CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-2-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **five** sections – **Section A, B, C, D** and **E**.

(iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculators **is not** allowed.

Section A (16 marks)

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

1. The product of oxidation of SO_3^{2-} with MnO_4^- in acidic medium is : [1 mark]

(A) SO_2

(B) SO_4^{2-}

(C) S^{2-}

(D) $S_2O_3^{2-}$

Correct Answer: (B) SO_4^{2-}

Solution:

Concept:

- Oxidation increases an element's oxidation number; acidic permanganate is a strong oxidising agent.
- Oxygen has oxidation number -2 in sulphite and sulphate. The sum of oxidation numbers equals the ion's charge.

Step 1: Compare sulphur oxidation numbers In SO_3^{2-}, $x + 3(-2) = -2$, so sulphur is $+4$. In SO_4^{2-}, $x + 4(-2) = -2$, so it is $+6$. The increase corresponds to loss of two electrons:

$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2\,H^+ + 2\,e^-.$$

Step 2: Eliminate the other products Sulphur remains $+4$ in SO_2, so that is not oxidation. It is -2 in S^{2-} and has average oxidation number $+2$ in $S_2O_3^{2-}$; neither represents oxidation of sulphite by permanganate. Acidic permanganate accepts electrons and is reduced to Mn^{2+}.

Step 3: Conclusion Sulphite is oxidised to sulphate, SO_4^{2-}. Hence, the correct option is (B).

Quick Tip to Solve: Compare sulphur's oxidation number: permanganate raises it from $+4$ in sulphite to $+6$ in sulphate.

2. The coordination number of Co in $[Co(en)_3]^{3+}$ is : [1 mark]

(A) 3

(B) 4

(C) 5

(D) 6

Correct Answer: (D) 6

Solution:

Concept:

- Coordination number is the number of ligand donor atoms directly bonded to the central metal ion.

Quick Tip to Solve: Multiply the number of en ligands by two; the complex charge does not determine its coordination number.

- Ethane-1,2-diamine, abbreviated en, is a bidentate ligand: its two nitrogen atoms each donate a lone pair to the metal.

Step 1: Identify the donor atoms Each en ligand has structure $H_2N-CH_2-CH_2-NH_2$. Both nitrogen atoms coordinate to the same cobalt centre, so one en ligand contributes two coordinate bonds. Counting ligand molecules alone would miss half the donor atoms.

Step 2: Count all metal-ligand bonds There are three en ligands in $[Co(en)_3]^{3+}$. Thus the donor-atom count is $3 \times 2 = 6$. The value 3 counts ligands or gives cobalt's oxidation state here; neither is the coordination number. The values 4 and 5 do not count all six bonded nitrogen atoms.

Step 3: Conclusion The coordination number of cobalt is 6. Hence, the correct option is (D).

Quick Tip to Solve: Multiply the number of en ligands by two; the complex charge does not determine its coordination number.

3. Which one of the following complexes is non-ionisable ? [1 mark]

(A) $[Co(NH_3)_3Cl_3]$

(B) $[Co(NH_3)_4Cl_2]Cl$

(C) $[Co(NH_3)_5Cl]Cl_2$

(D) $[Co(NH_3)_6]Cl_3$

Correct Answer: (A) $[Co(NH_3)_3Cl_3]$

Solution:

Concept:

- The square brackets enclose the coordination sphere. Ligands inside it remain bonded to the metal during ordinary ionic dissociation.
- Counter-ions outside the brackets dissociate in water. A neutral complex without counter-ions is non-ionisable in this sense.

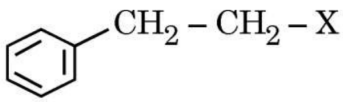
Step 1: Inspect the neutral complex In $[Co(NH_3)_3Cl_3]$, all three chloride ligands are inside the coordination sphere. Neutral ammonia contributes no charge, while cobalt in the $+3$ state balances three chlorido ligands. There is no chloride ion outside the brackets available for ionic dissociation.

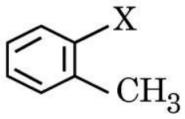
Step 2: Compare the remaining complexes $[Co(NH_3)_4Cl_2]Cl$, $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]Cl_3$ have respectively one, two and three chloride counter-ions outside their brackets. On dissolution, each produces a complex cation and its counter-ions. They are therefore ionisable, unlike the neutral first complex.

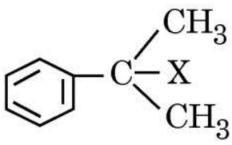
Step 3: Conclusion The non-ionisable complex is $[Co(NH_3)_3Cl_3]$. Hence, the correct option is (A).

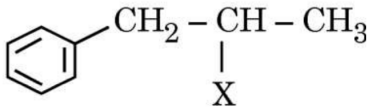
Quick Tip to Solve: Look outside the square brackets first: external chloride ions make these coordination compounds ionisable.

4. Which of the following is a benzylic halide ? [1 mark]

(A) 

(B) 

(C) 

(D) 

(A) $C_6H_5-CH_2-CH_2-X$

(B) o-$CH_3-C_6H_4-X$

(C) $C_6H_5-C(CH_3)_2-X$

(D) $C_6H_5-CH_2-CH(X)-CH_3$

Correct Answer: (C) $C_6H_5-C(CH_3)_2-X$

Solution:

Concept:

- A benzylic halide has its halogen bonded to an sp^3-hybridised carbon directly attached to a benzene ring.
- If the halogen is directly attached to a ring carbon, the compound is an aryl halide. A carbon farther along the side chain is not benzylic.

Step 1: Locate the halogen-bearing carbon In option (C), $C_6H_5-C(CH_3)_2-X$, the carbon bearing X is bonded directly to the phenyl group and to two methyl groups. It is an sp^3 carbon at the benzylic position, so this is a tertiary benzylic halide.

Step 2: Check the other positions In (A), X is on the second side-chain carbon, separated from the ring by CH_2. In (B), X is directly on the benzene ring, making an aryl halide. In (D), the halogen-bearing CH is again separated from the ring by CH_2. Neither (A) nor (D) has halogen at the benzylic position.

Step 3: Conclusion The benzylic halide is $C_6H_5-C(CH_3)_2-X$. Hence, the correct option is (C).

Quick Tip to Solve: Start at the carbon bonded to X: it must be outside the benzene ring and directly joined to a ring carbon.

5. Phenol is less acidic than : [1 mark]

(A) ethanol

(B) o-nitrophenol

(C) o-methoxyphenol

(D) o-methylphenol

Correct Answer: (B) o-nitrophenol

Solution:

Concept:

- Acid strength depends on conjugate-base stability: greater stabilisation of the anion favours loss of H^+.
- Electron-withdrawing groups increase phenol's acidity by stabilising phenoxide; electron-donating groups generally reduce it.

Step 1: Examine the nitro substituent The nitro group in *o*-nitrophenol withdraws electron density through both inductive and resonance effects. It stabilises the negative charge of the conjugate phenoxide ion, making proton loss more favourable than in unsubstituted phenol.

Step 2: Compare the other choices Ethanol gives ethoxide, which lacks phenoxide's resonance stabilisation, and is less acidic than phenol. The methyl group donates electron density, so *o*-methylphenol is less acidic. The methoxy group's resonance donation also makes *o*-methoxyphenol less acidic than phenol in the standard comparison. Thus only the nitro-substituted choice is more acidic than phenol.

Step 3: Conclusion Phenol is less acidic than *o*-nitrophenol. Hence, the correct option is (B).

Quick Tip to Solve: For substituted phenols, identify electron withdrawal: an ortho nitro group stabilises phenoxide and increases acidity.

6. $(CH_3)_3C-O-CH_3$ reacts with HI to give : [1 mark]

(A) $(CH_3)_3C-I + CH_3OH$

(B) $(CH_3)_3C-I + CH_3-I$

(C) $(CH_3)_3C-OH + CH_3-I$

(D) $(CH_3)_3C-OH + CH_3OH$

Correct Answer: (A) $(CH_3)_3C-I + CH_3OH$

Solution:

Concept:

- Hydrogen iodide protonates an ether oxygen, making carbon-oxygen bond cleavage easier.
- For an ether containing a tertiary alkyl group, cleavage proceeds through a stable tertiary carbocation, followed by attack of iodide.

Step 1: Cleave the protonated ether In tert-butyl methyl ether, $(CH_3)_3C-O-CH_3$, protonation gives an oxonium ion. The bond between oxygen and the tertiary carbon breaks, producing a tertiary butyl

Quick Tip to Solve: Check for a tertiary alkyl group before applying the usual least-hindered-carbon rule for cleavage of ethers by HI.

carbocation and methanol. Iodide then bonds to the carbocation:

$$(CH_3)_3C{-}O{-}CH_3 + HI \longrightarrow (CH_3)_3C{-}I + CH_3OH.$$

Step 2: Distinguish the listed products The stable tertiary carbocation favours formation of tert-butyl iodide, rather than the tert-butyl alcohol and methyl iodide in (C). Option (D) does not represent iodide substitution. Option (B) would require further conversion of the methanol by additional HI; it is not the direct ether-cleavage pair asked for here.

Step 3: Conclusion The products are tert-butyl iodide and methanol, $(CH_3)_3C{-}I + CH_3OH$. Hence, the correct option is (A).

Quick Tip to Solve: Check for a tertiary alkyl group before applying the usual least-hindered-carbon rule for cleavage of ethers by HI.

7. Aspirin is formed by the acetylation of : [1 mark]

(A) Benzoic acid

(B) Phenol

(C) Salicylic acid

(D) Phthalic acid

Correct Answer: (C) Salicylic acid

Solution:

Concept:

- Acetylation introduces the acetyl group, CH_3CO, into a molecule having a suitable reactive group.
- Aspirin is acetylsalicylic acid; its ester group is formed by acetylating the phenolic hydroxyl group of salicylic acid.

Step 1: Identify the functional group that reacts Salicylic acid is 2-hydroxybenzoic acid. It contains a phenolic $-OH$ group adjacent to a $-COOH$ group on the benzene ring. Acetic anhydride acetylates this hydroxyl group, converting $-OH$ into $-OCOCH_3$, while the carboxyl group remains present.

Step 2: Compare the other starting materials Benzoic acid has no phenolic hydroxyl group. Acetylation of phenol gives phenyl acetate, which lacks the carboxyl group needed in aspirin. Phthalic acid has two carboxyl groups rather than the required adjacent hydroxyl and carboxyl groups. These structures therefore do not give aspirin by the stated acetylation.

Step 3: Conclusion Aspirin is formed by acetylation of salicylic acid. Hence, the correct option is (C).

Quick Tip to Solve: Remember aspirin as acetylsalicylic acid: acetylate the phenolic hydroxyl group of salicylic acid and retain its carboxyl group.

8. An azeotropic solution of two liquids has boiling point higher than either of them when it : [1 mark]

(A) is saturated

(B) shows positive deviation from Raoult's law

(C) shows negative deviation from Raoult's law

(D) shows no deviation from Raoult's law

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

Solution:

Concept:

- A liquid boils when its vapour pressure equals the external pressure. Lower vapour pressure at a given temperature therefore implies a higher boiling point.
- Negative deviation from Raoult's law occurs when attraction between unlike molecules is stronger than that in the pure liquids; sufficiently strong negative deviation gives a maximum-boiling azeotrope.

Step 1: Relate molecular attraction to boiling Stronger attraction between the two components holds molecules in the liquid and reduces their tendency to escape. The total vapour pressure falls below its ideal value. More heating is then needed to reach atmospheric pressure, so the azeotrope can boil above both pure components.

Step 2: Eliminate the other behaviours Positive deviation raises vapour pressure and can produce a minimum-boiling azeotrope, the opposite of the observation. An ideal solution, with no deviation, does not form a maximum-boiling azeotrope. Saturation describes a solubility limit and does not explain this boiling-point maximum.

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

Quick Tip to Solve: For azeotropes, connect a maximum boiling point with a minimum vapour pressure and therefore negative deviation.

9. During electrolysis of aqueous $CuCl_2$: [1 mark]

(A) $H_2(g)$ is liberated at cathode

(B) Cu is formed at cathode

(C) $O_2(g)$ is liberated at anode

(D) $Cl_2(g)$ is liberated at cathode

Correct Answer: (B) Cu is formed at cathode

Solution:

Concept:

- Reduction occurs at the cathode during electrolysis: dissolved cations can gain electrons and deposit as metals.
- In aqueous $CuCl_2$, Cu^{2+} is reduced preferentially to water under the usual electrolysis conditions,

Quick Tip to Solve: First write $Cu^{2+} + 2e^- \longrightarrow Cu$: it immediately fixes both the product and its electrode as the cathode.

while chloride is oxidised at an inert anode.

Step 1: Identify the cathode product Copper(II) ions accept two electrons at the cathode. The electrode reaction is

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

Copper deposition is favoured over hydrogen evolution because copper(II) ions are more readily reduced than water in this aqueous solution. Thus hydrogen is not the expected cathode product.

Step 2: Check the electrode assignments In the usual electrolysis of aqueous copper(II) chloride using inert electrodes, chloride ions undergo oxidation:

$$\mathrm{2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^-}.$$

Chlorine is therefore associated with the anode, never with reduction at the cathode. Oxygen evolution is not the expected anode process for the usual chloride electrolysis described here; the definite cathode process is copper deposition.

Step 3: Conclusion Copper is formed at the cathode. Hence, the correct option is (B).

Quick Tip to Solve: First write $\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu}$: it immediately fixes both the product and its electrode as the cathode.

10. Half-life period of a first order reaction is 1386 seconds. The rate constant (k) of the reaction is : [1 mark]

(A) $0.5 \times 10^{-3}\ \mathrm{s^{-1}}$

(B) $5.0 \times 10^{-3}\ \mathrm{s^{-1}}$

(C) $5 \times 10^{-2}\ \mathrm{s^{-1}}$

(D) $0.5 \times 10^{-2}\ \mathrm{s^{-1}}$

Correct Answer: (A) $0.5 \times 10^{-3}\ \mathrm{s^{-1}}$

Solution:

Concept:

- For a first-order reaction, the half-life is $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- A first-order rate constant has units of reciprocal time; a half-life in seconds gives k in $\mathrm{s^{-1}}$.

Step 1: Rearrange the half-life relation The half-life is $1386\,\mathrm{s}$. Isolate the rate constant and substitute this value:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386\,\mathrm{s}}.$$

No initial concentration is needed because a first-order half-life is independent of initial concentration.

Step 2: Calculate and compare the powers of ten Since $1386 = 2 \times 693$, the numerical quotient is

$$\frac{0.693}{1386} = \frac{693 \times 10^{-3}}{2 \times 693} = 0.5 \times 10^{-3}.$$

Quick Tip to Solve: Use $k = 0.693/t_{1/2}$, then rewrite the numerical result in exactly the coefficient-and-exponent form printed in each option.

The printed values in (B) and (D) both equal $5.0 \times 10^{-3}\,s^{-1}$, ten times this value, while (C) is one hundred times this value. Keeping the decimal coefficient with its exponent prevents choosing a wrong power of ten.

Step 3: Conclusion $k = 0.5 \times 10^{-3}\,s^{-1} = 5.0 \times 10^{-4}\,s^{-1}$. Hence, the correct option is (A).

Quick Tip to Solve: Use $k = 0.693/t_{1/2}$, then rewrite the numerical result in exactly the coefficient-and-exponent form printed in each option.

11. The relative lowering of vapour pressure of an aqueous solution containing non-volatile solute is 0.0225. The mole fraction of the non-volatile solute is : [1 mark]

(A) 0.80

(B) 0.725

(C) 0.15

(D) 0.0225

Correct Answer: (D) 0.0225

Solution:

Concept:

- For a solution of a non-volatile solute, Raoult's law gives $p = x_1 p^0$, where p^0 is the pure solvent's vapour pressure and x_1 is its mole fraction.
- The mole fractions satisfy $x_1 + x_2 = 1$, where x_2 is the mole fraction of the solute. Relative lowering means $(p^0 - p)/p^0$.

Step 1: Express the relative lowering Substitute Raoult's law into the definition and simplify:

$$\frac{p^0 - p}{p^0} = \frac{p^0 - x_1 p^0}{p^0} = 1 - x_1 = x_2.$$

The non-volatile solute contributes no vapour pressure, so only the solvent contribution appears in this relation.

Step 2: Apply the given dimensionless value The stated relative lowering is 0.0225, so it directly supplies the solute mole fraction. The solvent mole fraction would instead be $1 - 0.0225 = 0.9775$. The values 0.80, 0.725 and 0.15 do not equal the specified relative lowering and therefore cannot be the required solute mole fraction.

Step 3: Conclusion The mole fraction of the non-volatile solute is 0.0225. Hence, the correct option is (D).

Quick Tip to Solve: For a non-volatile solute, read its mole fraction directly from the relative lowering; subtract from one only when the solvent mole fraction is asked.

12. The rate of the reaction $2A + B_2 \rightarrow 2AB$ is given by Rate = $k[A]^2[B_2]$. The value of rate constant (k) can be increased by : [1 mark]

(A) increasing the concentration of A

(B) increasing the concentration of B

(C) increasing the temperature

(D) all the above three

Correct Answer: (C) increasing the temperature

Solution:

Concept:

- In the rate law $r = k[\mathrm{A}]^2[\mathrm{B}_2]$, r is the reaction rate and k is the rate constant. At a fixed temperature, changing reactant concentrations changes the rate but not k.
- The Arrhenius relation is $k = A_0 e^{-E_a/(RT)}$, where A_0 is the frequency factor, E_a is the activation energy, R is the gas constant and T is absolute temperature.

Step 1: Separate concentration effects from the constant Increasing the concentration of A increases the rate through its squared concentration factor. Increasing the other reactant concentration also increases the rate through its concentration factor. Neither change increases the rate constant when temperature and other conditions remain fixed, so the concentration choices confuse rate with rate constant.

Step 2: Apply the temperature dependence With positive activation energy, increasing T makes $-E_a/(RT)$ less negative. The exponential factor and hence k increase. In molecular terms, a larger fraction of collisions have enough energy to overcome the activation barrier. Thus the temperature choice changes k, whereas the combined choice is incorrect because its concentration changes do not.

Step 3: Conclusion The rate constant can be increased by increasing the temperature. Hence, the correct option is (C).

Quick Tip to Solve: When asked about k, hold concentration factors separate: concentration affects the rate, while temperature changes the Arrhenius exponential.

13. Assertion (A): Aromatic primary amines can be prepared by Gabriel phthalimide synthesis.
Reason (R): Alkyl halide undergoes nucleophilic substitution with anion formed by phthalimide.

[1 mark]

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

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

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

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

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

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylation of the phthalimide anion followed by hydrolysis.
- Ordinary aryl halides do not undergo the nucleophilic substitution required in this synthesis.

Step 1: Evaluate the assertion The assertion is false. Preparing an aromatic primary amine would require substitution on an aryl halide. Its halogen is attached directly to the aromatic ring, and the carbon–halogen bond has partial double-bond character. It does not undergo the required substitution with the phthalimide anion under Gabriel synthesis conditions.

Step 2: Evaluate the reason The reason is true. Treatment of phthalimide with alkali forms its nitrogen-centred anion. This nucleophile displaces halide from an alkyl halide to give an N-alkylphthalimide, whose hydrolysis releases a primary aliphatic amine.

Step 3: Check the logical connection The reason describes reaction with an alkyl halide, not an aryl halide, and therefore cannot establish the assertion about aromatic amines. Options (A), (B) and (C) all require a true assertion and are excluded.

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

Quick Tip to Solve: In Gabriel synthesis, check whether the halogen-bearing carbon is alkyl or aryl; direct aryl substitution is the obstacle to preparing aniline.

14. Assertion (A): Uracil base is present in RNA.

Reason (R): RNA undergoes self-replication. [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:

- RNA contains the nitrogenous bases adenine, guanine, cytosine and uracil; DNA normally contains thymine in place of uracil.
- In the usual cellular account, DNA undergoes replication, while RNA participates in protein synthesis and is produced by transcription.

Step 1: Evaluate the assertion The assertion is true. Uracil is one of the four bases present in RNA. The presence of uracil, together with ribose sugar, helps distinguish RNA from DNA.

Step 2: Evaluate the reason The reason is false in the standard cellular context of this question. Self-replication is the characteristic function attributed to DNA. Cellular RNA is generally transcribed from a DNA template; it does not ordinarily make copies of itself.

Step 3: Check the explanatory link The identity of the bases in RNA is a statement about its chemical composition. It is not explained by the proposed self-replication. Options (A) and (B) require a true reason, while (D) requires a false assertion; none agrees with these evaluations.

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

Quick Tip to Solve: Remember RNA as ribose plus uracil, and distinguish its role in protein synthesis from the usual cellular replication of DNA.

15. Assertion (A): Diazonium salts of aliphatic amines are more stable than those of aromatic amines.
Reason (R): Diazonium salts of aromatic amines show resonance. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Aliphatic diazonium salts readily decompose with liberation of N_2 and are highly unstable.
- Aromatic diazonium salts are relatively more stable because the diazonium group is conjugated with the aromatic ring; they can be maintained in cold solution at 273–$278\,\text{K}$.

Step 1: Evaluate the assertion The assertion is false: it reverses the stability order. Diazonium salts derived from aliphatic primary amines are less stable than those derived from aromatic primary amines. The aliphatic salts decompose readily, releasing nitrogen gas.

Step 2: Evaluate the reason The reason is true. In an aromatic diazonium ion, the diazonium group interacts with the conjugated aromatic ring. Resonance delocalisation provides additional stabilisation that an alkyl group cannot provide in the same way.

Step 3: Relate resonance to the stability order Resonance supports greater relative stability of the aromatic salt, which is opposite to the assertion. Options (A), (B) and (C) assume that the assertion is true, so they cannot describe the given statements.

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

Quick Tip to Solve: Associate the aromatic ring with resonance stabilisation; the claim that an aliphatic diazonium salt is more stable has the order reversed.

16. Assertion (A): Acetanilide ($C_6H_5-NHCOCH_3$) is less basic than aniline.

Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen in acetanilide.

[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:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton.
- Acetylation converts aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$; its nitrogen lone pair is delocalised towards the carbonyl group.

Step 1: Evaluate the assertion The assertion is true. In acetanilide, the nitrogen lone pair participates in amide resonance with the adjacent carbonyl group. It is therefore less available for proton acceptance than the lone pair in aniline, making acetanilide less basic.

Step 2: Evaluate the reason The reason is true. The acetyl group introduced on nitrogen withdraws electron density through its carbonyl group. Delocalisation of the nitrogen lone pair towards the carbonyl oxygen decreases electron density and lone-pair availability at nitrogen.

Step 3: Check whether the reason explains the assertion The decrease in electron density at nitrogen directly reduces its tendency to accept a proton. Thus the stated electronic effect explains the lower basicity. Option (B) incorrectly denies this connection, and options (C) and (D) incorrectly declare one statement false.

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

Quick Tip to Solve: Identify the amide linkage in acetanilide: a nitrogen lone pair delocalised towards a carbonyl group is less available for basic behaviour.

Section B (10 marks)

17. Define the following terms :

(a) Essential amino acids

(b) Nucleotide [2 marks]

Solution:

Concept:

- Amino acids are the building units of proteins. Their classification as essential or non-essential depends on the body's ability to synthesise them in adequate amounts.
- Nucleotides are the building units of nucleic acids. Each contains a nitrogenous base, a pentose sugar and a phosphate group.

Step 1: Define essential amino acids **(a)** Essential amino acids are those amino acids that the human body cannot synthesise in sufficient amounts and must therefore obtain through the diet. Valine and leucine are examples. The word essential describes the dietary requirement; it does not mean that the other amino acids are unnecessary for making proteins.

Step 2: Define a nucleotide **(b)** A nucleotide is a compound formed from a nitrogenous base, a pentose sugar and a phosphate group. The base and sugar together form a nucleoside; attachment of phosphate makes it a nucleotide. The sugar is ribose in RNA nucleotides and 2-deoxyribose in DNA nucleotides. Nucleotides join through phosphodiester linkages to form nucleic-acid chains.

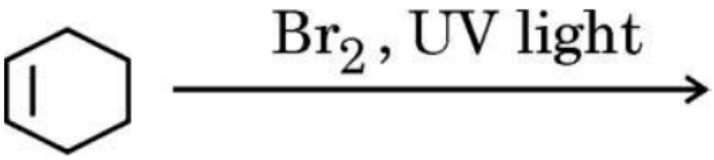
Step 3: Conclusion Essential amino acids must be supplied by the diet because the body cannot make enough of them. A nucleotide consists of a nitrogenous base, a pentose sugar and phosphate.

Quick Tip to Solve: For essential amino acids, mention the dietary need; for a nucleotide, list all three components so that it is not confused with a nucleoside.

18. (a) In the following pair of compounds, which compound undergoes S_N1 reaction faster and why?

(b) Write the major product in the following: [2 marks]





Solution:

Concept:

- An S_N1 reaction proceeds through slow carbon–halogen bond ionisation. A more stable carbocation is formed more readily and gives a faster reaction.

Quick Tip to Solve: First distinguish a benzene ring from a saturated ring; then use the UV-light condition to recognise allylic bromination of cyclohexene.

- Bromination under ultraviolet light proceeds by a free-radical pathway. In cyclohexene, substitution at an allylic carbon gives a resonance-stabilised intermediate.

Step 1: (a) Compare the carbocations Benzyl chloride, $C_6H_5CH_2Cl$, gives the benzyl carbocation, $C_6H_5CH_2^+$. Its positive charge is delocalised into the benzene ring by resonance. The other compound is cyclohexylmethyl chloride, $C_6H_{11}CH_2Cl$: its saturated ring cannot provide this resonance stabilisation to the initially formed primary carbocation. Therefore benzyl chloride ionises more readily and undergoes S_N1 substitution faster.

Step 2: (b) Apply allylic bromination The printed substrate is cyclohexene. Ultraviolet light causes homolytic cleavage of Br_2. A bromine radical removes an allylic hydrogen, and the resulting resonance-stabilised allylic radical reacts with Br_2. Thus one hydrogen on the carbon adjacent to the double bond is replaced by bromine; the double bond is retained. The major product is 3-bromocyclohex-1-ene, with HBr as the by-product.

Step 3: Conclusion (a) Benzyl chloride reacts faster because the benzyl carbocation is resonance-stabilised. (b) The major product is **3-bromocyclohex-1-ene**.

Quick Tip to Solve: First distinguish a benzene ring from a saturated ring; then use the UV-light condition to recognise allylic bromination of cyclohexene.

19. A first order reaction has a rate constant 1.25×10^{-3} s^{-1}. How long will 5 g of this reactant take to reduce to 2.5 g ?

[log 2 = 0.301, log 3 = 0.4771, log 4 = 0.6021] [2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0, [A]_t$ are the initial and remaining reactant concentrations.
- At constant volume, the concentration ratio equals the ratio of masses of the same reactant. Reduction to half of the initial mass takes one half-life, independent of the initial amount.

Step 1: Identify the fraction remaining The initial mass is $m_0 = 5\,\text{g}$, and the remaining mass is $m_t = 2.5\,\text{g}$. Thus $m_t/m_0 = 1/2$, so the required time is one half-life. The ratio entering the logarithm is

$$\frac{[A]_0}{[A]_t} = \frac{m_0}{m_t} = \frac{5}{2.5} = 2.$$

Step 2: Substitute the rate constant Using $k = 1.25 \times 10^{-3}\,\text{s}^{-1}$ and the supplied $\log 2 = 0.301$,

$$\begin{aligned} t &= \frac{2.303}{1.25 \times 10^{-3}} \log 2 \\ &= \frac{2.303 \times 0.301}{1.25 \times 10^{-3}} \\ &= 554.56\,\text{s}. \end{aligned}$$

The logarithm is dimensionless, so dividing by a rate constant in s^{-1} gives time in seconds.

Quick Tip to Solve: Since 2.5 g is exactly half of 5 g, use the first-order shortcut $t_{1/2} = 0.693/k$ immediately.

Step 3: Conclusion The reactant takes approximately $\boxed{5.55 \times 10^2\,\text{s}}$, or $9.24\,\text{min}$, to decrease from $5\,\text{g}$ to $2.5\,\text{g}$.

Quick Tip to Solve: Since 2.5 g is exactly half of 5 g, use the first-order shortcut $t_{1/2} = 0.693/k$ immediately.

20(a). What is lanthanoid contraction ? Actinoid contraction is greater from element to element than lanthanoid contraction. Why ? [2 marks]

Solution:

Concept:

- Atomic and ionic radii reflect the effective nuclear charge experienced by the outer electrons: stronger nuclear attraction draws the electron cloud inward.
- Electrons in f orbitals shield the increasing nuclear charge poorly. The successive filling of f orbitals therefore produces a contraction across an f-block series.

Step 1: Define lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic and ionic radii with increasing atomic number across the lanthanoid series. It is especially evident when comparing the radii of their Ln^{3+} ions. As nuclear charge increases, the added electrons enter the $4f$ subshell and do not effectively shield one another from that increase. Consequently the effective nuclear attraction increases and the radii decrease.

Step 2: Compare the shielding in actinoids In the actinoid series, the added electrons enter the $5f$ subshell. The shielding of one $5f$ electron by another is poorer than the shielding of one $4f$ electron by another in the lanthanoids. Hence the increase in nuclear charge is compensated less effectively in actinoids. Their electron clouds experience a greater increase in effective nuclear attraction, producing the greater contraction from element to element.

Step 3: Conclusion Lanthanoid contraction is the progressive decrease in atomic and ionic radii across the lanthanoids. Actinoid contraction is greater because $5f$ electrons shield the increasing nuclear charge more poorly than $4f$ electrons.

Quick Tip to Solve: Link the comparison in this order: poorer $5f$ shielding, greater effective nuclear attraction, and greater actinoid contraction.

OR

20(b). Why do transition metals have high enthalpy of atomization ? Which element of 3d-series has lowest enthalpy of atomization? [2 marks]

Solution:

Concept:

- Enthalpy of atomisation is the enthalpy required to convert one mole of a solid metal into separated gaseous atoms: $\text{M}(\text{s}) \longrightarrow \text{M}(\text{g})$. Stronger metallic bonding requires more energy for this process.

Quick Tip to Solve: For the lowest atomisation enthalpy in the 3d series, look for zinc's fully filled $3d^{10}$ subshell and absence of unpaired d electrons.

- Transition-metal bonding involves valence ns and $(n-1)d$ electrons. Several unpaired d electrons generally contribute to strong interatomic bonding.

Step 1: Explain the high atomisation enthalpies Most transition metals have several unpaired electrons in their partially filled d subshells. Participation of these d electrons along with the outer s electrons produces strong metallic bonding between the atoms. Considerable energy must therefore be supplied to separate the solid into individual gaseous atoms, accounting for their high enthalpies of atomisation.

Step 2: Identify the lowest value in the 3d series Zinc has the lowest enthalpy of atomisation among the elements of the 3d series. Its electronic configuration is $[\mathrm{Ar}]\,3d^{10}4s^2$. The d subshell is completely filled and has no unpaired d electrons, so zinc does not have the same strong d-electron contribution to metallic bonding as the other members. Its comparatively weak metallic bonding makes atom separation easier.

Step 3: Conclusion Transition metals generally have high atomisation enthalpies because their d and s valence electrons produce strong metallic bonding. $\boxed{\text{Zinc (Zn)}}$ has the lowest enthalpy of atomisation in the 3d series.

Quick Tip to Solve: For the lowest atomisation enthalpy in the 3d series, look for zinc's fully filled $3d^{10}$ subshell and absence of unpaired d electrons.

21. A 4% solution of urea (molar mass = 60 g mol^{-1}) is isotonic with 5.2% solution of an unknown organic substance. Calculate the molecular weight of the unknown organic substance. [2 marks]

Solution:

Concept:

- Isotonic solutions have the same osmotic pressure at the same temperature. For a dilute solution of a non-electrolyte, $\pi = CRT$, where C is molar concentration, R is the gas constant and T is absolute temperature.
- The molar concentration is $C = w/(MV)$, where w is solute mass, M its molar mass and V solution volume. Urea and the organic solute are treated as non-electrolytes without association or dissociation.

Step 1: Express the concentrations on the same volume basis A 4% urea solution contains 4 g urea per 100 mL solution, while the 5.2% solution contains 5.2 g unknown solute in the same volume. Let the unknown molar mass be M_x. The respective solute amounts are $4/60$ mol and $5.2/M_x$ mol.

Step 2: Equate the osmotic pressures Since temperature and solution volume are common, $\pi_1 = \pi_2$ makes the factors RT/V cancel. Therefore the two samples contain equal numbers of moles:

$$\frac{4}{60} = \frac{5.2}{M_x}, \qquad M_x = \frac{5.2 \times 60}{4}.$$

The more concentrated solution by mass must have the larger molar mass to give the same number of solute particles per unit volume.

Quick Tip to Solve: For isotonic non-electrolyte solutions expressed on the same percentage basis, use $M_x/M_{\text{urea}} = 5.2/4$; the common volume and temperature cancel.

Step 3: Conclusion The molar mass of the unknown organic substance is $\boxed{78\,\text{g mol}^{-1}}$; its relative molecular mass is 78.

Quick Tip to Solve: For isotonic non-electrolyte solutions expressed on the same percentage basis, use $M_x/M_{\text{urea}} = 5.2/4$; the common volume and temperature cancel.

Section C (21 marks)

22. The rate of a gaseous reaction triples when temperature is increased from 17°C to 27°C. Calculate the energy of activation for this reaction.

[Given : 2.303 R = 19.15 JK^{-1} mol^{-1}, log 3 = 0.48] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A is the pre-exponential factor and E_a is the activation energy. Temperature T must be in kelvin.
- For the same reaction at two temperatures, $\log(k_2/k_1) = \dfrac{E_a}{2.303R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$, taking A and E_a as constant over this small interval. At the same reactant concentrations, the ratio of rates equals the ratio of rate constants.

Step 1: Convert temperatures and identify the rate ratio Convert the Celsius values to absolute temperatures before using their reciprocals:

$$T_1 = 17 + 273 = 290\,\text{K}, \qquad T_2 = 27 + 273 = 300\,\text{K}.$$

The reaction rate triples, so the temperature comparison gives $k_2/k_1 = 3$. Thus $\log(k_2/k_1) = \log 3 = 0.48$, using the supplied value.

Step 2: Substitute in the two-temperature Arrhenius equation Substituting the given $2.303R = 19.15\,\text{J K}^{-1}\text{mol}^{-1}$,

$$0.48 = \frac{E_a}{19.15}\left(\frac{1}{290} - \frac{1}{300}\right) = \frac{E_a}{19.15}\frac{10}{87000}.$$

Rearranging gives

$$E_a = \frac{0.48 \times 19.15 \times 87000}{10} = 79970.4\,\text{J mol}^{-1}.$$

Dividing by 1000 converts joules to kilojoules. Both the logarithm of the rate ratio and $1/T_1 - 1/T_2$ are positive, so the calculated activation energy is positive, as expected for a rate that increases with temperature.

Step 3: Conclusion The energy of activation is $\boxed{E_a \approx 79.97\,\text{kJ mol}^{-1} \approx 80\,\text{kJ mol}^{-1}}$.

Quick Tip to Solve: Use 290 K and 300 K in the reciprocals, even though the temperature difference remains 10 K; Celsius temperatures cannot be substituted into the Arrhenius equation.

23. Calculate emf of the following cell:

$$\mathrm{Zn\,(s)} \mid \mathrm{Zn^{2+}\,(0.1\,M)} \parallel \mathrm{Sn^{2+}\,(0.001\,M)} \mid \mathrm{Sn\,(s)}$$

Given: $E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76\,\mathbf{V}$, $E^\circ_{\mathrm{Sn^{2+}/Sn}} = -0.14\,\mathbf{V}$.
[$\log 10 = 1$**]** [3 marks]

Solution:

Concept:

- The standard emf is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using the tabulated reduction potentials for both electrodes. The left electrode of the cell as written is the anode.
- At the usual temperature of $298\,\mathrm{K}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, in volts. Here n is the number of electrons transferred and Q is the reaction quotient; pure solids have unit activity.

Step 1: Write the electrode reactions Zinc is oxidised at the anode and tin(II) ions are reduced at the cathode:

$$\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$\mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Sn\,(s)}.$$

Adding them gives $\mathrm{Zn\,(s)} + \mathrm{Sn^{2+}(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + \mathrm{Sn\,(s)}$. Thus $n = 2$. The solid metals are omitted from Q, so

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Sn^{2+}}]} = \frac{0.1}{0.001} = 100.$$

Step 2: Find the standard emf Subtract the zinc reduction potential from the tin reduction potential, retaining both negative signs:

$$E^\circ_{\text{cell}} = (-0.14) - (-0.76) = 0.62\,\mathrm{V}.$$

The more positive reduction potential belongs to the tin electrode, in agreement with its role as the cathode.

Step 3: Apply the concentration correction With $\log 100 = 2\log 10 = 2$, the Nernst equation gives

$$E_{\text{cell}} = 0.62 - \frac{0.0591}{2}\log 100$$
$$= 0.62 - 0.0591\,\mathrm{V}.$$

Since $Q > 1$, the concentration correction lowers the emf relative to the standard value. In particular, the low concentration of the reacting $\mathrm{Sn^{2+}}$ ions makes their reduction less favourable.

Step 4: Conclusion The cell emf at $298\,\mathrm{K}$ is $\boxed{0.5609\,\mathrm{V} \approx 0.56\,\mathrm{V}}$.

Quick Tip to Solve: Write the net cell reaction first: its products put $[\mathrm{Zn^{2+}}]$ in the numerator of Q, and the two electrons give the factor $0.0591/2$.

24. The vapour pressure of a solvent at 283 K is 100 mm Hg. Calculate the vapour pressure of a dilute solution containing 1 mole of a strong electrolyte AB in 50 moles of the solvent at 283 K (assuming complete dissociation of solute AB). [3 marks]

Solution:

Concept:

- Raoult's law for a non-volatile solute is $p = x_1 p^0$, where p^0 is the vapour pressure of pure solvent and x_1 is the solvent mole fraction.
- The van't Hoff factor i counts the particles obtained per formula unit of solute. Complete dissociation $\mathrm{AB} \rightarrow \mathrm{A}^+ + \mathrm{B}^-$ gives $i = 2$.

Step 1: Count the solute particles after dissociation The given amount is 1 mol of AB and 50 mol of solvent. Each mole of AB supplies one mole of each ion, so the effective amount of solute particles is

$$n_{\text{particles}} = i n_{\mathrm{AB}} = 2 \times 1 = 2\,\text{mol}.$$

The total amount of independently moving particles is therefore $50 + 2 = 52$ mol. Counting AB as one undissociated particle would underestimate the lowering of vapour pressure.

Step 2: Apply Raoult's law at the stated temperature Both vapour pressures refer to 283 K, so no temperature correction is needed. The solvent mole fraction and solution pressure are

$$x_1 = \frac{50}{50+2} = \frac{25}{26}, \qquad p = 100 \times \frac{25}{26} = 96.1538\,\text{mm Hg}.$$

Thus the lowering is $100 - 96.1538 = 3.8462$ mm Hg, as expected for adding a non-volatile solute. If the usual dilute-solution approximation is used, the solute particles are neglected in the denominator:

$$\frac{p^0 - p}{p^0} \simeq \frac{i n_{\mathrm{AB}}}{n_1} = \frac{2}{50} = 0.04,$$

which gives the approximate pressure $100(1 - 0.04) = 96$ mm Hg.

Step 3: Conclusion The vapour pressure is $\boxed{96.15\,\text{mm Hg}}$ using the full mole fraction, or $\boxed{96\,\text{mm Hg}}$ with the usual dilute-solution approximation.

Quick Tip to Solve: Dissociate AB before counting moles: use 2 moles of ions, and include them in the denominator for the full mole fraction.

25. Write the structures of A, B and C in the following reactions: [3 marks]

(a) $CH_3 - CH_2 - Br \xrightarrow{KCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C$

(b)  $\xrightarrow{Fe + HCl} A \xrightarrow[273 - 278\ K]{NaNO_2 + HCl} B \xrightarrow{C_2H_5OH} C$

Solution:

Concept:

- KCN substitutes bromide through carbon to form a nitrile, adding one carbon to the chain. Partial hydrolysis of a nitrile gives the corresponding amide.
- Hofmann bromamide degradation with $Br_2/NaOH$ converts $RCONH_2$ to RNH_2, removing the carbonyl carbon.
- Aromatic primary amines form diazonium salts with $NaNO_2/HCl$ at 273–278 K. Ethanol replaces the diazonium group by hydrogen.

Step 1: Part (a): form the nitrile and amide Cyanide ion attacks bromoethane through its carbon end. Therefore A is propanenitrile, whose structure is $CH_3CH_2C \equiv N$:

$$CH_3CH_2Br + KCN \longrightarrow CH_3CH_2CN + KBr.$$

The specified partial hydrolysis converts the nitrile group into an amide group, so B is propanamide, $CH_3CH_2C(=O)NH_2$. The carbon skeleton still contains three carbon atoms.

Step 2: Part (a): perform Hofmann degradation Bromine and sodium hydroxide convert propanamide into ethanamine. The amide carbonyl carbon is removed as carbonate. Hence C has the structure $CH_3CH_2NH_2$, with two carbon atoms.

Step 3: Part (b): reduce and diazotise nitrobenzene Iron and hydrochloric acid reduce the nitro group to an amino group. A is therefore aniline, $C_6H_5NH_2$. Diazotisation at the printed low temperature gives B, benzenediazonium chloride: $[C_6H_5{-}N \equiv N]^+Cl^-$. The phenyl group is bonded to the positively charged nitrogen of the diazonium group.

Step 4: Part (b): replace the diazonium group by hydrogen Ethanol reduces benzenediazonium chloride to benzene while itself being oxidised to ethanal. Nitrogen gas is released. Thus C is benzene, C_6H_6, and the benzene ring remains intact throughout this sequence.

Step 5: Conclusion (a) $A = CH_3CH_2C \equiv N$, $B = CH_3CH_2C(=O)NH_2$, $C = CH_3CH_2NH_2$.
(b) A is aniline, $C_6H_5NH_2$; B is $[C_6H_5{-}N \equiv N]^+Cl^-$; C is benzene, C_6H_6.

Quick Tip to Solve: Track carbon count in (a): KCN adds one carbon and Hofmann degradation removes it; ethanol replaces the diazonium group by H in (b).

26. Write the reaction involved in the following :

(a) Wolff-Kishner reduction

(b) Decarboxylation reaction

(c) Cannizzaro reaction [3 marks]

Solution:

Concept:

- Wolff-Kishner reduction replaces the carbonyl oxygen of an aldehyde or ketone by two hydrogen atoms, using hydrazine and strong base on heating.
- Decarboxylation of a sodium carboxylate with soda lime gives an alkane containing one carbon atom fewer than the original carboxylate.
- Aldehydes without an α-hydrogen undergo Cannizzaro disproportionation in concentrated alkali: one molecule is reduced and another is oxidised.

Step 1: (a) Wolff-Kishner reduction The carbonyl compound first reacts with hydrazine to form a hydrazone. Heating it with KOH in a high-boiling solvent such as ethylene glycol gives the hydrocarbon, with liberation of nitrogen. For example, propanone gives propane:

$$\mathrm{CH_3COCH_3 + H_2NNH_2} \xrightarrow[\text{ethylene glycol, heat}]{\text{KOH}} \mathrm{CH_3CH_2CH_3 + N_2 + H_2O}.$$

The three-carbon chain is retained; only the carbonyl group is reduced to a methylene group.

Step 2: (b) Decarboxylation reaction Heat the sodium salt of a carboxylic acid with soda lime, a mixture of NaOH and CaO. The general equation is

$$\mathrm{RCOONa + NaOH} \xrightarrow[\Delta]{\text{CaO}} \mathrm{RH + Na_2CO_3}.$$

Sodium ethanoate, for example, gives methane:

$$\mathrm{CH_3COONa + NaOH} \xrightarrow[\Delta]{\text{CaO}} \mathrm{CH_4 + Na_2CO_3}.$$

Its carboxyl carbon enters the carbonate, so the hydrocarbon has one carbon fewer than the acid salt.

Step 3: (c) Cannizzaro reaction Benzaldehyde has no α-hydrogen and reacts with concentrated sodium hydroxide as follows:

$$\mathrm{2C_6H_5CHO + NaOH \longrightarrow C_6H_5CH_2OH + C_6H_5COONa}.$$

One benzaldehyde molecule is reduced to benzyl alcohol, while another is oxidised to sodium benzoate. The carboxylate salt, rather than free benzoic acid, is formed in this alkaline reaction mixture.

Step 4: Conclusion The required reactions are: (a) propanone to propane by Wolff-Kishner reduction; (b) sodium ethanoate to methane by soda-lime decarboxylation; (c) benzaldehyde to benzyl alcohol and sodium benzoate by Cannizzaro reaction, as shown in the balanced equations above.

Quick Tip to Solve: Remember the distinguishing conditions: hydrazine/KOH for Wolff-Kishner, soda lime for decarboxylation, and no alpha-H with concentrated alkali for Cannizzaro.

27. Give the equations of reactions for the preparation of : (any three)

(a) Phenol from chlorobenzene

(b) Salicylaldehyde from phenol

(c) 2-Methoxyacetophenone from anisole

(d) Picric acid from phenol [3 marks]

Solution:

Concept:

- Chlorobenzene undergoes nucleophilic substitution with aqueous alkali at high temperature and pressure; acidification of the phenoxide gives phenol.
- Phenol undergoes ortho formylation in the Reimer–Tiemann reaction and extensive nitration with concentrated nitric acid.
- The methoxy group activates anisole towards electrophilic substitution and directs an incoming acyl group to the ortho and para positions.

Step 1: (a) Hydrolyse chlorobenzene and acidify Heat chlorobenzene with aqueous sodium hydroxide at $623\,\text{K}$ and $300\,\text{atm}$, then acidify the sodium phenoxide obtained:

$$\text{C}_6\text{H}_5\text{Cl} + 2\,\text{NaOH} \xrightarrow{623\,\text{K},\,300\,\text{atm}} \text{C}_6\text{H}_5\text{ONa} + \text{NaCl} + \text{H}_2\text{O}$$

$$\text{C}_6\text{H}_5\text{ONa} + \text{HCl} \longrightarrow \text{C}_6\text{H}_5\text{OH} + \text{NaCl}$$

Step 2: (b) Formylate phenol by the Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, followed by acid work-up. The overall equation after work-up is:

$$\text{C}_6\text{H}_5\text{OH} + \text{CHCl}_3 + 3\,\text{NaOH} \longrightarrow \text{o-HOC}_6\text{H}_4\text{CHO} + 3\,\text{NaCl} + 2\,\text{H}_2\text{O}$$

The main product is salicylaldehyde (2-hydroxybenzaldehyde).

Step 3: (c) Acetylate anisole by Friedel–Crafts acylation React anisole with acetyl chloride in the presence of anhydrous aluminium chloride:

$$\text{C}_6\text{H}_5\text{OCH}_3 + \text{CH}_3\text{COCl} \xrightarrow{\text{anhyd}\cdot\,\text{AlCl}_3} \text{o-CH}_3\text{OC}_6\text{H}_4\text{COCH}_3 + \text{HCl}$$

Separate the required ortho product, 2-methoxyacetophenone, from the mixture; the para isomer is the major product.

Step 4: (d) Nitrate phenol exhaustively Treat phenol with concentrated nitric acid to obtain 2,4,6-trinitrophenol, called picric acid:

$$\text{C}_6\text{H}_5\text{OH} + 3\,\text{HNO}_3 \xrightarrow{\text{conc}\cdot} \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH} + 3\,\text{H}_2\text{O}$$

The three nitro groups occupy the two ortho positions and the para position relative to the hydroxyl group.

Step 5: Conclusion Any three preparations above answer the question; their products are phenol, salicylaldehyde, 2-methoxyacetophenone and picric acid, respectively.

Quick Tip to Solve: Match the new group to the reagent: use chloroform/alkali for ortho $-\text{CHO}$, acetyl chloride/AlCl_3 for $-\text{COCH}_3$, and concentrated HNO_3 for three nitro groups.

28. Give reasons for the following :

(a) Chlorine is ortho/para directing in electrophilic aromatic substitution reactions, though chlorine is an electron withdrawing group.

(b) Racemic mixture is optically inactive.

(c) Allyl chloride is hydrolysed more readily than n-propyl chloride. [3 marks]

Solution:

Concept:

- Inductive and resonance effects have different roles: the overall electron density affects aromatic reactivity, while relative intermediate stability determines orientation.
- Enantiomers rotate plane-polarised light by equal angles in opposite directions under identical conditions.
- Resonance delocalisation stabilises an allylic carbocation and assists nucleophilic substitution at an allylic carbon.

Step 1: (a) Distinguish chlorine's deactivation from its orientation Chlorine is electronegative and withdraws electron density through its strong negative inductive effect, $-I$. This effect predominates overall, so chlorobenzene is less reactive than benzene towards electrophilic substitution. However, a chlorine lone pair can donate into the aromatic ring by resonance, the $+R$ effect. This donation increases electron density particularly at the ortho and para positions and provides extra resonance stabilisation to the intermediates produced by attack at those positions. The meta intermediate lacks this corresponding stabilisation. Hence an electron-withdrawing chlorine substituent can still direct substitution to ortho and para positions.

Step 2: (b) Add the rotations of the enantiomers A racemic mixture contains equal amounts of the dextrorotatory and laevorotatory enantiomers. Each enantiomer is optically active, but their rotations have equal magnitude and opposite signs. Therefore,

$$\alpha_{\text{net}} = (+\alpha) + (-\alpha) = 0.$$

Its optical inactivity is due to external compensation between different molecules, not the absence of chirality in either enantiomer.

Step 3: (c) Compare the stability of the substitution intermediates Loss of chloride from allyl chloride gives an allylic carbocation whose positive charge is delocalised over two terminal carbon atoms:

$$\mathrm{CH_2{=}CH{-}CH_2^+} \longleftrightarrow \mathrm{CH_2^+{-}CH{=}CH_2}.$$

Resonance stabilisation makes this ion easier to form during hydrolysis. In contrast, loss of chloride from n-propyl chloride would produce the localised primary carbocation $\mathrm{CH_3CH_2CH_2^+}$, with no adjacent double bond for resonance. The allylic position also favours substitution through stabilisation of the transition state in a bimolecular pathway. Thus allyl chloride undergoes hydrolysis more readily.

Step 4: Conclusion Chlorine's resonance donation accounts for ortho/para direction despite inductive deactivation; equal opposite optical rotations cancel in a racemate; and resonance stabilisation enhances the hydrolysis of allyl chloride relative to n-propyl chloride.

Quick Tip to Solve: Keep the comparisons separate: $-I$ explains deactivation, $+R$ explains direction, equal enantiomer amounts explain cancellation, and allylic resonance explains easier substitution.

Section D (8 marks)

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

29(a). Case study: Transition metals have incomplete d-subshell either in neutral atom or in their ions. The presence of partly filled d-orbitals in their atoms makes transition elements different from that of the non-transition elements. With partly filled d-orbitals, these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic properties and paramagnetic behaviour. The transition metals are very hard and have low volatility. An examination of the $E^{\circ}_{M^{2+}/M}$ values shows the varying trends :

(a) On what basis can we say that Cu is a transition element but Zn is not ? (Atomic number : Cu = 29, Zn = 30) [1 mark]

	$E^{o}_{M^{2+}/M}$
V	– 1·18
Cr	– 0·91
Mn	– 1·18
Fe	– 0·44
Co	– 0·28
Ni	– 0·25
Cu	+ 0·34
Zn	– 0·76

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its usual ions.
- The $4s$ electrons are removed before $3d$ electrons when these atoms form positive ions; a full d subshell contains ten electrons.

Step 1: Examine copper and its common divalent ion Copper has the configuration $[\mathrm{Ar}]\,3d^{10}4s^{1}$, but its common ion Cu^{2+} has $[\mathrm{Ar}]\,3d^{9}$. The ion therefore contains a partially filled d subshell, so copper satisfies the definition even though the neutral atom has $3d^{10}$.

Step 2: Examine zinc and its usual ion Zinc has $[\mathrm{Ar}]\,3d^{10}4s^{2}$, and its usual ion Zn^{2+} has $[\mathrm{Ar}]\,3d^{10}$. Both have a completely filled d subshell. Merely belonging to the d-block is therefore insufficient to make zinc a transition element.

Step 3: Conclusion Copper is a transition element because Cu^{2+} is $3d^{9}$; zinc is not, because both its atom and usual ion retain $3d^{10}$.

Quick Tip to Solve: For the Cu–Zn comparison, write the divalent-ion configurations: d^{9} qualifies, whereas d^{10} does not.

29(b). Why do transition elements show variety of oxidation states ? [1 mark]

Solution:

Concept:

- The outer ns and penultimate $(n-1)d$ subshells of transition elements have comparable energies, where n is the outer principal quantum number.
- Oxidation state depends on the number of electrons lost or used in bonding; electrons from both these subshells can participate.

Step 1: Identify the electrons available for bonding The small energy difference between the ns and $(n-1)d$ orbitals allows a transition metal to use its outer s electrons as well as a variable number of d electrons in forming compounds. Bonding is therefore not restricted to a single fixed number of valence electrons.

Step 2: Relate different electron counts to oxidation states Participation of different numbers of these electrons produces several oxidation states. For example, iron, with configuration $[\mathrm{Ar}]\,3d^6 4s^2$, forms Fe^{2+} by losing its two $4s$ electrons and Fe^{3+} by losing one additional $3d$ electron.

Step 3: Conclusion Transition elements show variable oxidation states because their ns and $(n-1)d$ electrons have comparable energies and different numbers can participate in bonding.

Quick Tip to Solve: State both the cause and consequence: similar $ns/(n-1)d$ energies allow variable participation of s and d electrons.

29(c). (i) Why do $E^{\circ}_{\mathrm{M}^{2+}/\mathrm{M}}$ values show irregular trend from Vanadium to Zinc ?
(ii) How is the variability in oxidation states of transition metals different from that of the non-transition elements ?

[2 marks]

Solution:

Concept:

- The standard reduction potential for $\mathrm{M}^{2+}(\mathrm{aq}) + 2\,\mathrm{e}^- \longrightarrow \mathrm{M}\,(\mathrm{s})$ depends on the net energy change in forming the aqueous ion from the metal.
- Transition metals can use both $(n-1)d$ and ns electrons in bonding; their energies are close.

Step 1: Explain the irregular electrode potentials (i) Formation of $\mathrm{M}^{2+}(\mathrm{aq})$ involves atomisation of the metal, removal of two electrons and hydration of the gaseous ion. Thus the potential reflects the combined effects of atomisation enthalpy, the first two ionisation enthalpies and hydration enthalpy. These quantities do not vary uniformly from vanadium to zinc. Extra stability of particular electronic configurations, such as d^5 for Mn^{2+} and d^{10} for Zn^{2+}, also affects this energy balance and produces an irregular trend.

Step 2: Compare the spacing of oxidation states (ii) Transition metals commonly show successive oxidation states differing by one unit because different numbers of the nearby d and s electrons can participate. For example, manganese shows $+2, +3, +4, +5, +6, +7$. In non-transition elements, the commonly observed variable oxidation states generally differ by two units; examples are $+2, +4$ in tin

Quick Tip to Solve: For electrode potentials, combine atomisation, ionisation and hydration effects; for oxidation-state variability, compare the gaps between successive states.

and $+3, +5$ in phosphorus.

Step 3: Conclusion (i) Non-uniform atomisation, ionisation and hydration energy changes cause the irregular electrode-potential trend. (ii) Transition-metal oxidation states commonly differ by one, whereas those of non-transition elements generally differ by two.

Quick Tip to Solve: For electrode potentials, combine atomisation, ionisation and hydration effects; for oxidation-state variability, compare the gaps between successive states.

OR

29(c). (i) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing. Why ? (Atomic number : Cr = 24, Mn = 25)

(ii) Complete the following ionic equation : $2MnO_4^- + H_2O + I^- \rightarrow$ [2 marks]

Solution:

Concept:

- A reducing agent loses electrons and is oxidised; an oxidising agent gains electrons and is reduced. The stability of the resulting electronic configuration helps determine the direction.
- In neutral or weakly alkaline medium, permanganate is reduced to MnO_2, while iodide can be oxidised to iodate, IO_3^-.

Step 1: Compare the stable ions formed from the two d-four species (i) Both Cr^{2+} and Mn^{3+} have the configuration $[Ar]3d^4$. Chromium(II) readily loses an electron to form the more stable chromium(III), with a $3d^3$ configuration (t_{2g}^3 in its octahedral aqua complex):

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

Therefore Cr^{2+} reduces another species. In contrast, manganese(III) readily gains an electron to form manganese(II), whose $3d^5$ configuration is especially stable because it is half-filled:

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

Hence Mn^{3+} oxidises another species.

Step 2: Balance the permanganate-iodide reaction (ii) The given reactants use water rather than acid. Manganese changes from $+7$ in MnO_4^- to $+4$ in MnO_2, gaining three electrons per manganese atom. Iodine changes from -1 to $+5$ in IO_3^-, losing six electrons. Therefore two permanganate ions react with one iodide ion. Balancing oxygen, hydrogen and charge gives

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

The equation has nine oxygen atoms and two hydrogen atoms on each side; the total charge is -3 on each side.

Step 3: Conclusion Cr^{2+} is reducing because it forms stable Cr^{3+} (d^3); Mn^{3+} is oxidising because it forms stable Mn^{2+} (d^5). The ionic products are $2\,MnO_2 + IO_3^- + 2\,OH^-$.

Quick Tip to Solve: Compare the configurations reached by losing or gaining an electron; in the ionic equation, match the six-electron iodide change with two permanganate ions.

30(a). **Case study: Carbohydrates are essential for life in both plants and animals. Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Chemically they are polyhydroxy aldehydes or ketones. On the basis of their behaviour on hydrolysis, carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides. All monosaccharides are reducing sugars, i.e., they are oxidized by Tollens' reagent and Fehling's solution. A monosaccharide like glucose is aldohexose and its molecular formula was found to be $C_6H_{12}O_6$. After reacting with different reagents like HI, H_2N-OH, Bromine water, $(CH_3CO)_2O$, etc. its structure was found to contain one aldehyde group, one primary alcoholic group ($-CH_2OH$) and four secondary alcoholic groups ($>CHOH$). Despite having the aldehyde group, glucose does not give some of the reactions of aldehyde group like Schiff's test, $NaHSO_3$ addition. This explains the existence of glucose in two cyclic hemiacetal forms which differ only in the configuration of the hydroxyl group at C-1.**

(a) What are reducing sugars ? [1 mark]

Solution:

Concept:

- A reducing sugar reduces a mild oxidising reagent while its own functional group is oxidised.
- Tollens' reagent and Fehling's solution are standard tests for reducing sugars.

Step 1: Identify the chemical behaviour Sugars that reduce Tollens' reagent or Fehling's solution are called reducing sugars. In these reactions the sugar itself is oxidised; the word reducing describes its action on the reagent.

Step 2: Relate the definition to examples Glucose and fructose are examples, and all monosaccharides are reducing sugars. Glucose can supply a free aldehyde group through its open-chain form. Fructose, a ketose, also responds because it rearranges to aldoses in the alkaline test medium.

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

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

30(b). **Classify the following into monosaccharide and disaccharide : Fructose, Sucrose, Lactose, Galactose** [1 mark]

Solution:

Concept:

- A monosaccharide is a single carbohydrate unit that cannot be hydrolysed to a simpler carbohydrate.
- A disaccharide yields two monosaccharide molecules on hydrolysis of its glycosidic bond.

Step 1: Identify the single sugar units Fructose and galactose are monosaccharides. Each is one hexose unit; fructose is a ketohexose, whereas galactose is an aldohexose. Neither can be hydrolysed into smaller carbohydrate units.

Step 2: Identify the sugars made from two units Sucrose and lactose are disaccharides. On hydrolysis,

Quick Tip to Solve: Recall the hydrolysis pairs: sucrose gives glucose plus fructose; lactose gives glucose plus galactose.

sucrose yields glucose and fructose, whereas lactose yields glucose and galactose. Each therefore contains two monosaccharide units joined through a glycosidic linkage.

Step 3: Conclusion **Monosaccharides:** fructose and galactose. **Disaccharides:** sucrose and lactose.

Quick Tip to Solve: Recall the hydrolysis pairs: sucrose gives glucose plus fructose; lactose gives glucose plus galactose.

30(c). Name the polysaccharide which is known as 'animal starch'. Why is it called 'animal starch' ? [2 marks]

Solution:

Concept:

- A storage polysaccharide contains many linked monosaccharide units and can be broken down to provide glucose when energy is required.
- Starch is the main storage carbohydrate in plants, whereas glycogen performs the corresponding function in animals.

Step 1: Identify the animal storage polysaccharide The polysaccharide known as animal starch is **glycogen**. It is a highly branched polymer of α-D-glucose and is stored mainly in the liver and muscles of animals. Its glucose residues are linked primarily by $\alpha(1 \rightarrow 4)$ bonds, with $\alpha(1 \rightarrow 6)$ bonds at branch points.

Step 2: Explain its resemblance to starch Starch stores glucose in plants for later use, and glycogen serves the same storage role in animals. When glucose is needed, glycogen can be broken down to supply it. Its branched structure also resembles amylopectin, the branched component of starch, although glycogen is more extensively branched. The name therefore expresses both its animal occurrence and its similarity to starch in structure and function.

Step 3: Conclusion **Glycogen** is called animal starch because it is the reserve carbohydrate in animals, analogous to starch in plants, and is a branched glucose polymer resembling amylopectin.

Quick Tip to Solve: Pair the names with their storage sites: starch in plants and glycogen mainly in animal liver and muscles; this also explains the term animal starch.

OR

30(c). (i) Name the isomers of glucose which in the cyclic form differ only in the configuration of the $-$OH group at C-1.

(ii) Presence of which functional group was detected when glucose reacted with Br_2 water ? [2 marks]

Solution:

Concept:

- Anomers are cyclic sugar stereoisomers that differ only in configuration at the anomeric carbon, which is C-1 in glucose.

Quick Tip to Solve: A difference only at C-1 of cyclic glucose identifies anomers; oxidation with bromine water identifies its aldehyde group.

- Bromine water is a mild oxidising agent that converts the aldehyde group, $-\mathrm{CHO}$, into a carboxyl group, $-\mathrm{COOH}$.

Step 1: (i) Identify the two cyclic isomers The isomers are α-D-glucose and β-D-glucose, called **anomers**. Ring formation converts the aldehydic carbon C-1 into a new stereocentre. In the conventional Haworth structures of D-glucose, the C-1 hydroxyl group is below the ring in the α form and above it in the β form; the configurations at the other stereocentres remain unchanged.

Step 2: (ii) Identify the group oxidised by bromine water The reaction detects an **aldehyde group**. The open-chain form of glucose is oxidised to gluconic acid, while its terminal primary alcohol group remains unchanged under these mild conditions:

$$\mathrm{CHO(CHOH)_4CH_2OH + Br_2 + H_2O \longrightarrow COOH(CHOH)_4CH_2OH + 2\,HBr.}$$

Thus oxidation of the aldehydic end, rather than the alcoholic end, establishes the presence of $-\mathrm{CHO}$ in glucose.

Step 3: Conclusion (i) The cyclic isomers are α-D-glucose and β-D-glucose (anomers). (ii) Bromine water detects the aldehyde group, $-\mathrm{CHO}$.

Quick Tip to Solve: A difference only at C-1 of cyclic glucose identifies anomers; oxidation with bromine water identifies its aldehyde group.

Section E (15 marks)

31(a). (i) The resistance of 0.05 M CH_3COOH solution is found to be 100 ohm. If the cell constant is 0.0354 cm^{-1}, calculate the molar conductivity of the acetic acid solution.

(ii) State Faraday's first law of electrolysis. How much charge in Faraday is required for the reduction of 1 mol of MnO_4^- to Mn^{2+} ? [5 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. Conductivity is $\kappa = G(l/A)$, where l/A is the cell constant.
- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when κ is in S $\mathrm{cm^{-1}}$ and concentration c is in mol $\mathrm{L^{-1}}$.
- Faraday's first law relates the mass deposited or liberated to the charge passed: $m = ZQ = ZIt$, where Z is the electrochemical equivalent, I the current and t the time. One faraday, F, is the charge of one mole of electrons.

Step 1: (i) Calculate the conductance and conductivity The solution has resistance $R = 100\,\Omega$, so its conductance is

$$G = \frac{1}{R} = \frac{1}{100} = 0.0100\,\mathrm{S}.$$

Multiply by the given cell constant $0.0354\,\mathrm{cm^{-1}}$ to remove the effect of the cell geometry:

$$\kappa = G\frac{l}{A} = 0.0100 \times 0.0354 = 3.54 \times 10^{-4}\,\mathrm{S\ cm^{-1}}.$$

Quick Tip to Solve: Use $\Lambda_m = 1000(l/A)/(Rc)$ directly when resistance is given. For charge in faradays, multiply moles of ions by the decrease in oxidation number per ion.

Step 2: (i) Convert conductivity to molar conductivity For $c = 0.05\,\text{mol L}^{-1}$, substitute into the molar-conductivity expression:

$$\Lambda_m = \frac{1000 \times 3.54 \times 10^{-4}}{0.05} = 7.08\,\text{S cm}^2\,\text{mol}^{-1}.$$

The factor 1000 converts litres to cubic centimetres because conductivity uses centimetre units.

Step 3: (ii) State Faraday's first law The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte:

$$m \propto Q, \qquad m = ZQ = ZIt.$$

Here Z is the mass deposited per coulomb for the specified electrode reaction.

Step 4: (ii) Count the electrons required for permanganate reduction In MnO_4^-, the oxidation number x of manganese satisfies $x + 4(-2) = -1$, so $x = +7$. Reduction to Mn^{2+} lowers it to $+2$, requiring five electrons per ion:

$$\text{MnO}_4^- + 8\,\text{H}^+ + 5\,\text{e}^- \longrightarrow \text{Mn}^{2+} + 4\,\text{H}_2\text{O}.$$

One mole of permanganate therefore requires five moles of electrons. One mole of electrons carries one faraday, hence

$$Q = 5F \approx 5 \times 96485 = 4.82425 \times 10^5\,\text{C}.$$

Step 5: Conclusion (i) The molar conductivity is $\boxed{7.08\,\text{S cm}^2\,\text{mol}^{-1}}$. (ii) Faraday's first law is $m = ZQ$; reduction of 1 mol of MnO_4^- to Mn^{2+} requires $\boxed{5\text{ faradays}}$.

Quick Tip to Solve: Use $\Lambda_m = 1000(l/A)/(Rc)$ directly when resistance is given. For charge in faradays, multiply moles of ions by the decrease in oxidation number per ion.

OR

31(b). (i) The conductivity of $0.0025\,\text{mol L}^{-1}$ acetic acid is $5.25 \times 10^{-5}\,\text{S cm}^{-1}$. Calculate its degree of dissociation if Λ_m° for acetic acid is $390\,\text{S cm}^2\,\text{mol}^{-1}$.

(ii) Write anode, cathode and overall reaction of lead storage battery. [5 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$, when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1}. The factor 1000 converts litres into cubic centimetres.
- For a weak electrolyte such as acetic acid, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^\circ$, where Λ_m° is the molar conductivity at infinite dilution, corresponding to complete dissociation.
- During discharge of a lead storage battery, oxidation occurs at the lead anode and reduction occurs at the lead dioxide cathode. Both electrodes form PbSO_4, and sulphuric acid is consumed.

Quick Tip to Solve: Convert κ to Λ_m using $1000\kappa/c$ before dividing by 390. In the battery, both electrodes become PbSO_4 during discharge; balance the cathode in acidic medium.

Step 1: (i) Calculate the molar conductivity The given conductivity is $\kappa = 5.25 \times 10^{-5}\ \text{S cm}^{-1}$ and the concentration is $c = 0.0025\ \text{mol L}^{-1}$. Hence,

$$\Lambda_m = \frac{1000\kappa}{c} = \frac{1000(5.25 \times 10^{-5})}{0.0025} = 21\ \text{S cm}^2\ \text{mol}^{-1}.$$

Conductivity must first be converted into molar conductivity because the dissociation relation compares conductivities per mole at the given concentration and at infinite dilution.

Step 2: (i) Obtain the fraction of acid molecules dissociated Acetic acid dissociates according to $\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$. Using the given limiting molar conductivity,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\circ} = \frac{21}{390} = 0.05385.$$

The degree of dissociation is dimensionless because the conductivity units cancel. Expressed as a percentage, it is $100\alpha = 5.385\%$. The small value is consistent with acetic acid being a weak electrolyte at this concentration.

Step 3: (ii) Write the anode and cathode reactions during discharge At the negative anode, lead is oxidised from oxidation state 0 to +2 and releases two electrons:

$$\text{Pb(s)} + {\text{SO}_4}^{2-}\text{(aq)} \longrightarrow \text{PbSO}_4\text{(s)} + 2\,\text{e}^-.$$

At the positive cathode, lead in PbO_2 is reduced from +4 to +2. In the acidic electrolyte the balanced reduction half-reaction is

$$\text{PbO}_2\text{(s)} + {\text{SO}_4}^{2-}\text{(aq)} + 4\,\text{H}^+\text{(aq)} + 2\,\text{e}^- \longrightarrow \text{PbSO}_4\text{(s)} + 2\,\text{H}_2\text{O(l)}.$$

Sulphate ions supply the insoluble lead sulphate formed on both electrodes. The two electrons lost at the anode equal the two electrons gained at the cathode.

Step 4: (ii) Add the half-reactions Cancel the electrons and combine $4\,\text{H}^+$ and $2\,{\text{SO}_4}^{2-}$ as two formula units of sulphuric acid. The overall discharge reaction is

$$\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\,\text{H}_2\text{SO}_4\text{(aq)} \longrightarrow 2\,\text{PbSO}_4\text{(s)} + 2\,\text{H}_2\text{O(l)}.$$

This equation conserves lead, sulphur, oxygen and hydrogen. Acid concentration decreases during discharge. Supplying electrical energy during charging reverses the overall reaction, regenerating lead, lead dioxide and sulphuric acid.

Step 5: Conclusion (i) The degree of dissociation is $\boxed{\alpha \approx 0.0538}$, or approximately $\boxed{5.38\%}$. (ii) During discharge, the lead anode is oxidised and the lead dioxide cathode is reduced to PbSO_4; the overall reaction is $\text{Pb} + \text{PbO}_2 + 2\,\text{H}_2\text{SO}_4 \longrightarrow 2\,\text{PbSO}_4 + 2\,\text{H}_2\text{O}$.

Quick Tip to Solve: Convert κ to Λ_m using $1000\kappa/c$ before dividing by 390. In the battery, both electrodes become PbSO_4 during discharge; balance the cathode in acidic medium.

32. Answer any five of the following :

(a) How is the crystal field splitting energy for octahedral complex (Δ_o) related to that of tetrahedral complex (Δ_t) ?

(b) Write the IUPAC name of the following complex : $[PtCl_2(en)_2](NO_3)_2$

(c) Write the geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ on the basis of Valency Bond Theory (VBT).

(d) What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

(e) For the coordination compound on the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$. Is the coordination compound a high spin or low spin complex ?

(f) Out of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_4Cl_2]^+$, which complex is heteroleptic and why ?

(g) Draw the structures of optical isomers of $[PtCl_2(en)_2]^{2+}$. [5 marks]

Solution:

Concept:

- Crystal field splitting depends on ligand arrangement. For the same metal ion and ligands, tetrahedral splitting is approximately $\Delta_t = \frac{4}{9}\Delta_o$. The competition between octahedral splitting Δ_o and pairing energy P determines spin state.
- In naming a coordination compound, name ligands alphabetically, then the metal with its oxidation state, and finally the counter-ion. Ethane-1,2-diamine (en) is a neutral bidentate ligand.
- Valence bond theory relates hybridisation to geometry; unpaired electrons cause paramagnetism. A complex with all electrons paired is diamagnetic.
- Heteroleptic complexes contain more than one kind of ligand. Optical isomers are non-superimposable mirror images; chelating ligands can make an octahedral cis complex chiral.

Step 1: (a) Relate the splitting energies A tetrahedral field produces a smaller separation between its two sets of d orbitals than an octahedral field for the same metal ion and ligands. The standard relation is

$$\Delta_t = \frac{4}{9}\Delta_o, \qquad \Delta_o = \frac{9}{4}\Delta_t.$$

Thus, tetrahedral splitting is about 44% of the corresponding octahedral splitting.

Step 2: (b) Determine the oxidation state and name the salt The two nitrate counter-ions contribute charge -2, so the complex ion has charge $+2$. Each chlorido ligand has charge -1, whereas each en ligand is neutral. If the oxidation state of platinum is x, then

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

The name is **dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate**. The prefix bis is used for two ligands whose name already contains a numerical prefix; nitrate is named after the complex cation.

Step 3: (c) Apply VBT to nickel tetracarbonyl In $[Ni(CO)_4]$, carbon monoxide is neutral, so nickel is in oxidation state zero. Free nickel has configuration $[Ar]3d^8 4s^2$. In the presence of the strong-field CO ligands, the electrons pair to give a filled $3d^{10}$ set. The empty $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals, each accepting an electron pair from a ligand. Consequently the complex is **tetrahedral** and, with no unpaired electrons, **diamagnetic**.

Quick Tip to Solve: First calculate the metal oxidation state from the counter-ions. For the optical pair, place the two chlorido ligands cis, join each en ligand to adjacent sites, and reflect the entire arrangement including the chelate links.

Step 4: (d) Identify the isomerism involving both complex ions Both the cation and anion in $[Co(NH_3)_6][Cr(CN)_6]$ are coordination entities. Interchanging ligands between the two metal centres gives the coordination isomer $[Cr(NH_3)_6][Co(CN)_6]$. Therefore the compound shows **coordination isomerism**. This is distinct from ionisation isomerism, in which a coordinated ligand exchanges with a counter-ion outside the coordination sphere.

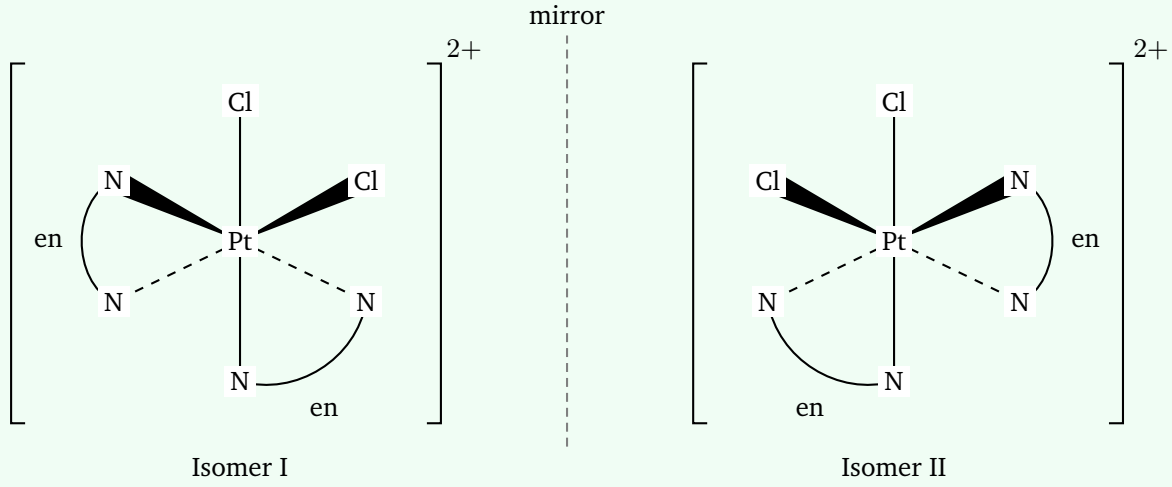
Step 5: (e) Fill the octahedral d orbitals Since $\Delta_o < P$, promoting the fourth electron to the higher e_g set costs less energy than pairing it in the lower t_{2g} set. The first three electrons singly occupy the three t_{2g} orbitals and the fourth singly occupies an e_g orbital:

$$d^4: \quad t_{2g}^3 e_g^1.$$

All four electrons are unpaired, so it is a **high-spin complex**.

Step 6: (f) Count the different kinds of ligand $[Co(NH_3)_4Cl_2]^+$ contains two types of ligand, ammine (NH_3) and chlorido (Cl^-), and is therefore **heteroleptic**. In contrast, $[Co(NH_3)_6]^{3+}$ contains only ammine ligands and is homoleptic. The distinction concerns the kinds of ligand, not the total number of donor atoms.

Step 7: (g) Construct the pair of optical isomers Platinum(IV) has six donor atoms around it: two chlorido ligands and the four nitrogen donors of two en ligands. In the **cis** arrangement, the chlorido ligands are adjacent. The two ways of arranging the chelate rings form the non-superimposable mirror images drawn below. Each curved N-to-N link represents one $-CH_2-CH_2-$ bridge, so the linked donor atoms belong to the same en ligand. Solid wedges point towards the reader and dashed bonds point away. The pair may be designated Δ and Λ; the trans arrangement is optically inactive.



Optical isomers of cis-$[PtCl_2(en)_2]^{2+}$. Each curved link joins the two nitrogen donors of one en ligand.

Step 8: Conclusion (a) $\Delta_t = \frac{4}{9}\Delta_o$. (b) Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate. (c) sp^3, tetrahedral, diamagnetic. (d) Coordination isomerism. (e) $t_{2g}^3 e_g^1$, high spin. (f) $[Co(NH_3)_4Cl_2]^+$, because it has two types of ligand. (g) The cis complex has the mirror-image pair shown. Any five of these seven parts may be attempted.

Quick Tip to Solve: First calculate the metal oxidation state from the counter-ions. For the optical pair, place the two chlorido ligands cis, join each en ligand to adjacent sites, and reflect the entire arrangement including the chelate links.

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

(1) Oxidation of aldehydes is easier as compared to ketones.

(2) The alpha (α) hydrogen atoms of aldehydes are acidic in nature.

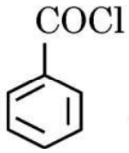
(ii) Write the products in the following reactions :

(1) $C_6H_5COCH_3 \xrightarrow{NaOH/I_2} ? + ?$

(2) $C_6H_5COCl + (CH_3)_2Cd \longrightarrow ? + CdCl_2$

(iii) Give a simple chemical test to distinguish between ethanoic acid and ethanal. [5 marks]

(1)  $\xrightarrow{NaOH\,/\,I_2}$? + ?

(2)  + $(CH_3)_2Cd \longrightarrow$? + $CdCl_2$

Solution:

Concept:

- An aldehyde has a hydrogen on its carbonyl carbon and is readily oxidised to a carboxylic acid. Oxidation of a ketone generally needs stronger conditions and cleavage of a carbon-carbon bond.
- An α-hydrogen is attached to the carbon next to the carbonyl group. Its removal gives a resonance-stabilised enolate ion.
- Methyl ketones, containing $-COCH_3$, undergo the iodoform reaction with iodine and alkali. Acid chlorides react with dialkylcadmium reagents to form ketones.
- Carboxylic acids liberate CO_2 from aqueous sodium hydrogencarbonate; aldehydes do not.

Step 1: (i)(1) Compare the bonds involved in oxidation An aldehyde RCHO can be converted to the corresponding carboxylic acid without breaking its carbon skeleton:

$$RCHO + [O] \longrightarrow RCOOH.$$

It has a hydrogen attached directly to the carbonyl carbon, which makes this oxidation easy; even mild oxidising agents such as Tollens' reagent oxidise aldehydes. A ketone has two carbon groups attached to its carbonyl carbon and no such hydrogen. Its oxidation usually involves breaking a strong carbon-carbon bond adjacent to the carbonyl group and therefore requires vigorous conditions. Thus aldehydes are more readily oxidised than ketones.

Step 2: (i)(2) Explain the acidity of the alpha hydrogen The electron-withdrawing carbonyl group polarises the bonds at the neighbouring carbon. When an α-hydrogen is removed as a proton, the conjugate base is stabilised by delocalisation of its negative charge between the alpha carbon and oxygen. For ethanal, the two important resonance contributors are

$$^{-}CH_2-CH=O \longleftrightarrow CH_2=CH-O^{-}.$$

Quick Tip to Solve: For an iodoform reaction, split $RCOCH_3$ into RCOONa and CHI_3; retain the salt form because the medium is alkaline.

Stabilisation of this enolate favours proton removal relative to an ordinary alkane. Hence aldehydes having an α-hydrogen show acidic character at that position; this does not mean they behave as strong acids in water.

Step 3: (ii)(1) Apply the iodoform reaction to acetophenone Acetophenone contains the required $-COCH_3$ group. Iodination of the methyl group followed by alkaline cleavage produces sodium benzoate and yellow iodoform. The balanced equation is

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow + 3\,NaI + 3\,H_2O.$$

The aromatic fragment remains as the benzoate salt in the alkaline medium; the methyl carbon becomes CHI_3.

Step 4: (ii)(2) Form the ketone from benzoyl chloride Dimethylcadmium supplies a methyl group to the acyl carbon of benzoyl chloride. The acid chloride is converted to a ketone, acetophenone, rather than undergoing the further addition typical of a Grignard reagent. With stoichiometric coefficients included,

$$2\,C_6H_5COCl + (CH_3)_2Cd \longrightarrow 2\,C_6H_5COCH_3 + CdCl_2.$$

The required organic product is therefore acetophenone (1-phenylethan-1-one).

Step 5: (iii) Perform the sodium hydrogencarbonate test Add aqueous sodium hydrogencarbonate separately to the two samples. Ethanoic acid gives brisk effervescence of carbon dioxide:

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2\uparrow.$$

Ethanal gives no such effervescence. The gas from the acid sample can be confirmed by passing it through limewater, which turns milky. This distinguishes the acid from the aldehyde directly.

Step 6: Conclusion (i) Aldehydes oxidise without carbon-carbon bond cleavage, whereas ketones generally require it; their α-hydrogens are acidic because the enolate is resonance-stabilised. (ii)(1) The products are C_6H_5COONa and CHI_3; (ii)(2) the organic product is $C_6H_5COCH_3$. (iii) With $NaHCO_3$, ethanoic acid evolves CO_2, while ethanal does not.

Quick Tip to Solve: For an iodoform reaction, split $RCOCH_3$ into $RCOONa$ and CHI_3; retain the salt form because the medium is alkaline.

OR

33(b). (i) Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(ii) Arrange the following in increasing order of their reactivity towards HCN: CH_3COCH_3, $(CH_3)_3C-COCH_3$, CH_3CHO.

(iii) How can you convert phenyl magnesium bromide to benzoic acid?

(iv) Give a simple chemical test to distinguish between benzaldehyde and ethanal.

(v) Write the main product in the following reaction: [5 marks]

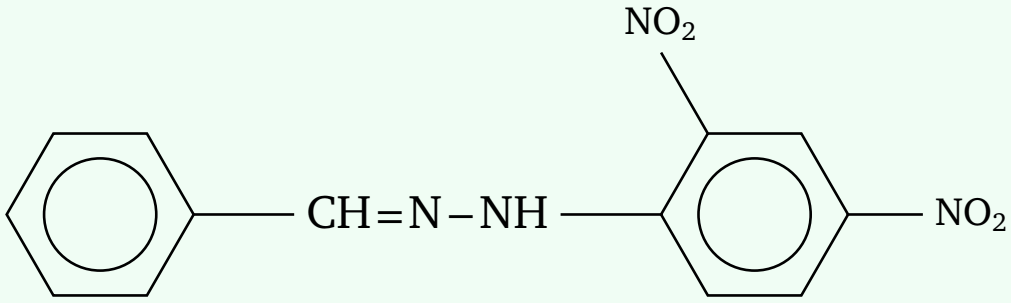
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-COOC_2H_5 \xrightarrow[(ii)\ H^+]{(i)\ NaBH_4} ?$$

Solution:

Concept:

- Aldehydes condense with 2,4-dinitrophenylhydrazine through their carbonyl group, eliminating water and forming a hydrazone containing C=N–NH.
- Addition of CN^- is favoured by a more electrophilic and less crowded carbonyl carbon; alkyl groups reduce electrophilicity through their electron-releasing effect.
- Grignard reagents add to CO_2 to form magnesium carboxylates; acidic hydrolysis gives the corresponding carboxylic acid.
- Ethanal gives the iodoform test, whereas benzaldehyde does not. $NaBH_4$ reduces an aldehyde or ketone carbonyl but normally leaves an ester group unchanged.

Step 1: (i) Form the benzaldehyde hydrazone The terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine reacts with the carbonyl group of benzaldehyde. Loss of water replaces C=O by C=N–NH, giving the structure drawn below. Its condensed formula is $C_6H_5CH{=}NNHC_6H_3(NO_2)_2$; the two nitro groups occupy positions 2 and 4 relative to the ring carbon bonded to –NH–. The hydrogen originally attached to the aldehyde carbon remains attached to the hydrazone carbon.



Benzaldehyde 2,4-dinitrophenylhydrazone: nitro groups are ortho and para to the hydrazone attachment.

Step 2: (ii) Compare electronic effects and steric hindrance Ethanal contains only one electron-releasing methyl group and one small hydrogen atom at the carbonyl carbon. It is therefore more electrophilic and less hindered than either ketone. Among the ketones, the bulky tert-butyl group obstructs attack by CN^- more strongly than a methyl group; its electron-releasing effect also reduces

Quick Tip to Solve: For a molecule containing both ketone and ester groups, mark the ketone before applying $NaBH_4$: change only that C=O into CH(OH) and retain the ester.

the carbonyl carbon's electrophilicity. Hence the increasing order is

$$(CH_3)_3C{-}COCH_3 < CH_3COCH_3 < CH_3CHO.$$

Step 3: (iii) Carboxylate the Grignard reagent and hydrolyse Treat phenyl magnesium bromide with dry carbon dioxide in anhydrous ether. Then perform acidic hydrolysis of the magnesium benzoate formed:

$$C_6H_5MgBr + CO_2 \xrightarrow{\text{dry ether}} C_6H_5COOMgBr,$$
$$C_6H_5COOMgBr + HCl \longrightarrow C_6H_5COOH + MgBrCl.$$

Carbon dioxide supplies the additional carbon atom of the carboxyl group. Water or acid is introduced only after the carbon dioxide reaction, since it would otherwise destroy the Grignard reagent.

Step 4: (iv) Apply the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Ethanal gives a yellow precipitate of iodoform, CHI_3; benzaldehyde gives no yellow iodoform precipitate. The positive reaction is

$$CH_3CHO + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3\downarrow + HCOONa + 3\,NaI + 3\,H_2O.$$

Ethanal has the required $CH_3{-}C(=O)$ arrangement with hydrogen as the remaining substituent. Benzaldehyde lacks this methyl-carbonyl unit. Tollens' test cannot distinguish this pair because both compounds are aldehydes and give a positive test.

Step 5: (v) Reduce only the ketone group In ethyl acetoacetate, $CH_3COCH_2COOC_2H_5$, the first carbonyl is a ketone, while the second belongs to an ester. Sodium borohydride reduces the ketone carbonyl to a secondary alcohol; the ester group remains unchanged. Protonation during acidic work-up gives

$$CH_3COCH_2COOC_2H_5 \xrightarrow[2.\ H^+]{1.\ NaBH_4} CH_3CH(OH)CH_2COOC_2H_5.$$

The product is ethyl 3-hydroxybutanoate. Numbering begins at the ester carbonyl carbon, so the new hydroxyl group is at carbon 3.

Step 6: Conclusion (i) The derivative is $C_6H_5CH{=}NNHC_6H_3(NO_2)_2$, with nitro groups at 2 and 4, as drawn. (ii) Reactivity increases as $(CH_3)_3C{-}COCH_3 < CH_3COCH_3 < CH_3CHO$. (iii) Use CO_2 in dry ether, then acid hydrolysis, to obtain benzoic acid. (iv) Ethanal alone gives yellow iodoform. (v) The main product is $CH_3CH(OH)CH_2COOC_2H_5$.

Quick Tip to Solve: For a molecule containing both ketone and ester groups, mark the ketone before applying $NaBH_4$: change only that $C{=}O$ into $CH(OH)$ and retain the ester.