalpies. Their divalent ions have the configurations

$$Mn^{2+} : [Ar]\,3d^5, \qquad Zn^{2+} : [Ar]\,3d^{10}.$$

The $3d^5$ configuration is half-filled and the $3d^{10}$ configuration is completely filled. The third ionisation removes an electron from these particularly stable arrangements, so it requires relatively high energy.

Step 2: (ii) Compare the magnetic behaviour of permanganate and manganate In $KMnO_4$, the oxidation state of manganese is $+7$, since $+1 + x - 8 = 0$. Thus manganese has a $3d^0$ configuration with no unpaired electron, and permanganate is diamagnetic. In K_2MnO_4, $+2 + x - 8 = 0$ gives manganese the oxidation state $+6$. It has a $3d^1$ configuration, with one unpaired electron, making potassium manganate paramagnetic.

Step 3: (iii) State a consequence of lanthanoid contraction Zirconium and hafnium have nearly equal atomic radii and therefore very similar chemical properties. The lanthanoids occur before hafnium in the sixth period; contraction across this series largely offsets the expected size increase on going from zirconium to hafnium. Consequently, these two elements are difficult to separate.

Step 4: (iv) Prepare potassium manganate from pyrolusite Pyrolusite is MnO_2. Fuse it with potassium hydroxide in the presence of air or another oxidising agent. Oxygen oxidises manganese from $+4$ in the ore to $+6$ in the green potassium manganate:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O.$$

The reaction conserves all atoms and shows the strongly alkaline, oxidising conditions needed to

Quick Tip to Solve: For manganese oxoanions, find the oxidation state first: +7 gives d0 and +6 gives d1; for third ionisation, inspect the stable configuration of the divalent ion.

obtain manganate.

Step 5: (v) Explain why oxygen stabilises higher oxidation states better Oxygen can form multiple bonds with transition metals, whereas fluorine forms only single bonds. The strong metal–oxygen multiple bonding helps stabilise very high metal oxidation states. For example, manganese attains $+7$ in Mn_2O_7, while its highest fluoride, MnF_4, contains manganese in $+4$. Thus fluorine's high electronegativity alone does not make it as effective as oxygen in stabilising the highest oxidation states.

Step 6: Conclusion (i) Manganese and zinc. (ii) K_2MnO_4 is paramagnetic because it has one unpaired electron. (iii) Zr and Hf have nearly equal radii and similar properties. (iv) Oxidising fusion of MnO_2 with KOH yields K_2MnO_4. (v) Oxygen stabilises higher oxidation states through metal–oxygen multiple bonds.

Quick Tip to Solve: For manganese oxoanions, find the oxidation state first: $+7$ gives d0 and $+6$ gives d1; for third ionisation, inspect the stable configuration of the divalent ion.

32(a). (i) An organic compound (X) having molecular formula $C_5H_{10}O$ can show various properties depending on its structures. Draw each of the structures if it:

(I) shows Cannizzaro reaction.

(II) reduces Tollens' reagent and has a chiral carbon.

(III) gives positive iodoform test.

(ii) Write the reaction involved in the following:

(I) Clemmensen reduction

(II) Etard reaction [5 marks]

Solution:

Concept:

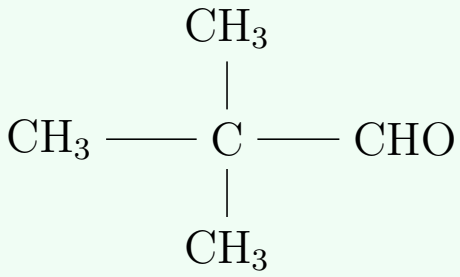
- Cannizzaro reaction is disproportionation of an aldehyde without any α-hydrogen in concentrated alkali. The α-carbon is the carbon immediately adjacent to the $-CHO$ group.
- Aldehydes reduce Tollens' reagent, producing silver. A chiral carbon is attached to four different groups.
- A methyl ketone, $CH_3CO\,R$, gives the iodoform test with $I_2/NaOH$, producing yellow CHI_3. Clemmensen reduction changes a carbonyl group into a methylene group, while Etard oxidation changes the side-chain methyl group of toluene into an aldehyde.

Step 1: (i)(I) Select an aldehyde without alpha-hydrogen The required structure is 2,2-dimethylpropanal, $(CH_3)_3CCHO$. Its α-carbon is bonded to three methyl groups and the aldehyde carbon, so it bears no hydrogen. It therefore undergoes Cannizzaro reaction:

$$2(CH_3)_3CCHO + NaOH \longrightarrow (CH_3)_3CCH_2OH + (CH_3)_3CCOONa.$$

One aldehyde molecule is reduced to an alcohol and the other is oxidised to a carboxylate salt. The structure contains five carbon atoms and ten hydrogen atoms, as required.

Quick Tip to Solve: For the three structures, check in order: no alpha-H beside CHO, four different groups on one carbon, and a CH3CO group; then count all five carbons.

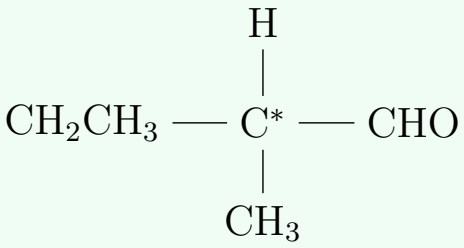


2,2-Dimethylpropanal: its alpha-carbon has no hydrogen.

Step 2: (i)(II) Select a chiral aldehyde The required compound is 2-methylbutanal:

$$CH_3CH_2CH(CH_3)CHO.$$

The aldehyde group reduces Tollens' reagent to metallic silver. The carbon indicated by an asterisk has four different substituents: $-H$, $-CH_3$, $-CH_2CH_3$ and $-CHO$; hence it is chiral. The molecular formula is again $C_5H_{10}O$. A ketone would not satisfy the Tollens condition, and an unbranched aldehyde would not supply the required chiral carbon.



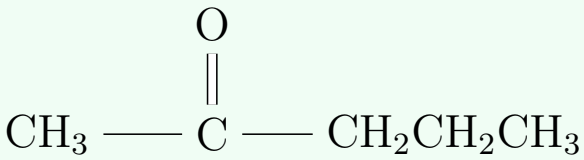
2-Methylbutanal: the asterisk identifies the chiral carbon.

Step 3: (i)(III) Select a methyl ketone Pentan-2-one, $CH_3COCH_2CH_2CH_3$, is a suitable structure. It contains the CH_3CO- group responsible for the positive iodoform test:

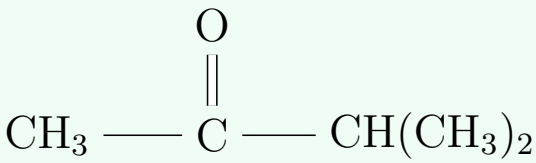
$$CH_3COCH_2CH_2CH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3 + CH_3CH_2CH_2COONa + 3NaI + 3H_2O.$$

Another acceptable isomer is 3-methylbutan-2-one, $CH_3COCH(CH_3)_2$; its structure is also shown. Both ketones have formula $C_5H_{10}O$ and the same diagnostic methyl-ketone group. Pentan-3-one lacks this group and does not give the test.

Quick Tip to Solve: For the three structures, check in order: no alpha-H beside CHO, four different groups on one carbon, and a CH3CO group; then count all five carbons.



Pentan-2-one



3-Methylbutan-2-one

Two methyl ketones that satisfy the formula and the iodoform test.

Step 4: (ii)(I) Write Clemmensen reduction Aldehydes and ketones are reduced with zinc amalgam, $\mathrm{Zn(Hg)}$, and concentrated hydrochloric acid. The carbonyl oxygen is removed and the carbonyl carbon becomes a saturated carbon:

$$\mathrm{RCHO} + 4[\mathrm{H}] \xrightarrow{\mathrm{Zn(Hg),\ conc.\ HCl}} \mathrm{RCH_3} + \mathrm{H_2O},$$
$$\mathrm{CH_3COCH_3} + 4[\mathrm{H}] \xrightarrow{\mathrm{Zn(Hg),\ conc.\ HCl}} \mathrm{CH_3CH_2CH_3} + \mathrm{H_2O}.$$

Here R denotes a hydrocarbon group and $[\mathrm{H}]$ denotes reducing hydrogen equivalents.

Step 5: (ii)(II) Write Etard reaction Toluene reacts with chromyl chloride, $\mathrm{CrO_2Cl_2}$, in carbon disulphide to form an Etard complex. Hydrolysis of the complex gives benzaldehyde:

$$\mathrm{C_6H_5CH_3} \xrightarrow[\mathrm{CS_2}]{\mathrm{CrO_2Cl_2}} \text{Etard complex} \xrightarrow{\mathrm{H_2O}} \mathrm{C_6H_5CHO}.$$

Thus the side-chain methyl group is oxidised to $-\mathrm{CHO}$, while the benzene ring remains intact; the product is benzaldehyde, rather than benzoic acid.

Step 6: Conclusion (i) The structures are (I) $(\mathrm{CH_3})_3\mathrm{CCHO}$, (II) $\mathrm{CH_3CH_2CH(CH_3)CHO}$, and (III) $\mathrm{CH_3COCH_2CH_2CH_3}$ (or $\mathrm{CH_3COCH(CH_3)_2}$). (ii) Clemmensen reduction converts $\mathrm{C{=}O}$ to $\mathrm{CH_2}$ using $\mathrm{Zn(Hg)}$, conc. HCl; Etard reaction converts toluene into benzaldehyde using chromyl chloride followed by hydrolysis.

Quick Tip to Solve: For the three structures, check in order: no alpha-H beside CHO, four different groups on one carbon, and a CH3CO group; then count all five carbons.

OR

Answer the following questions:

32(b)(i). Draw structure of the methyl hemiacetal of methanal. [1 mark]

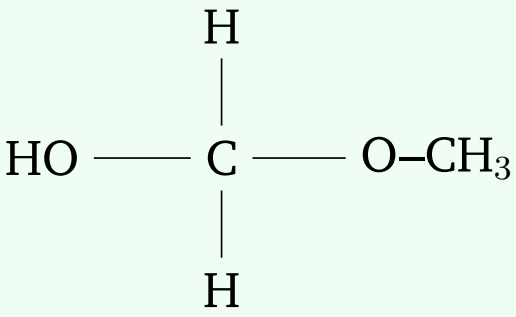
Solution:

Concept:

- A hemiacetal has an $-OH$ group and an $-OR$ group attached to the same carbon atom.
- The methyl hemiacetal forms by addition of methanol, CH_3OH, to the carbonyl group of methanal, $HCHO$.

Step 1: Identify the groups on the former carbonyl carbon Methanal has two hydrogen atoms bonded to its carbonyl carbon. On addition of methanol, the carbonyl oxygen becomes $-OH$, while the methanol oxygen supplies $-OCH_3$. Both original hydrogen atoms remain attached to that carbon.

Step 2: Draw the hemiacetal structure The connectivity is $HO-CH_2-O-CH_3$. The drawing below explicitly shows both hydrogens and the two different oxygen-containing groups on the central carbon. There is only one methoxy group: replacing the hydroxyl group with another methoxy group would give an acetal instead.



Methyl hemiacetal of methanal

Step 3: Conclusion The methyl hemiacetal of methanal is $\boxed{HO-CH_2-O-CH_3}$, with $-OH$ and $-OCH_3$ on the same carbon.

Quick Tip to Solve: Keep both hydrogens of methanal on carbon and change its carbonyl into one OH group and one OCH3 group.

32(b)(ii). There are two $-NH_2$ groups in semicarbazide. However only one is involved in the formation of semicarbazones. Give reason. [1 mark]

Solution:

Concept:

- Semicarbazide has the structure $H_2N-NH-C(=O)-NH_2$; its two $-NH_2$ groups occupy different chemical environments.
- Semicarbazone formation requires a nucleophilic nitrogen with a lone pair available to attack the

Quick Tip to Solve: Locate the NH2 directly bonded to C=O: resonance makes that amide nitrogen the less nucleophilic one.

carbonyl carbon of an aldehyde or ketone.

Step 1: Examine the amino group directly attached to carbonyl The lone pair on the nitrogen of the $-C(=O)-NH_2$ group is delocalised by resonance into the adjacent carbonyl group. This amide nitrogen therefore has much lower nucleophilicity and does not participate in the condensation.

Step 2: Identify the reacting terminal amino group The terminal $-NH_2$ group in $H_2N-NH-CO-NH_2$ is not directly attached to the carbonyl carbon. Its lone pair is available for nucleophilic attack, followed by loss of water, giving the semicarbazone linkage $R_2C=N-NH-CO-NH_2$.

Step 3: Conclusion Only the terminal hydrazino $-NH_2$ group reacts; the other $-NH_2$ group's lone pair is delocalised into the carbonyl group by resonance.

Quick Tip to Solve: Locate the NH2 directly bonded to C=O: resonance makes that amide nitrogen the less nucleophilic one.

32(b)(iii). How will you convert ethanol to 3-hydroxybutanal? [1 mark]

Solution:

Concept:

- Ethanol gives ethanal on passing its vapour over heated copper at $573\,K$, by dehydrogenation.
- Ethanal contains alpha-hydrogen atoms and undergoes aldol addition with cold, dilute aqueous alkali to form a beta-hydroxy aldehyde.

Step 1: Convert ethanol into ethanal Pass ethanol vapour over copper heated to $573\,K$:

$$CH_3CH_2OH \xrightarrow{Cu,\ 573\ K} CH_3CHO + H_2.$$

This removes hydrogen from the primary alcohol without oxidising the aldehyde further to a carboxylic acid.

Step 2: Carry out aldol addition Treat ethanal with cold, dilute aqueous $NaOH$. Two ethanal molecules combine:

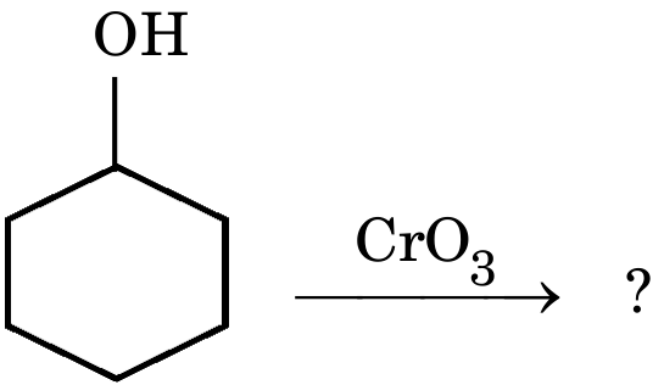
$$2\,CH_3CHO \xrightarrow{dil\cdot\ NaOH,\ cold} CH_3CH(OH)CH_2CHO.$$

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Avoid heating the aldol product, since dehydration would instead produce but-2-enal.

Step 3: Conclusion CH_3CH_2OH is first converted to CH_3CHO, then aldol addition with cold dilute $NaOH$ gives $\boxed{CH_3CH(OH)CH_2CHO}$, 3-hydroxybutanal.

Quick Tip to Solve: Make ethanal first, then use cold dilute NaOH; heating the aldol would remove the OH group as water.

32(b)(iv). Complete the following equation: [1 mark]



Solution:

Concept:

- Chromium trioxide, CrO_3, oxidises secondary alcohols into ketones.
- In cyclohexanol, the carbon bearing $-OH$ is bonded to two other carbon atoms and one hydrogen atom; it is a secondary alcohol carbon.

Step 1: Identify the oxidation site The printed reactant is cyclohexanol. Oxidation removes the hydrogen from the hydroxyl group and the hydrogen from its carbon atom, converting the $>CHOH$ unit into a $>C{=}O$ unit.

Step 2: Preserve the ring and form the carbonyl group The six-membered carbon ring remains intact under the indicated alcohol oxidation. Its hydroxyl-bearing carbon becomes the ketone carbonyl carbon. Using $[O]$ for the oxidising equivalent, the equation is

$$C_6H_{11}OH + [O] \xrightarrow{CrO_3} C_6H_{10}O + H_2O.$$

The formula $C_6H_{10}O$ here denotes cyclohexanone.

Step 3: Conclusion The missing product is $\boxed{\text{cyclohexanone}}$, the six-membered cyclic ketone with a $C{=}O$ group at the former alcohol carbon.

Quick Tip to Solve: For a secondary cyclic alcohol, replace the CHOH unit by C=O and retain the entire carbon ring.

32(b)(v). Write the final product formed when phthalic acid is treated with NH_3 followed by strong heating. [1 mark]

Solution:

Concept:

- Phthalic acid is benzene-1,2-dicarboxylic acid, o-$C_6H_4(COOH)_2$, with adjacent carboxyl groups.
- Reaction with ammonia followed by strong heating causes dehydration and formation of a cyclic imide, in which one $-NH-$ group is bonded to two carbonyl carbons.

Quick Tip to Solve: Adjacent COOH groups plus ammonia and strong heat form a five-membered cyclic imide: phthalimide.

Step 1: React the acid with ammonia Ammonia first forms ammonium carboxylate groups with phthalic acid. On heating, condensation occurs between the carboxyl-derived groups and nitrogen. Their adjacent positions permit closure of a five-membered ring fused to the benzene ring.

Step 2: Identify the final cyclic imide Strong heating completes dehydration to phthalimide. The overall reaction can be written as

$$\text{o-}C_6H_4(COOH)_2 + NH_3 \xrightarrow{\text{strong heating}} C_6H_4(CO)_2NH + 2\,H_2O.$$

In $C_6H_4(CO)_2NH$, both neighbouring carbonyl groups are attached to the same nitrogen atom, giving the cyclic imide rather than a simple amide.

Step 3: Conclusion The final product is $\boxed{\text{phthalimide}}$, $C_6H_4(CO)_2NH$, also called benzene-1,2-dicarboximide.

Quick Tip to Solve: Adjacent COOH groups plus ammonia and strong heat form a five-membered cyclic imide: phthalimide.

33(a)(i). Calculate the emf of the following cell at 25°C:
Zn(s) | Zn^{2+} (0.1 M) || H^+ (0.01 M) | H_2(g) (1 bar), Pt(s)
[Given: $E^\circ_{Zn^{2+}/Zn}$ = -0.76 V, $E^\circ_{2H^+/H_2}$ = 0.00 V, log 10 = 1] [3 marks]

Solution:

Concept:

- For a galvanic cell written with the anode on the left, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using tabulated reduction potentials.
- The Nernst equation at 25°C is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$. Here n is the number of electrons transferred and Q is the dimensionless reaction quotient.
- Pure solids have unit activity. For this cell, the hydrogen pressure is divided by its standard pressure, 1 bar, while dissolved-ion activities are approximated by their molar concentrations relative to 1 mol L^{-1}.

Step 1: Identify the half-reactions and standard emf Zinc is oxidised at the left electrode and hydrogen ions are reduced at the platinum electrode. Platinum provides an inert conducting surface:

$$\begin{aligned} \text{Anode:} \quad & Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-, \\ \text{Cathode:} \quad & 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g). \end{aligned}$$

Thus the overall reaction is $Zn(s) + 2\,H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$, and $n = 2$. Use the supplied reduction potentials without reversing the sign of zinc twice:

$$E^\circ_{\text{cell}} = 0.00 - (-0.76) = 0.76\,\text{V}.$$

Step 2: Construct the reaction quotient Zinc metal does not appear in Q because it is a pure solid. The hydrogen-ion activity must be squared because two hydrogen ions are consumed in the balanced

Quick Tip to Solve: Balance the cell reaction before forming Q: the coefficient 2 on hydrogen ions means that 0.01 must be squared, while zinc metal is omitted.

reaction. With $p_{H_2} = 1\,\text{bar}$,

$$Q = \frac{[Zn^{2+}](p_{H_2}/p^\circ)}{[H^+]^2} = \frac{0.1 \times 1}{(0.01)^2} = 1000 = 10^3.$$

Concentration symbols in this numerical substitution stand for concentrations divided by the standard concentration. Therefore $\log Q = 3 \log 10 = 3$.

Step 3: Apply the Nernst correction Substituting the electron count and reaction quotient gives

$$\begin{aligned} E_{\text{cell}} &= 0.76 - \frac{0.0591}{2} \log(10^3) \\ &= 0.76 - 0.08865 \\ &= 0.67135\,\text{V}. \end{aligned}$$

The correction is subtracted since $Q > 1$. The non-standard concentrations therefore reduce the emf below the standard value while leaving it positive for the cell reaction as written.

Step 4: Conclusion The emf of the given zinc–hydrogen cell at 25°C is $\boxed{E_{\text{cell}} \approx 0.671\,\text{V}}$, or about $0.67\,\text{V}$.

Quick Tip to Solve: Balance the cell reaction before forming Q: the coefficient 2 on hydrogen ions means that 0.01 must be squared, while zinc metal is omitted.

33(a)(ii). State Faraday's second law of electrolysis. How much electricity is required in terms of Faraday for the reduction of 1 mol of $Cr_2O_7^{2-}$ to Cr^{3+}? [2 marks]

Solution:

Concept:

- Faraday's second law: when the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated are proportional to their equivalent masses.
- One Faraday, F, is the charge carried by one mole of electrons. For reduction, the required charge is obtained from the number of moles of electrons accepted.

Step 1: State the mass relation If m_1, m_2 are the deposited masses and E_1, E_2 are their equivalent masses, the law gives

$$\frac{m_1}{m_2} = \frac{E_1}{E_2}.$$

An equivalent mass is the molar mass divided by the number of electrons transferred per formula unit in the electrode reaction.

Step 2: Count the electrons accepted by dichromate In $Cr_2O_7^{2-}$, each chromium has oxidation state $+6$. Reduction to Cr^{3+} requires three electrons per chromium atom. Since one dichromate ion contains two chromium atoms, it accepts six electrons:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O.$$

Quick Tip to Solve: Count both chromium atoms: each changes from $+6$ to $+3$, so the electron requirement is twice three.

Therefore, one mole of dichromate ions requires six moles of electrons, whose total charge is $6F$.

Step 3: Conclusion Faraday's second law states that deposited masses are proportional to equivalent masses for equal charge. The electricity required to reduce $1\,\text{mol}$ of $Cr_2O_7^{2-}$ to Cr^{3+} is $\boxed{6F}$.

Quick Tip to Solve: Count both chromium atoms: each changes from +6 to +3, so the electron requirement is twice three.

OR

33(b)(i). The conductivity of 0.20 M solution of KCl is 2.48 $\times$ 10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).
[Given: $\lambda^\circ_{(K^+)}$ = 73.5 S cm^2 mol^{-1}, $\lambda^\circ_{(Cl^-)}$ = 76.5 S cm^2 mol^{-1}] [2 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/C$ when conductivity κ is in $\text{S}\,\text{cm}^{-1}$ and concentration C is in $\text{mol}\,\text{L}^{-1}$.
- Kohlrausch's law gives $\Lambda_m^\circ = \lambda^\circ_{K^+} + \lambda^\circ_{Cl^-}$. The conductivity ratio used to calculate the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$.

Step 1: Calculate molar conductivity Substitute $\kappa = 2.48 \times 10^{-2}\,\text{S}\,\text{cm}^{-1}$ and $C = 0.20\,\text{mol}\,\text{L}^{-1}$:

$$\Lambda_m = \frac{1000(2.48 \times 10^{-2})}{0.20} = 124\,\text{S}\,\text{cm}^2\,\text{mol}^{-1}.$$

The factor 1000 converts the solution volume from litres to cubic centimetres, keeping the conductivity and concentration units consistent.

Step 2: Use the limiting ionic conductivities KCl supplies one potassium ion and one chloride ion per formula unit. Hence,

$$\Lambda_m^\circ = 73.5 + 76.5 = 150.0\,\text{S}\,\text{cm}^2\,\text{mol}^{-1}.$$

The required conductivity-based degree of dissociation is

$$\alpha = \frac{124}{150.0} = 0.8267 \simeq 0.827.$$

This ratio is dimensionless because the numerator and denominator have the same units. Expressed as a percentage, it is approximately 82.7%.

Step 3: Conclusion $\boxed{\Lambda_m = 124\,\text{S}\,\text{cm}^2\,\text{mol}^{-1}}$ and $\boxed{\alpha \simeq 0.827}$, or approximately 82.7%, using the given conductivity data.

Quick Tip to Solve: With conductivity in S per centimetre and concentration in mol per litre, retain the factor 1000 before dividing by concentration.

33(b)(ii). Calculate $\Delta_r G^\circ$ of the following cell:

$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$

[Given: $E^\circ_{Mg^{2+}/Mg}$ = -2.37 V, $E^\circ_{Cu^{2+}/Cu}$ = +0.34 V, 1 F = 96500 C mol^{-1}] [2 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, with both tabulated values taken as reduction potentials.
- Standard reaction Gibbs energy is $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per reaction as written and F is the Faraday constant.

Step 1: Identify the electrodes and electron transfer Magnesium is oxidised and copper(II) ions are reduced:

$$\text{Mg(s)} \longrightarrow \text{Mg}^{2+}\text{(aq)} + 2\text{e}^-,$$
$$\text{Cu}^{2+}\text{(aq)} + 2\text{e}^- \longrightarrow \text{Cu(s)}.$$

Thus magnesium is the anode, copper is the cathode, and $n = 2$. The two electrons released at the anode are consumed at the cathode; they are counted once in the overall reaction.

Step 2: Calculate the standard cell potential and Gibbs energy Using the supplied reduction potentials,

$$E^\circ_{\text{cell}} = 0.34 - (-2.37) = 2.71\,\text{V}.$$

Therefore,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(2.71)\\ &= -523030\,\text{J mol}^{-1}\\ &= -523.03\,\text{kJ mol}^{-1}.\end{aligned}$$

Since $1\,\text{C} \times 1\,\text{V} = 1\,\text{J}$, the unit is energy per mole of the cell reaction. Its negative sign agrees with the positive standard cell potential.

Step 3: Conclusion For $\text{Mg(s)} + \text{Cu}^{2+}\text{(aq)} \longrightarrow \text{Mg}^{2+}\text{(aq)} + \text{Cu(s)}$, $\boxed{\Delta_r G^\circ = -523.03\,\text{kJ mol}^{-1}}$ (approximately $-523\,\text{kJ mol}^{-1}$).

Quick Tip to Solve: Subtract the magnesium reduction potential, including its minus sign; then use two electrons, not four, in the Gibbs-energy formula.

33(b)(iii). What type of cell is mercury cell? Why is it more advantageous than dry cell? [1 mark]

Solution:

Concept:

- A primary cell supplies current through a chemical reaction that is not practically reversed by recharging; the mercury cell is a primary cell.
- A cell maintains nearly constant voltage when its overall discharge reaction does not cause an appreciable change in the electrolyte concentration.

Quick Tip to Solve: Link the constant mercury-cell voltage to cancellation of hydroxide ions in the overall discharge reaction.

Step 1: Identify the type of cell The mercury cell is a primary cell. Its anode is a zinc-mercury amalgam, its cathode contains mercury(II) oxide, and its alkaline electrolyte contains KOH and ZnO.

Step 2: Explain its advantage over a dry cell The overall discharge reaction is

$$\mathrm{Zn(Hg) + HgO(s) \longrightarrow ZnO(s) + Hg(l).}$$

Hydroxide ions consumed in the cathode reaction are regenerated in the anode reaction. Thus, the overall reaction does not change the electrolyte concentration appreciably. The mercury cell consequently provides an almost constant potential of about $1.35\,\mathrm{V}$ during its useful life, whereas a dry cell's voltage decreases with use.

Step 3: Conclusion The mercury cell is a $\boxed{\text{primary cell}}$. Its advantage over a dry cell is its nearly constant output voltage of approximately $1.35\,\mathrm{V}$ throughout its useful life.

Quick Tip to Solve: Link the constant mercury-cell voltage to cancellation of hydroxide ions in the overall discharge reaction.