CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-3-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of 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. Which of the following ligands can show linkage isomerism in a coordination compound ? [1 mark]

(A) NH_3

(B) SO_4^{2-}

(C) NO_2^-

(D) $C_2O_4^{2-}$

Correct Answer: (C) NO_2^-

Solution:

Concept:

- Linkage isomerism arises when an ambidentate ligand coordinates through either of two different donor atoms.
- An ambidentate ligand binds through one donor atom at a time; this differs from a chelating ligand, which binds through two donor atoms simultaneously.

Step 1: Identify the alternative donor atoms The nitrite ion, NO_2^-, can attach to a metal through nitrogen (nitro form) or through oxygen (nitrito form). These different metal–ligand linkages produce linkage isomers without changing the ligand's composition.

Step 2: Check the other ligands Ammonia coordinates through nitrogen. Sulphate coordinates through oxygen, while oxalate normally chelates through two oxygen atoms. These options do not offer the nitrogen-versus-oxygen donor choice responsible for the linkage isomerism tested here.

Step 3: Conclusion NO_2^- shows linkage isomerism. Hence, the correct option is (C).

Quick Tip to Solve: For linkage isomerism, look for two different possible donor atoms in the same ligand, as N and O in nitrite.

2. On adding $AgNO_3$ solution to 1 mole of complex $NiCl_2 \cdot 4NH_3$, two moles of AgCl are formed. The secondary valency of Ni in the complex will be : [1 mark]

(A) 4

(B) 2

(C) 3

(D) 6

Correct Answer: (A) 4

Solution:

Concept:

- Werner's secondary valency is the coordination number, the number of donor atoms directly bonded to the central metal.
- Chloride ions outside the coordination sphere are ionisable and precipitate with silver ions:

Quick Tip to Solve: First use the amount of AgCl to count outer-sphere chlorides, then count only the ligands inside the brackets.

$Ag^+ + Cl^- \longrightarrow AgCl(s)$.

Step 1: Locate the chloride ions One mole of the complex yields two moles of silver chloride. Thus, both chloride ions in $NiCl_2 \cdot 4NH_3$ are outside the coordination sphere; neither occupies a coordination site on nickel.

Step 2: Count the coordinated donor atoms The complex is therefore written $[Ni(NH_3)_4]Cl_2$. Each of the four ammonia molecules supplies one nitrogen donor atom. The value 2 is nickel's oxidation state (primary valency), not its coordination number; values 3 and 6 do not match the four coordinated ligands.

Step 3: Conclusion The secondary valency of nickel is 4. Hence, the correct option is (A).

Quick Tip to Solve: First use the amount of AgCl to count outer-sphere chlorides, then count only the ligands inside the brackets.

3. Transition elements form alloys easily because they have : [1 mark]

(A) same electronic configuration

(B) same enthalpies of atomisation

(C) same oxidation states

(D) nearly the same atomic size

Correct Answer: (D) nearly the same atomic size

Solution:

Concept:

- An alloy is a metallic mixture in which atoms of another element can occupy positions in a metal lattice.
- Similar atomic radii allow substitution of one metal atom by another with little distortion of the lattice.

Step 1: Relate atomic size to alloy formation Transition metals have nearly similar atomic sizes. Therefore, an atom of one transition metal can readily replace an atom of another in its crystal lattice, while preserving a stable metallic structure. This favours the formation of substitutional alloys.

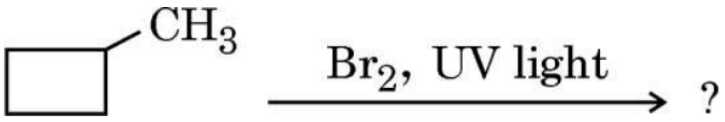
Step 2: Eliminate the other explanations Transition elements do not all have the same electronic configuration, the same enthalpy of atomisation or the same oxidation states. Those proposed equalities in (A), (B) and (C) are therefore incorrect. The size similarity in (D) directly explains the ease of atomic substitution.

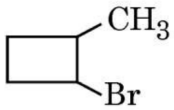
Step 3: Conclusion Transition elements form alloys easily because they have nearly the same atomic size. Hence, the correct option is (D).

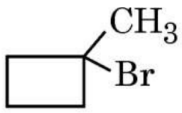
Quick Tip to Solve: For alloy formation, picture one metal atom replacing another in a lattice: similar size makes the substitution easier.

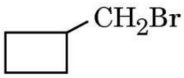
4. Consider the following reaction :

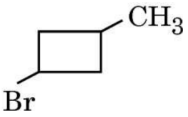
The major product obtained is : [1 mark]

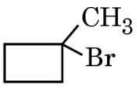


(A) 

(B) 

(C) 

(D) 

Correct Answer: (B) 

Solution:

Concept:

- Bromine under ultraviolet light reacts with an alkane by free-radical substitution; light causes homolytic cleavage of Br_2.
- Bromination is selective: hydrogen abstraction preferentially produces the more stable alkyl radical, with stability $3^\circ > 2^\circ > 1^\circ$.

Step 1: Identify the preferred hydrogen The printed reactant is methylcyclobutane. Its ring carbon bearing the methyl group is bonded to three carbon atoms and has one tertiary hydrogen. Abstraction of this hydrogen gives a tertiary radical; abstraction at the other ring carbons or the methyl group gives secondary or primary radicals, respectively.

Step 2: Match substitution at that carbon The tertiary radical takes bromine from Br_2, so Br replaces the hydrogen on the same ring carbon that bears CH_3. This is structure (B). Structures (A) and (D) represent secondary ring substitution, while (C) represents substitution in the primary methyl group; these are less favoured.

Step 3: Conclusion The major product is 1-bromo-1-methylcyclobutane. Hence, the correct option is (B).

Quick Tip to Solve: With bromine and UV light, count carbon neighbours at each hydrogen-bearing carbon and select the tertiary C–H site.

5. Which one of the following compounds has the highest pK_a value ? [1 mark]

(A) p-Nitrophenol

(B) m-Nitrophenol

(C) p-Cresol

(D) 2,4,6-Trinitrophenol

Correct Answer: (C) p-Cresol

Solution:

Concept:

- $\mathrm{p}K_a = -\log_{10} K_a$: a higher $\mathrm{p}K_a$ means a smaller acid dissociation constant and hence a weaker acid.
- Electron-withdrawing substituents stabilise the phenoxide ion and increase acidity; electron-donating substituents have the opposite effect.

Step 1: Examine the methyl substituent In p-cresol, the methyl group donates electron density through its positive inductive effect and hyperconjugation. This makes formation of the negatively charged phenoxide ion less favourable, so p-cresol is less acidic than phenol.

Step 2: Compare the nitro-substituted options Nitro groups withdraw electrons. The nitro group in m-nitrophenol increases acidity mainly through its inductive effect; at the para position it also stabilises phenoxide by resonance. Three nitro groups make 2,4,6-trinitrophenol especially acidic. Thus all three nitrophenols are stronger acids, with lower $\mathrm{p}K_a$, than p-cresol.

Step 3: Conclusion p-Cresol has the highest $\mathrm{p}K_a$. Hence, the correct option is (C).

Quick Tip to Solve: Translate highest pKa into weakest acid first, then choose the electron-donating methyl group over nitro groups.

6. $C_6H_5-O-CH_3$ when treated with HI gives : [1 mark]

(A) $C_6H_5-I + CH_3-OH$

(B) $C_6H_5-OH + CH_3-I$

(C) $C_6H_5-OH + CH_3-OH$

(D) $C_6H_5-I + CH_3-I$

Correct Answer: (B) $C_6H_5-OH + CH_3-I$

Solution:

Concept:

- Hydrogen iodide cleaves an ether after protonation of its oxygen atom, which makes the C–O bond easier to break.
- In an aryl methyl ether, iodide attacks the methyl carbon by the S_N2 mechanism; the aryl C–O bond has partial double-bond character due to resonance.

Step 1: Locate the bond that breaks Anisole, $C_6H_5OCH_3$, is protonated at oxygen. Iodide attacks its unhindered methyl carbon and breaks the $O - CH_3$ bond. Direct S_N2 attack at the aromatic sp^2

Quick Tip to Solve: For anisole plus HI, retain oxygen on the phenyl ring and attach iodine to the methyl group.

carbon does not occur, so the phenyl–oxygen bond remains intact.

Step 2: Identify the products Cleavage gives phenol and methyl iodide:

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I.$$

Options (A) and (D) incorrectly require formation of iodobenzene by breaking the aryl–oxygen bond. Option (C) gives methanol instead of the methyl iodide formed by iodide attack.

Step 3: Conclusion The products are C_6H_5OH and CH_3I. Hence, the correct option is (B).

Quick Tip to Solve: For anisole plus HI, retain oxygen on the phenyl ring and attach iodine to the methyl group.

7. Which of the following compounds on treatment with benzene sulphonyl chloride forms product insoluble in alkali ? [1 mark]

(A) $(CH_3)_3N$

(B) $(CH_3)_2NH$

(C) $CH_3CH_2NH_2$

(D) $C_6H_5NH_2$

Correct Answer: (B) $(CH_3)_2NH$

Solution:

Concept:

- In the Hinsberg test, primary and secondary amines react with benzene sulphonyl chloride to form sulphonamides.
- A sulphonamide containing an N–H bond can lose its acidic hydrogen and dissolve in alkali as a salt; an N,N-disubstituted sulphonamide has no such hydrogen.

Step 1: Examine the secondary amine Dimethylamine, $(CH_3)_2NH$, reacts to give $C_6H_5SO_2N(CH_3)_2$. Both nitrogen substituents are methyl groups, so the product has no N–H bond. It cannot form the corresponding salt with alkali and remains insoluble.

Step 2: Check the other amines Ethylamine and aniline, options (C) and (D), are primary amines; their sulphonamide products retain an acidic N–H bond and dissolve in alkali. Trimethylamine, option (A), is a tertiary amine and does not form a sulphonamide in this test. The question asks for an insoluble reaction product, not an unreacted amine.

Step 3: Conclusion $(CH_3)_2NH$ forms the alkali-insoluble sulphonamide. Hence, the correct option is (B).

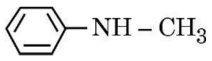
Quick Tip to Solve: Count N–H bonds in the sulphonamide product: a secondary amine leaves none, so its product is insoluble in alkali.

8. Which of the following amines gives carbylamine reaction ? [1 mark]

(A) $C_2H_5NH_2$

(B) $(C_2H_5)_2NH$

(C) $(C_2H_5)_3N$

(D) 

Correct Answer: (A) $C_2H_5NH_2$

Solution:

Concept:

- The carbylamine test is given only by primary amines, both aliphatic and aromatic, which contain the $-NH_2$ group.
- Heating a primary amine with chloroform and alcoholic potassium hydroxide produces an offensive-smelling isocyanide.

Step 1: Identify the primary amine In $C_2H_5NH_2$, nitrogen is attached to one ethyl group and two hydrogen atoms. It is therefore a primary amine and undergoes the reaction

$$C_2H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_2H_5NC + 3\,KCl + 3\,H_2O.$$

The reaction is carried out with alcoholic KOH on heating.

Step 2: Check the remaining options $(C_2H_5)_2NH$ and $C_6H_5NHCH_3$ are secondary amines because nitrogen is bonded to two carbon groups. $(C_2H_5)_3N$ is a tertiary amine. None contains the primary amino group needed for this test, so options (B), (C) and (D) fail.

Step 3: Conclusion Ethylamine, $C_2H_5NH_2$, gives the carbylamine reaction. Hence, the correct option is (A).

Quick Tip to Solve: Count the carbon groups directly bonded to nitrogen: only the option with one such group and two N–H bonds passes the carbylamine test.

9. 'Night-Blindness' is caused by the deficiency of Vitamin : [1 mark]

(A) B

(B) C

(C) K

(D) A

Correct Answer: (D) A

Solution:

Concept:

- Vitamins are organic nutrients needed in small amounts for normal physiological functions; their deficiency causes characteristic disorders.
- Vitamin A is required for normal vision, especially adaptation to dim light, because its derivative retinal forms part of the visual pigment in rod cells.

Step 1: Relate the disorder to its function Night-blindness is difficulty seeing in dim light. A deficiency

Quick Tip to Solve: For vitamin-deficiency questions, pair A with dim-light vision, C with scurvy, and K with blood clotting before selecting the option letter.

of vitamin A impairs the normal functioning and regeneration of the visual pigment rhodopsin in the retina, so dim-light vision is affected.

Step 2: Eliminate the other vitamins Vitamin B is a group of vitamins associated with functions such as metabolism and nerve health. Vitamin C deficiency causes scurvy, while vitamin K is needed for normal blood clotting. These do not match the standard deficiency association for night-blindness.

Step 3: Conclusion Night-blindness is caused by deficiency of vitamin A. Hence, the correct option is (D).

Quick Tip to Solve: For vitamin-deficiency questions, pair A with dim-light vision, C with scurvy, and K with blood clotting before selecting the option letter.

10. A 1% solution of solute 'X' is isotonic with a 6% solution of sucrose (molar mass = 342 g mol^{-1}). The molar mass of solute 'X' is : [1 mark]

(A) 34.2 g mol^{-1}

(B) 57 g mol^{-1}

(C) 114 g mol^{-1}

(D) 3.42 g mol^{-1}

Correct Answer: (B) 57 g mol^{-1}

Solution:

Concept:

- Isotonic solutions have equal osmotic pressures at the same temperature. For a dilute nonelectrolyte solution, $\pi = CRT$, where C is molar concentration, R the gas constant and T absolute temperature.
- On the mass-per-volume percentage basis used here, a 1% solution contains 1 g solute per 100 mL solution; molarity equals mass divided by molar mass and volume in litres.

Step 1: Equate the molar concentrations Treat the solutes as non-dissociating, as in the stated osmotic-pressure comparison. Taking 100 mL of each solution gives 1 g of X and 6 g of sucrose. If M_X is the molar mass of X, equality of osmotic pressures gives

$$\frac{1}{M_X(0.100)}RT = \frac{6}{342(0.100)}RT.$$

Step 2: Solve the mass-ratio relation Cancel the common volume and RT, then rearrange:

$$\frac{1}{M_X} = \frac{6}{342}, \qquad M_X = \frac{342}{6} = 57\ \text{g mol}^{-1}.$$

Options (A), (C) and (D) give unequal numbers of solute particles in the same volume, so they do not satisfy the isotonic condition.

Step 3: Conclusion The molar mass of X is 57 g mol^{-1}. Hence, the correct option is (B).

Quick Tip to Solve: For isotonic nonelectrolyte solutions expressed on the same percentage basis, divide the percentages by the respective molar masses and equate.

11. When the initial concentration of a reactant is doubled in the reaction, the half life period remains same. The order of reaction is : [1 mark]

(A) First

(B) Second

(C) Zero

(D) $\frac{1}{2}$

Correct Answer: (A) First

Solution:

Concept:

- Half-life $t_{1/2}$ is the time required for the reactant concentration to decrease to half its initial value, denoted by $[A]_0$.
- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant. It is independent of $[A]_0$.

Step 1: Use the stated half-life behaviour Doubling $[A]_0$ leaves the observed half-life unchanged. In the first-order expression, initial concentration does not occur, so this behaviour follows directly from $t_{1/2} = 0.693/k$ at a fixed temperature.

Step 2: Test the other orders For zero order, $t_{1/2} = [A]_0/(2k)$, so doubling concentration doubles half-life. For second order, $t_{1/2} = 1/(k[A]_0)$, so it halves. For order $1/2$, half-life is proportional to $[A]_0^{1/2}$, so it increases by $\sqrt{2}$. Thus none of the other printed options predicts an unchanged half-life.

Step 3: Conclusion The reaction is first order. Hence, the correct option is (A).

Quick Tip to Solve: An unchanged half-life when initial concentration changes is the direct signature of first-order kinetics at fixed temperature.

12. Which of the following is a secondary cell ? [1 mark]

(A) Dry cell

(B) Lead storage cell

(C) Mercury cell

(D) Daniell cell

Correct Answer: (B) Lead storage cell

Solution:

Concept:

- A secondary cell is a rechargeable electrochemical cell: an external current can reverse its discharge reaction and regenerate the active electrode materials.
- A lead storage cell uses lead and lead dioxide electrodes with aqueous sulphuric acid. Its discharge products can be converted back during charging.

Step 1: Identify the reversible storage reaction During discharge of a lead storage cell, both electrodes

Quick Tip to Solve: Look for regeneration of the original electrode materials on charging; lead storage cells meet this defining feature of secondary cells.

form lead sulphate:

$$Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O.$$

Applying a suitable external charging voltage reverses this reaction, regenerating Pb, PbO_2 and sulphuric acid. This makes the cell reusable.

Step 2: Compare the other listed cells The usual dry cell and mercury cell are primary cells whose chemicals are not conveniently regenerated by charging. The Daniell cell is a galvanic cell used to illustrate spontaneous electricity generation and is not the rechargeable storage cell among these choices.

Step 3: Conclusion The lead storage cell is a secondary cell. Hence, the correct option is (B).

Quick Tip to Solve: Look for regeneration of the original electrode materials on charging; lead storage cells meet this defining feature of secondary cells.

13. Assertion (A): $\Delta_{mix}H$ and $\Delta_{mix}V$ are zero for non-ideal solutions.

Reason (R): Solute-solvent interactions are not same as pure solute-solute and pure solvent-solvent interactions in non-ideal solutions. [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:

- Ideal solutions obey Raoult's law over the entire concentration range and have $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$, where these denote enthalpy and volume changes on mixing.
- Non-ideal solutions have unlike solute–solvent interactions differing from the like interactions in the pure components, causing departures from ideal mixing behaviour.

Step 1: Evaluate the assertion The assertion assigns zero enthalpy and volume changes on mixing to non-ideal solutions. These are the characteristic ideal-solution conditions. Non-ideal mixing generally involves heat absorption or release and a volume change, so the assertion is false.

Step 2: Evaluate the reason In a non-ideal solution, the attraction between unlike solute and solvent molecules differs from the attractions between molecules in each pure component. This difference gives rise to deviations from Raoult's law. The reason is therefore true.

Step 3: Check the explanatory relation The stated difference in interactions accounts for non-ideal behaviour, including nonzero mixing changes, rather than supporting the assertion of zero changes. Since the assertion is false and the reason true, the options treating the assertion as true are excluded.

Quick Tip to Solve: Associate zero enthalpy and volume changes on mixing with ideal solutions; unequal unlike and like interactions signal non-ideality.

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

Quick Tip to Solve: Associate zero enthalpy and volume changes on mixing with ideal solutions; unequal unlike and like interactions signal non-ideality.

14. Assertion (A): Rate of reaction increases with increase in temperature.

Reason (R): Number of effective collisions increase with increase in temperature. [1 mark]

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

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

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

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

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

Solution:

Concept:

- An effective collision has sufficient energy to overcome the activation-energy barrier and a suitable molecular orientation for reaction.
- Increasing temperature increases the fraction of molecules having energy equal to or greater than the activation energy, thereby increasing effective collisions per unit time.

Step 1: Evaluate the assertion In the usual collision-theory description of a reaction, increasing temperature increases the rate constant and hence the reaction rate at the same concentrations. The assertion is true.

Step 2: Evaluate the reason At a higher temperature, molecular kinetic energies are greater and a larger fraction of collisions crosses the activation-energy barrier. Thus the number of effective collisions per unit time increases. The reason is true; it refers to successful collisions, not merely every collision between molecules.

Step 3: Link effective collisions to the rate Effective collisions produce chemical change. More such collisions per unit time directly cause faster product formation, so the reason correctly explains the assertion. Option (B) incorrectly denies this link, while (C) and (D) incorrectly treat one of the statements as 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: When temperature is raised, focus on the increased fraction of collisions with sufficient energy; this is the direct link to a faster reaction.

15. Assertion (A): The boiling point of ethanol is higher than that of dimethyl ether.
Reason (R): Dimethyl ether molecules are associated through hydrogen bonding. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Intermolecular hydrogen bonding requires a hydrogen bonded directly to an electronegative atom such as oxygen.
- Stronger intermolecular attractions require more energy to separate molecules and therefore raise the boiling point.

Step 1: Evaluate the assertion Ethanol, CH_3CH_2OH, has an $O-H$ group and forms intermolecular hydrogen bonds. Dimethyl ether, CH_3OCH_3, has the same molecular formula but lacks this group. Ethanol therefore has a higher boiling point, so Assertion (A) is true.

Step 2: Evaluate the reason Dimethyl ether contains oxygen with lone pairs but has no hydrogen directly attached to oxygen. Its pure molecules cannot form hydrogen bonds with one another. Thus Reason (R) is false; accepting hydrogen bonds from water would not establish self-association.

Step 3: Check the explanation and options The higher boiling point is explained by hydrogen bonding between ethanol molecules. The stated reason assigns this association to the ether, so it cannot explain the assertion. Options (A) and (B) incorrectly treat R as true, while (D) incorrectly treats A as false.

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

Quick Tip to Solve: For isomeric alcohols and ethers, check for an oxygen-bound hydrogen: the alcohol can hydrogen-bond with itself.

16. Assertion (A): Aniline undergoes Friedel-Crafts reaction.

Reason (R): Aniline forms salt with $AlCl_3$, the Lewis acid in Friedel-Crafts reaction. [1 mark]

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

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

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

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

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

Solution:

Concept:

- Friedel-Crafts alkylation and acylation use the Lewis acid $AlCl_3$ to generate an electrophile.
- Aniline is a Lewis base: the nitrogen lone pair can bind to the Lewis acid, changing the reactivity of its aromatic ring.

Step 1: Evaluate the assertion Aniline does not undergo the usual Friedel-Crafts reaction. Although the free amino group activates the benzene ring, the catalyst interacts with this group under Friedel-Crafts conditions. Assertion (A) is therefore false.

Step 2: Evaluate the reason Aniline forms a salt with $AlCl_3$, the Lewis acid catalyst. Nitrogen donates its lone pair to the Lewis acid, and the resulting nitrogen-containing group strongly deactivates the ring towards electrophilic substitution. Reason (R) is true.

Step 3: Relate the statements Salt formation explains why the normal Friedel-Crafts reaction fails for aniline. It does not support the assertion that the reaction occurs. Options (A) and (B) require a true assertion, and (C) requires a false reason; neither condition applies here.

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

Quick Tip to Solve: Before applying the activating effect of an amino group, check whether the Lewis acid catalyst binds its nitrogen lone pair.

Section B (10 marks)

17. Write the reactions of glucose with :

(a) H_2N-OH

(b) Br_2 water [2 marks]

Solution:

Concept:

- The open-chain form of glucose contains an aldehyde group, $-CHO$, which undergoes characteristic carbonyl reactions.
- Hydroxylamine converts an aldehyde to an oxime; bromine water mildly oxidises an aldehyde to a carboxylic acid.

Quick Tip to Solve: Track only the aldehyde end: hydroxylamine changes it to $CH=NOH$, whereas bromine water changes it to $COOH$.

Step 1: React glucose with hydroxylamine (a) The carbonyl group condenses with hydroxylamine, NH_2OH, eliminating water to give glucose oxime:

$$HOCH_2(CHOH)_4CHO + NH_2OH \longrightarrow HOCH_2(CHOH)_4CH{=}NOH + H_2O.$$

The terminal aldehyde carbon becomes the carbon of the $CH{=}NOH$ group. The remaining hydroxyl groups are unchanged. This reaction establishes the presence of a carbonyl group in glucose.

Step 2: Oxidise glucose with bromine water (b) Bromine water oxidises the aldehyde end to a carboxyl group, producing gluconic acid:

$$HOCH_2(CHOH)_4CHO + Br_2 + H_2O \longrightarrow HOCH_2(CHOH)_4COOH + 2\,HBr.$$

This mild oxidising agent leaves the terminal CH_2OH group intact. Formation of gluconic acid therefore confirms that the carbonyl group is aldehydic; oxidation of both ends would require a stronger oxidising agent.

Step 3: Conclusion Glucose gives glucose oxime with hydroxylamine and gluconic acid with bromine water, according to the balanced equations above.

Quick Tip to Solve: Track only the aldehyde end: hydroxylamine changes it to $CH{=}NOH$, whereas bromine water changes it to $COOH$.

18. Complete and balance the following chemical equations :

(a) $KMnO_4 \xrightarrow{\Delta}$ **?**

(b) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow$ **?** [2 marks]

Solution:

Concept:

- Heating potassium permanganate produces potassium manganate, manganese dioxide and oxygen.
- In acidic medium, permanganate is reduced to Mn^{2+}, while oxalate is oxidised to carbon dioxide. Balance both atoms and net ionic charge.

Step 1: Balance the thermal decomposition (a) The balanced decomposition equation is

$$2\,KMnO_4 \xrightarrow{\Delta} K_2MnO_4 + MnO_2 + O_2.$$

Two potassium atoms require one unit of potassium manganate. Of the two manganese atoms, one occurs in manganate and one in manganese dioxide. The eight oxygen atoms on the left are distributed as four, two and two on the right.

Step 2: Combine the redox half-reactions (b) The reduction and oxidation half-reactions are

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O,$$
$$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^-.$$

Quick Tip to Solve: In acid, each permanganate ion gains five electrons and each oxalate ion loses two, immediately giving the ratio $2 : 5$.

Multiply the first by 2 and the second by 5 to cancel ten electrons. Adding gives

$$2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O.$$

The net charge is $+4$ on each side; manganese, carbon, oxygen and hydrogen are all balanced.

Step 3: Conclusion (a) The products are $K_2MnO_4 + MnO_2 + O_2$, with $2KMnO_4$ on the left. (b) The products are $2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$, with the printed reactant coefficients unchanged.

Quick Tip to Solve: In acid, each permanganate ion gains five electrons and each oxalate ion loses two, immediately giving the ratio $2 : 5$.

19(a). Define molal depression constant. How is it related to enthalpy of fusion ? [2 marks]

Solution:

Concept:

- For a dilute ideal solution of a nonvolatile, non-dissociating solute, freezing-point depression is $\Delta T_f = K_f m$, where m is molality.
- The molal depression constant K_f is a property of the solvent; it depends on its normal freezing temperature and molar enthalpy of fusion.

Step 1: Define the molal depression constant The molal depression constant, or cryoscopic constant, is the depression in freezing point produced when one mole of a nonvolatile solute is dissolved in one kilogram of solvent, for an ideal dilute solution with no association or dissociation. Equivalently, $K_f = \Delta T_f / m$, so its unit is $\mathrm{K\,kg\,mol^{-1}}$.

Step 2: Relate the constant to enthalpy of fusion The thermodynamic relation for a dilute solution is

$$\Delta T_f = \frac{R(T_f^0)^2}{\Delta_{\mathrm{fus}} H}\, x_2,$$

where x_2 is the solute mole fraction. If the solvent molar mass M_1 is expressed in $\mathrm{g\,mol^{-1}}$, then $x_2 \simeq mM_1/1000$. Comparing with $\Delta T_f = K_f m$ yields

$$K_f = \frac{R(T_f^0)^2 M_1}{1000\,\Delta_{\mathrm{fus}} H}.$$

Here T_f^0 is the freezing temperature of the pure solvent in kelvin, R is the gas constant, and $\Delta_{\mathrm{fus}} H$ is the molar enthalpy of fusion in $\mathrm{J\,mol^{-1}}$. If M_1 is in $\mathrm{kg\,mol^{-1}}$, omit the factor 1000.

Step 3: Conclusion K_f is the freezing-point depression per unit molality, and

$$K_f = \frac{R(T_f^0)^2 M_1}{1000\,\Delta_{\mathrm{fus}} H}$$

for M_1 in $\mathrm{g\,mol^{-1}}$.

Quick Tip to Solve: Use the pure solvent's freezing point in kelvin, and retain the factor 1000 only when its molar mass is entered in grams per mole.

OR

19(b). What type of deviation is shown by ethanol and acetone mixture ? Give reason. What type of azeotropic mixture is formed by that deviation ? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution is $p_i = x_i p_i^\circ$, where x_i is the liquid mole fraction and p_i° is the pure-component vapour pressure.
- Weaker attractions between unlike molecules allow easier escape into the vapour phase, producing positive deviation from Raoult's law.

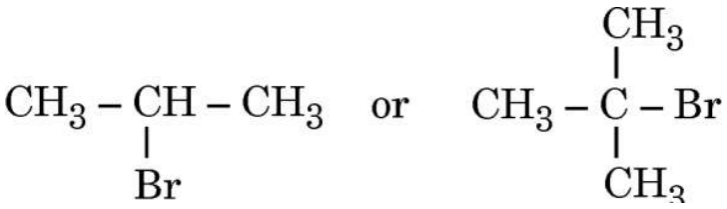
Step 1: Compare the intermolecular attractions Pure ethanol molecules are associated through intermolecular hydrogen bonding. Adding acetone disrupts some of these ethanol–ethanol hydrogen bonds. Although ethanol and acetone can interact, their effective unlike-molecule attractions are weaker than the attractions in the pure liquids. Thus the molecules escape more readily and the vapour pressure is higher than the ideal value: the mixture shows positive deviation.

Step 2: Connect vapour pressure with the boiling point A liquid boils when its vapour pressure equals the external pressure. An unusually high vapour pressure therefore allows the mixture to boil at a lower temperature. A sufficiently large positive deviation gives a minimum-boiling azeotrope. At its azeotropic composition, the liquid and vapour have the same composition and the mixture distils at a constant temperature.

Step 3: Conclusion The ethanol–acetone mixture shows **positive deviation** because mixing weakens the net intermolecular attractions by disrupting ethanol hydrogen bonding. It forms a **minimum-boiling azeotrope**.

Quick Tip to Solve: Follow the chain: weaker attractions, higher vapour pressure, lower boiling point, then minimum-boiling azeotrope.

20. (a) Which halogen compound in the following pair will react faster in S_N1 reaction and why?
(b) Why is the dipole moment of chlorobenzene lower than that of cyclohexyl chloride? [2 marks]



Solution:

Concept:

- In an S_N1 reaction, slow heterolytic carbon–halogen bond cleavage forms a carbocation. A more stable carbocation is formed more readily.
- The dipole moment is $\mu = qr$, where q is the separated charge and r is the separation. Bond

Quick Tip to Solve: With the leaving group fixed, rank carbocation stability for SN1; for dipole moment, consider both charge separation and bond length.

polarity and bond length both influence its magnitude.

Step 1: Compare the carbocations in part (a) The two compounds have the same leaving group, bromide. 2-Bromopropane, $CH_3CH(Br)CH_3$, forms a secondary carbocation, whereas tert-butyl bromide, $(CH_3)_3CBr$, forms a tertiary carbocation:

$$(CH_3)_3CBr \longrightarrow (CH_3)_3C^+ + Br^-.$$

Three alkyl groups stabilise the tertiary carbocation by their electron-releasing inductive effect and hyperconjugation more effectively than the two alkyl groups stabilise the secondary carbocation. Hence ionisation, and therefore the S_N1 reaction, is faster for tert-butyl bromide.

Step 2: Explain the dipole-moment difference in part (b) In chlorobenzene, a chlorine lone pair is conjugated with the benzene ring. Resonance gives the carbon–chlorine bond partial double-bond character, making it shorter than the corresponding single bond in cyclohexyl chloride. Also, chlorine is attached to an sp^2-hybridised carbon in chlorobenzene; this carbon is more electronegative than the sp^3-hybridised carbon in cyclohexyl chloride, reducing the bond's charge separation. The shorter, less polar bond accounts for the lower dipole moment of chlorobenzene.

Step 3: Conclusion (a) $(CH_3)_3CBr$ reacts faster by S_N1, owing to its more stable tertiary carbocation. (b) Chlorobenzene has a shorter, less polar carbon–chlorine bond and therefore a lower dipole moment than cyclohexyl chloride.

Quick Tip to Solve: With the leaving group fixed, rank carbocation stability for SN1; for dipole moment, consider both charge separation and bond length.

21. (a) In a reaction, if the concentration of reactant 'X' is tripled, the rate of reaction becomes twenty-seven times. What is the order of the reaction ?

(b) State a condition under which a bimolecular reaction is kinetically a first-order reaction. Give an example of such a reaction. [2 marks]

Solution:

Concept:

- In the rate law $r = k[X]^n$, n is the order with respect to X, r is the reaction rate and k is the rate constant at the given temperature.
- If one reactant of a bimolecular reaction is in large excess, its concentration remains effectively constant and can be included in an observed rate constant.

Step 1: Use the rate ratio in part (a) Keep temperature and other reactant concentrations unchanged and write the rates before and after tripling $[X]$:

$$r_1 = k[X]^n, \qquad r_2 = k(3[X])^n.$$

Quick Tip to Solve: Convert the rate multiplier to a power of the concentration multiplier: $27 = 3^3$. For pseudo-first-order kinetics, identify the excess reactant.

Dividing cancels both the rate constant and the original concentration:

$$\frac{r_2}{r_1} = 3^n = 27 = 3^3.$$

Thus the order with respect to X, and the reaction order for the stated dependence, is $n = 3$.

Step 2: State the pseudo-first-order condition and example For $r = k[A][B]$, take B in such a large excess that its concentration changes negligibly during the reaction. Then $r = k'[A]$, with $k' = k[B]$ effectively constant. The observed kinetics is first order although the underlying reaction involves two reactant molecules. Acid-catalysed hydrolysis of ethyl ethanoate in excess water is an example:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH.$$

At fixed acid concentration, water acts as the solvent and is in large excess, so the observed rate is proportional to the ester concentration.

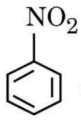
Step 3: Conclusion (a) The reaction is third order with respect to X. (b) A bimolecular reaction becomes pseudo-first-order when one reactant is in large excess; ester hydrolysis in excess water is an example.

Quick Tip to Solve: Convert the rate multiplier to a power of the concentration multiplier: $27 = 3^3$. For pseudo-first-order kinetics, identify the excess reactant.

Section C (21 marks)

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

(a) $CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0°C]{HNO_2} C$

(b)  $\xrightarrow{Fe/HCl} A \xrightarrow[273\ K]{NaNO_2 + HCl} B \xrightarrow{C_6H_5OH} C$

Solution:

Concept:

- Cyanide substitution adds one carbon; nitrile reduction changes $-CN$ into $-CH_2NH_2$ without altering the carbon skeleton.
- Nitrous acid converts primary aliphatic amines into alcohols, whereas aromatic primary amines form diazonium salts at low temperature.
- Benzenediazonium salts couple with phenol, mainly at its free para position, to form an azo linkage, $-N{=}N-$.

Step 1: Identify the three products in sequence (a) Cyanide from KCN replaces chloride through its carbon end. This forms propanenitrile, so $A = CH_3CH_2CN$. Its three-carbon chain includes the carbon introduced by cyanide. Reduction with $LiAlH_4$ converts the nitrile group to a primary amino

Quick Tip to Solve: Count the extra carbon introduced by KCN; then distinguish alcohol formation by an aliphatic amine from diazotisation and azo coupling of an aromatic amine.

group, giving propan-1-amine, B = $CH_3CH_2CH_2NH_2$:

$$CH_3CH_2CN + 4\,[H] \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2.$$

Nitrous acid then replaces the amino group with a hydroxyl group through an unstable aliphatic diazonium intermediate:

$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2 + H_2O.$$

Therefore C = $CH_3CH_2CH_2OH$, propan-1-ol.

Step 2: Identify the three products in sequence (b) Iron and hydrochloric acid reduce nitrobenzene's nitro group to an amino group, giving aniline after work-up: A = $C_6H_5NH_2$. Sodium nitrite and hydrochloric acid generate nitrous acid in situ. At 273 K, aniline undergoes diazotisation:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2{}^+Cl^- + NaCl + 2\,H_2O.$$

Thus B is benzenediazonium chloride, $[C_6H_5{-}N{\equiv}N]^+\,Cl^-$. Coupling with phenol, conventionally in mildly alkaline solution, occurs predominantly para to the activating hydroxyl group. It forms C, *p*-hydroxyazobenzene, $C_6H_5{-}N{=}N{-}C_6H_4{-}OH$, with OH para to the azo group. The two diazonium nitrogen atoms remain in the azo linkage.

Step 3: Conclusion (a) A = CH_3CH_2CN, B = $CH_3CH_2CH_2NH_2$, C = $CH_3CH_2CH_2OH$.
(b) A = $C_6H_5NH_2$, B = $[C_6H_5{-}N{\equiv}N]^+\,Cl^-$, and C = $C_6H_5{-}N{=}N{-}C_6H_4{-}OH$, with OH para to $-N{=}N-$.

Quick Tip to Solve: Count the extra carbon introduced by KCN; then distinguish alcohol formation by an aliphatic amine from diazotisation and azo coupling of an aromatic amine.

23. How will you bring about the following conversions ? (any three)

(a) Benzoic acid to Benzaldehyde

(b) Ethanal to Propanone

(c) Acetophenone to Benzoic acid

(d) Bromobenzene to 1-Phenylethanol [3 marks]

Solution:

Concept:

- Rosenmund reduction selectively converts an acid chloride to an aldehyde using hydrogen and poisoned $Pd/BaSO_4$.
- Grignard addition to an aldehyde followed by hydrolysis gives a secondary alcohol; oxidation gives a ketone. Methyl ketones undergo the haloform reaction to give carboxylate salts.

Step 1: (a) Form benzoyl chloride and reduce it Use thionyl chloride followed by Rosenmund

Quick Tip to Solve: Count carbons: methyl Grignard extends ethanal by one carbon; haloform reaction removes the methyl carbon of acetophenone.

reduction. The poisoned catalyst prevents further reduction to benzyl alcohol:

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$
$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$$

Step 2: (b) Add a methyl group and oxidise Add methylmagnesium bromide to ethanal in dry ether, then hydrolyse to propan-2-ol:

$$CH_3CHO + CH_3MgBr \xrightarrow{\text{dry ether}} CH_3CH(OMgBr)CH_3$$
$$CH_3CH(OMgBr)CH_3 + H_2O \longrightarrow CH_3CH(OH)CH_3 + Mg(OH)Br$$

Oxidise the secondary alcohol with acidified potassium dichromate:

$$CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$$

Step 3: (c) Remove the methyl carbon by haloform reaction Heat acetophenone with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate:

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow C_6H_5COONa + CHI_3 + 3\,NaI + 3\,H_2O$$
$$C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl$$

Step 4: (d) Form phenylmagnesium bromide and add ethanal Prepare the Grignard reagent in dry ether, add ethanal and only then introduce water for hydrolysis:

$$C_6H_5Br + Mg \xrightarrow{\text{dry ether}} C_6H_5MgBr$$
$$C_6H_5MgBr + CH_3CHO \longrightarrow C_6H_5CH(OMgBr)CH_3$$
$$C_6H_5CH(OMgBr)CH_3 + H_2O \longrightarrow C_6H_5CH(OH)CH_3 + Mg(OH)Br$$

Step 5: Conclusion The products are (a) benzaldehyde, (b) propanone, (c) benzoic acid and (d) 1-phenylethanol. Any three sequences may be presented.

Quick Tip to Solve: Count carbons: methyl Grignard extends ethanal by one carbon; haloform reaction removes the methyl carbon of acetophenone.

24. (a) Write the reactions involved in the following :

(i) Reimer-Tiemann reaction

(ii) Kolbe's reaction

(b) Name the reagent used in the bromination of phenol to form 2,4,6-Tribromophenol. [3 marks]

Solution:

Concept:

- The hydroxyl group activates the benzene ring of phenol and directs electrophilic substitution mainly to the ortho and para positions.
- Reimer-Tiemann formylation introduces a formyl group, $-CHO$, mainly ortho to the hydroxyl group. Kolbe's reaction introduces a carboxyl group at that position after acidification.

Step 1: (a)(i) Write the Reimer-Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The major product is salicylaldehyde (2-hydroxybenzaldehyde); a small amount of the para isomer also forms. The net reaction giving the major product is:

$$C_6H_5OH + CHCl_3 + 3\,NaOH \longrightarrow C_6H_4(OH)CHO + 3\,NaCl + 2\,H_2O$$

Here the hydroxyl and formyl groups in $C_6H_4(OH)CHO$ occupy adjacent ring positions. Chloroform and alkali generate the reactive dichlorocarbene intermediate, and hydrolysis followed by acid work-up yields the aldehyde.

Step 2: (a)(ii) Write Kolbe's reaction of phenol First convert phenol into sodium phenoxide:

$$C_6H_5OH + NaOH \longrightarrow C_6H_5ONa + H_2O$$

Heat sodium phenoxide with carbon dioxide under pressure at about $400\,K$. Sodium salicylate is formed, and acidification gives salicylic acid (2-hydroxybenzoic acid):

$$C_6H_5ONa + CO_2 \xrightarrow{400\,K,\ \text{pressure}} C_6H_4(OH)COONa$$

$$C_6H_4(OH)COONa + HCl \longrightarrow C_6H_4(OH)COOH + NaCl$$

In both products written here, the hydroxyl group is ortho to the carboxylate or carboxyl group.

Step 3: (b) Identify the reagent for tribromination The reagent is **bromine water**, that is, aqueous bromine. Phenol's activated ring undergoes substitution at both ortho positions and at the para position, forming a white precipitate of 2,4,6-tribromophenol:

$$C_6H_5OH + 3\,Br_2 \longrightarrow C_6H_2Br_3OH + 3\,HBr$$

A Lewis-acid catalyst is not required because phenol is much more reactive towards electrophilic substitution than benzene.

Step 4: Conclusion Reimer-Tiemann reaction gives mainly 2-hydroxybenzaldehyde; Kolbe's reaction followed by acidification gives 2-hydroxybenzoic acid. Bromine water converts phenol into 2,4,6-tribromophenol.

Quick Tip to Solve: Link the reagents to the new group: chloroform/alkali adds formyl, carbon dioxide/pressure adds carboxyl, and bromine water substitutes all three activated positions.

25. A first-order reaction is 25% complete in 40 minutes. Calculate the value of rate constant. In what time will the reaction be 80% complete ?

[Given : log 2 = 0.30, log 3 = 0.48, log 4 = 0.60, log 5 = 0.69] [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are initial and remaining reactant concentrations, t is elapsed time and k is the rate constant.
- Percentage completion gives the fraction reacted. The integrated rate equation uses the fraction remaining, $[A]_t/[A]_0 = 1 - x/100$, when $x\%$ has reacted. With time in minutes, k has units min^{-1}.

Step 1: Convert 25 percent completion to reactant remaining Choose an initial amount of 100 arbitrary units. After 40 minutes, 25 units have reacted and 75 units remain. Since the ratio is independent of the chosen initial amount,

$$\frac{[A]_0}{[A]_{40}} = \frac{100}{75} = \frac{4}{3}.$$

We must use 75 in the denominator, since the rate law refers to reactant still present, not reactant already consumed.

Step 2: Substitute the given logarithms to find the rate constant Using the supplied values $\log 4 = 0.60$ and $\log 3 = 0.48$,

$$\begin{aligned} k &= \frac{2.303}{40}\log\frac{4}{3} \\ &= \frac{2.303}{40}(0.60 - 0.48) \\ &= 0.006909\,\text{min}^{-1}. \end{aligned}$$

The positive result is consistent with a decreasing reactant concentration, since the initial-to-remaining concentration ratio exceeds one.

Step 3: Calculate the time for 80 percent completion At 80 percent completion, 20 percent remains, so the concentration ratio is $100/20 = 5$. Using the given $\log 5 = 0.69$ and the same rate constant,

$$\begin{aligned} t_{80} &= \frac{2.303}{k}\log 5 \\ &= \frac{2.303 \times 0.69}{0.006909} \\ &= 230\,\text{min}. \end{aligned}$$

This is the total time measured from the start of the reaction. It is not the extra time after the first 40 minutes. The given rounded logarithms have been used consistently in both calculations.

Step 4: Conclusion The rate constant is $\boxed{k = 6.909 \times 10^{-3}\,\text{min}^{-1}}$, and the reaction is 80 percent complete after $\boxed{230\,\text{min}}$ from the start, using the supplied logarithms.

Quick Tip to Solve: Convert completion to remaining percentage first; then use $t_{80}/40 = \log 5/\log(4/3) = 0.69/0.12$ to obtain the time directly.

26. (a) What type of nucleophilic substitution (S_N1 or S_N2) occurs in the hydrolysis of 2-Bromobutane to form ($\pm$)-Butan-2-ol ? Give reason.

(b) What happens when chlorobenzene and methyl chloride are treated with sodium metal in dry ether ? [3 marks]

Solution:

Concept:

- In an S_N1 substitution, the carbon-halogen bond first ionises to give a carbocation; the nucleophile then attacks this intermediate.
- A trigonal-planar carbocation can be attacked from either face, producing both configurations at an initially chiral carbon.
- The Wurtz-Fittig reaction couples an aryl halide with an alkyl halide using sodium in dry ether, forming an alkylbenzene.

Step 1: (a) Identify the mechanism from the racemic product The product specified is ($\pm$)-butan-2-ol, a racemic mixture of the two enantiomers. This indicates an S_N1 pathway. The slow ionisation step is

$$CH_3CH(Br)CH_2CH_3 \longrightarrow CH_3\overset{+}{C}HCH_2CH_3 + Br^-.$$

The secondary carbocation has an sp^2-hybridised, planar positively charged carbon. Water can approach this carbon from either face; after loss of a proton, the two enantiomers of butan-2-ol are obtained. Thus the original configuration is lost, giving racemisation in the idealised board-level mechanism. A single S_N2 attack instead occurs from the back side and gives inversion, so it does not account for the stated racemic outcome from one enantiomer.

Step 2: (b) Apply the Wurtz-Fittig coupling Sodium in dry ether couples the phenyl group of chlorobenzene with the methyl group of methyl chloride. The organic product is toluene (methylbenzene), and the two chlorine atoms form sodium chloride:

$$C_6H_5Cl + CH_3Cl + 2Na \xrightarrow{\text{dry ether}} C_6H_5CH_3 + 2NaCl.$$

This is the Wurtz-Fittig reaction because one reactant is an aryl halide and the other is an alkyl halide.

Step 3: Conclusion (a) S_N1 substitution: a planar carbocation permits attack from both faces and hence racemisation. (b) Toluene is formed by the Wurtz-Fittig reaction.

Quick Tip to Solve: Use the stated stereochemical outcome as the clue: racemisation signals a planar intermediate, whereas backside substitution gives inversion.

27. The conductivity of 0.2 M solution of KCl is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity and degree of dissociation (α).

Given : $\lambda^0_{K+} = 73.5$ **S cm^2 mol^{-1},** $\lambda^0_{Cl-} = 76.5$ **S cm^2 mol^{-1}** [3 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when conductivity κ is in $\mathrm{S\,cm^{-1}}$ and concentration c is in $\mathrm{mol\,L^{-1}}$. The factor 1000 converts litres to cubic centimetres.
- Kohlrausch's law gives $\Lambda^0_m = \lambda^0_{\mathrm{K^+}} + \lambda^0_{\mathrm{Cl^-}}$ for KCl, because one formula unit supplies one ion of each kind.
- The conductivity-based degree of dissociation requested in the question is obtained from $\alpha = \Lambda_m/\Lambda^0_m$.

Step 1: Calculate molar conductivity The given concentration is $c = 0.2\,\mathrm{mol\,L^{-1}}$ and the conductivity is $\kappa = 2.48 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$. Thus

$$\Lambda_m = \frac{1000(2.48 \times 10^{-2})}{0.2} = 124\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Equivalently, one mole occupies $1000/0.2 = 5000\,\mathrm{cm^3}$ of this solution; multiplying that volume per mole by conductivity gives the same molar conductivity.

Step 2: Find the limiting molar conductivity Add the limiting ionic conductivities with their 1:1 stoichiometric coefficients:

$$\Lambda^0_m = 73.5 + 76.5 = 150\,\mathrm{S\,cm^2\,mol^{-1}}.$$

Both terms have the same units, so their sum can be compared directly with Λ_m.

Step 3: Obtain the conductivity ratio Substituting the two molar conductivities,

$$\alpha = \frac{124}{150} = 0.8267, \qquad 100\alpha = 82.67\%.$$

The ratio is dimensionless. For this question this is the expected conductivity-based result. Physically, KCl is a strong electrolyte and is essentially dissociated; at finite concentration, interionic interactions also reduce ionic mobility. Therefore this ratio is an apparent dissociation value, rather than evidence that 17.33% of KCl remains as neutral molecules.

Step 4: Conclusion The molar conductivity is $\boxed{124\,\mathrm{S\,cm^2\,mol^{-1}}}$. The requested conductivity-based value is $\boxed{\alpha \approx 0.827}$, or 82.7%.

Quick Tip to Solve: With conductivity in S per cm and concentration in mol per litre, retain the factor 1000; then divide by the sum of the two limiting ionic conductivities.

28. A solution is prepared by dissolving 5 g of a non-volatile solute in 200 g of water. It has a vapour pressure of 31.84 mm Hg at 300 K. Calculate the molar mass of the solute. (Vapour pressure of pure water at 300 K = 32 mm Hg) [3 marks]

Solution:

Concept:

- For an ideal solution containing a non-volatile solute, Raoult's law is $p = x_1 p^0$, where p^0 is the pure-solvent vapour pressure, p is the solution vapour pressure and x_1 is the solvent mole fraction.
- Relative lowering of vapour pressure is $(p^0 - p)/p^0 = x_2 = n_2/(n_1 + n_2)$, where n_1 and n_2 are solvent and solute amounts in moles. For a dilute solution, $x_2 \approx n_2/n_1$.

Step 1: Find the relative lowering of vapour pressure Both pressures are measured at the same temperature, 300 K, and in the same units. Hence

$$\Delta p = 32 - 31.84 = 0.16\,\text{mm Hg}, \qquad \frac{\Delta p}{p^0} = \frac{0.16}{32} = 0.005.$$

Since the solute is non-volatile, this lowering is due to the reduction in the solvent mole fraction. The small value also supports using the dilute-solution approximation.

Step 2: Apply the standard dilute-solution relation Let the solute molar mass be M_2. For water, $M_1 = 18\,\text{g mol}^{-1}$, while the given masses are $w_1 = 200\,\text{g}$ and $w_2 = 5\,\text{g}$. Therefore

$$\frac{p^0 - p}{p^0} \approx \frac{n_2}{n_1} = \frac{w_2 M_1}{w_1 M_2}.$$

Substitution gives

$$0.005 = \frac{5 \times 18}{200 M_2}, \qquad M_2 \approx \frac{5 \times 18}{200 \times 0.005} = 90\,\text{g mol}^{-1}.$$

Step 3: Check the dilute approximation against the exact relation Keeping the solute moles in the denominator gives

$$0.005 = \frac{5/M_2}{200/18 + 5/M_2}.$$

Rearranging, $0.005(200/18) = 0.995(5/M_2)$, so the exact ideal-solution value is $89.55\,\text{g mol}^{-1}$. Its difference from 90 is only 0.5%, consistent with the small solute mole fraction and the usual dilute-solution treatment of this question.

Step 4: Conclusion The solute molar mass is approximately $\boxed{90\,\text{g mol}^{-1}}$ by the dilute-solution formula (the exact Raoult-law calculation gives $89.55\,\text{g mol}^{-1}$).

Quick Tip to Solve: Use the pressure lowering, 0.16 mm Hg, in the numerator and pure-water pressure, 32 mm Hg, in the denominator; use 18 g per mole for water.

Section D (8 marks)

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

29. Proteins are the most abundant biomolecules of the living system. Proteins are the polymers of about twenty different α-amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

On the basis of their molecular shape, proteins are classified into two types: Fibrous and Globular proteins. Structure and shape of proteins can be studied at four different levels i.e., primary, secondary, tertiary and quaternary, each level being more complex than the previous one. The secondary or tertiary structure of proteins get disturbed on change of pH or temperature and they are not able to perform their functions. This is called denaturation of proteins.

Answer the following questions: [4 marks]

29(a). What are essential amino acids ? [1 mark]

Solution:

Concept:

- Amino acids are the building units used by the body to synthesise proteins.
- Essential amino acids are classified by the body's inability to synthesise them, rather than by a special type of peptide bond.

Step 1: Identify the body's requirement The body requires a supply of amino acids for protein synthesis. Some amino acids can be synthesised within the body, whereas essential amino acids cannot be synthesised by it.

Step 2: Identify the source of these amino acids Since the body cannot make essential amino acids, they must be supplied through the diet. Valine and leucine are examples; protein-containing food provides these amino acids on digestion.

Step 3: Conclusion Essential amino acids are amino acids that cannot be synthesised by the body and must therefore be obtained through the diet.

Quick Tip to Solve: Use both phrases in the definition: cannot be synthesised by the body, and must be supplied in the diet.

29(b). What is meant by zwitter ionic form of amino acids ? [1 mark]

Solution:

Concept:

- An amino acid contains an acidic carboxyl group, $-COOH$, and a basic amino group, $-NH_2$.
- A zwitterion is a dipolar ion with both positive and negative charges within the same molecule and zero net charge.

Step 1: Transfer a proton internally In aqueous solution, the carboxyl group can donate a proton to

Quick Tip to Solve: Show both charges: the amino group accepts a proton and the carboxyl group loses one, leaving zero net charge.

the amino group. Thus the amino group becomes $-NH_3{}^+$ and the carboxyl group becomes $-COO-$.

Step 2: Identify the dipolar form The resulting amino-acid form is $H_3N^+-CH(R)-COO^-$, where R is the side chain. Its positive and negative charges coexist on different groups, but cancel to give an electrically neutral molecule overall.

Step 3: Conclusion The zwitterionic form of an amino acid is its dipolar form, $H_3N^+-CH(R)-COO^-$, containing both a positively charged ammonium group and a negatively charged carboxylate group.

Quick Tip to Solve: Show both charges: the amino group accepts a proton and the carboxyl group loses one, leaving zero net charge.

29(c). (i) Give one example each for Fibrous protein and Globular protein.
(ii) What type of linkages hold monomers of proteins together ? [2 marks]

Solution:

Concept:

- Fibrous proteins contain polypeptide chains arranged in elongated, fibre-like structures; globular proteins have chains folded into compact shapes.
- The monomers of proteins are α-amino acids. A peptide linkage, $-CO-NH-$, is an amide bond formed between two amino-acid residues.

Step 1: Give the two protein examples for part (i) Keratin, present in hair and wool, is a fibrous protein: its chains form elongated structural fibres. Insulin is a globular protein, whose polypeptide chains are folded into a compact three-dimensional form. These examples distinguish the two classes by molecular shape.

Step 2: Identify the linkage for part (ii) The carboxyl group of one amino acid reacts with the amino group of another, eliminating a water molecule and producing the covalent peptide linkage $-CO-NH-$. Repetition of this condensation links amino-acid residues into a polypeptide chain. Hydrogen bonds can stabilise the folded structure, but the monomers themselves are joined by peptide bonds.

Step 3: Conclusion (i) Fibrous protein: keratin; globular protein: insulin. (ii) Amino-acid monomers in proteins are joined by peptide linkages, $-CO-NH-$.

Quick Tip to Solve: Pair hair with fibrous keratin and insulin with globular protein; identify the monomer-joining bond as a peptide bond.

OR

29(c). (i) What is the structural feature which characterises a reducing sugar ?
(ii) What is the structural difference between nucleoside and nucleotide ? [2 marks]

Solution:

Concept:

- A reducing sugar has a free anomeric centre that permits formation of the open-chain carbonyl form; its aldehydic or ketonic group is not permanently locked in a glycosidic bond.
- A nucleoside contains a nitrogenous base and a pentose sugar. A nucleotide contains these two components together with a phosphate group.

Step 1: Identify the reducing-sugar feature for part (i) A reducing sugar possesses a free aldehydic or ketonic group in its open-chain form. In a cyclic sugar, a free hemiacetal or hemiketal anomeric hydroxyl group allows the ring to open and regenerate the carbonyl group. Thus the presence of a free anomeric centre, rather than simply several hydroxyl groups, is the structural test. Ketose sugars can also reduce the usual alkaline reagents by rearranging to aldoses.

Step 2: Compare the components for part (ii) In a nucleoside, a nitrogenous base is attached to the anomeric carbon of a pentose sugar through an N-glycosidic linkage. When phosphoric acid esterifies a sugar hydroxyl group of a nucleoside, a nucleotide is formed. Therefore, the additional phosphate group is the structural difference: a nucleoside has base and sugar, while a nucleotide has base, sugar and phosphate.

Step 3: Conclusion (i) A reducing sugar has a free aldehydic or ketonic group, accessible through ring opening at a free anomeric centre. (ii) A nucleotide is a phosphorylated nucleoside; the phosphate group is absent from a nucleoside.

Quick Tip to Solve: Check whether the anomeric centre is free for reducing behaviour; remember nucleotide = nucleoside + phosphate.

30. The involvement of $(n-1)$d electrons in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties and tendency for the formation of coloured ions. The transition metals react with a number of non-metals like oxygen, nitrogen and halogens. $KMnO_4$ and $K_2Cr_2O_7$ are common examples.

The two series of inner transition elements, lanthanoids and actinoids, constitute the f-block of the periodic table. In the lanthanoids, there is regular decrease in atomic size with increase in atomic number due to the imperfect shielding effect of 4f-orbital electrons which causes contraction.

Answer the following questions: [4 marks]

30(a). Why do transition metals and their compounds act as good catalysts ? [1 mark]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated during the reaction.
- Transition elements can show variable oxidation states and form intermediate complexes with reactants.

Step 1: Explain intermediate formation Transition metals and their compounds can accept and donate electrons by changing oxidation state. They therefore form temporary intermediates with reactants, allowing a reaction to proceed through easier steps.

Step 2: Relate surface adsorption to catalysis Finely divided transition metals also adsorb reactant molecules on their surfaces. Adsorption brings the reactants together and weakens their bonds, lowering the energy barrier to reaction.

Step 3: Conclusion Their variable oxidation states, intermediate-complex formation and ability to adsorb reactants make transition metals and their compounds good catalysts.

Quick Tip to Solve: Link variable oxidation states to intermediate formation; for solid metals, also mention adsorption on the surface.

30(b). What is the cause of contraction in the atomic size of lanthanoids ? [1 mark]

Solution:

Concept:

- Atomic size depends on the effective nuclear attraction experienced by the electrons.
- The $4f$ electrons shield the outer electrons from nuclear charge poorly.

Step 1: Track the increase in nuclear charge Across the lanthanoid series, each successive element has one more proton, and the added electron enters the inner $4f$ subshell. Thus the nuclear charge rises from one element to the next.

Step 2: Account for poor shielding The added $4f$ electron does not effectively screen the extra nuclear charge. Consequently, the effective nuclear attraction increases and pulls the electron cloud closer to the nucleus, causing a gradual decrease in atomic size.

Quick Tip to Solve: State both links in the cause: poor $4f$ shielding increases effective nuclear charge, which decreases atomic size.

Step 3: Conclusion Lanthanoid contraction is caused by the poor shielding effect of $4f$ electrons, which allows effective nuclear charge to increase across the series.

Quick Tip to Solve: State both links in the cause: poor $4f$ shielding increases effective nuclear charge, which decreases atomic size.

30(c). Define lanthanoid contraction. How does it affect the atomic radii of the third transition series and the second transition series ? [2 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series as atomic number increases.
- Poor shielding by $4f$ electrons increases effective nuclear attraction and affects the sizes of the elements following the lanthanoids.

Step 1: Define the contraction and its origin From lanthanum towards lutetium, atomic and corresponding ionic radii decrease gradually with increasing atomic number. The added electrons enter the $4f$ subshell and shield the added nuclear charge imperfectly. Hence, the electron cloud experiences greater attraction and contracts.

Step 2: Compare corresponding transition elements The lanthanoids precede the later members of the third, $5d$, transition series. Their contraction offsets the size increase expected from the additional electron shell. Corresponding elements of the second, $4d$, and third, $5d$, transition series therefore have nearly equal atomic radii. For example, zirconium and hafnium have radii of approximately $160\,\text{pm}$ and $159\,\text{pm}$, respectively.

Step 3: Conclusion Lanthanoid contraction is the gradual decrease in lanthanoid atomic and ionic size with increasing atomic number. It makes corresponding second- and third-transition-series elements, such as Zr and Hf, nearly equal in atomic radius.

Quick Tip to Solve: Use the pair Zr/Hf: the extra shell in hafnium is offset by contraction caused by the intervening $4f$ series.

OR

30(c). In aqueous media, which is a stronger reducing agent — Cr^{2+} or Fe^{2+} and why ? [2 marks]

Solution:

Concept:

- A reducing agent donates an electron and is itself oxidised. Compare the ease of oxidation from the $+2$ to the $+3$ state.
- The stability of the resulting aqueous ion depends on electronic configuration and hydration. For Cr^{3+}, the d^3 configuration is especially stable in an octahedral environment.

Quick Tip to Solve: Compare the reduction potentials of the $+3/+2$ couples: the more negative value identifies the stronger $+2$ reducing agent.

Step 1: Examine oxidation of chromium(II) The Cr^{2+} ion has a $3d^4$ configuration and readily loses an electron:

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

The resulting Cr^{3+} ion has a $3d^3$ configuration. In its octahedral aqua complex, its three electrons occupy the lower-energy t_{2g} orbitals, giving a stable t_{2g}^3 arrangement.

Step 2: Compare with iron(II) in aqueous solution Oxidation of Fe^{2+} changes $3d^6$ to the half-filled $3d^5$ configuration of Fe^{3+}. Nevertheless, the aqueous reduction potentials are approximately

$$E^\circ(Cr^{3+}/Cr^{2+}) = -0.41\,V,$$
$$E^\circ(Fe^{3+}/Fe^{2+}) = +0.77\,V.$$

The more negative reduction potential of the chromium couple shows that its reduced form, Cr^{2+}, has the greater tendency to donate an electron. Thus half-filled-shell stability alone does not determine reducing strength in water.

Step 3: Conclusion Cr^{2+} is the stronger reducing agent in aqueous media because it is more readily oxidised to stable Cr^{3+} with its $3d^3$, t_{2g}^3 configuration.

Quick Tip to Solve: Compare the reduction potentials of the $+3/+2$ couples: the more negative value identifies the stronger $+2$ reducing agent.

Section E (15 marks)

31. Attempt any five of the following :

(a) Write the IUPAC name of the complex : $[Co(H_2O)(CN)(en)_2]^{2+}$

(b) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal ion ?

(c) Arrange the following complex ions in increasing order of their crystal field splitting energy (Δ_o) : $[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$

(d) Write the hybridization and magnetic character of the complex $[Ni(CO)_4]$ on the basis of valence bond theory. [Atomic No. : Ni = 28]

(e) Out of $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, which one complex is : (i) more stable ? (ii) the high spin complex ?

(f) What is the difference between an ambidentate ligand and bidentate ligand ?

(g) Write the electronic configuration of d^5 in terms of t_{2g} and e_g in an octahedral field when : (i) $\Delta_o > P$, and (ii) $\Delta_o < P$ [5 marks]

Solution:

Concept:

- For coordination nomenclature, first determine the metal oxidation state from ligand charges, then list ligand names alphabetically before the metal name and its oxidation state.
- In an octahedral field, the lower-energy t_{2g} orbitals and higher-energy e_g orbitals are separated by

Quick Tip to Solve: Find the metal oxidation state before counting d electrons. For octahedral filling, compare Δ_o with P: a larger splitting favours pairing in t_{2g}, while a smaller splitting favours occupation of e_g.

Δ_o. The competition between Δ_o and pairing energy P determines the spin state.

- A bidentate ligand binds through two donor atoms simultaneously, whereas an ambidentate ligand has alternative donor atoms but binds through only one of them at a time.
- Chelation generally increases complex stability. In valence bond theory, hybridisation determines the geometry and unpaired electrons determine the magnetic character.

Step 1: (a) Determine the oxidation state and name the complex In $[\mathrm{Co(H_2O)(CN)(en)_2}]^{2+}$, water and ethane-1,2-diamine (en) are neutral ligands, while $\mathrm{CN^-}$ has charge -1. If the oxidation state of cobalt is x,

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

The ligand names are aqua, cyanido and ethane-1,2-diamine. They are placed in alphabetical order; the prefix bis is used for the two ethane-1,2-diamine ligands and is ignored for alphabetisation. The complex is cationic, so the metal name remains cobalt. Its IUPAC name is **aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion**.

Step 2: (b) Compare positions in a tetrahedral complex All four coordination positions of a tetrahedron are equivalent, and the angle between any pair of metal–ligand bonds is approximately 109.5°. Thus, with two different types of unidentate ligand, exchanging positions does not create distinct adjacent and opposite arrangements. For example, all placements of two identical ligands in a tetrahedral $\mathrm{MA_2B_2}$ complex are equivalent by rotation. Therefore, distinct cis and trans geometrical isomers are not possible.

Step 3: (c) Apply the spectrochemical series All three complexes contain cobalt in the $+3$ oxidation state and have six ligands. The relevant ligand field strength increases as

$$\mathrm{F^-} < \mathrm{NH_3} < \mathrm{CN^-}.$$

A stronger ligand field gives a greater octahedral splitting. Hence the increasing order of Δ_o is

$$[\mathrm{CoF_6}]^{3-} < [\mathrm{Co(NH_3)_6}]^{3+} < [\mathrm{Co(CN)_6}]^{3-}.$$

Step 4: (d) Apply valence bond theory to nickel tetracarbonyl Carbon monoxide is a neutral ligand, so nickel has oxidation state zero in $[\mathrm{Ni(CO)_4}]$. The isolated nickel atom has configuration $[\mathrm{Ar}]3d^8 4s^2$. In the presence of the strong-field CO ligands, the valence electrons pair to give a filled $3d^{10}$ set, leaving the $4s$ and $4p$ orbitals available for bonding. One $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals, which accept lone pairs from four CO ligands. The complex is therefore **sp^3-hybridised and tetrahedral**. Since all its electrons are paired, it is **diamagnetic**.

Step 5: (e) Compare stability and spin character (i) $[\mathrm{Co(C_2O_4)_3}]^{3-}$ is more stable because each oxalate ion is a bidentate ligand and forms a chelate ring with cobalt. This chelate effect favours its stability relative to the complex with unidentate fluoride ligands.
(ii) $[\mathrm{CoF_6}]^{3-}$ is the high-spin complex. Cobalt is $+3$, hence d^6, and fluoride is a weak-field ligand. Its splitting is too small to favour additional pairing in the lower orbitals, so the configuration is $t_{2g}^4 e_g^2$, with four unpaired electrons.

Step 6: (f) Distinguish the two kinds of ligand An **ambidentate ligand** has two different possible donor atoms but coordinates through only one of them at a time. For example, $\mathrm{NO_2^-}$ can bond

Quick Tip to Solve: Find the metal oxidation state before counting d electrons. For octahedral filling, compare Δ_o with P: a larger splitting favours pairing in t_{2g}, while a smaller splitting favours occupation of e_g.

through nitrogen or oxygen. It is therefore unidentate in either mode and can give linkage isomerism. A **bidentate ligand** coordinates to the same metal ion through two donor atoms simultaneously. For example, ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, binds through both nitrogen atoms, while oxalate, $C_2O_4{}^{2-}$, binds through two oxygen atoms. Such binding forms a chelate ring.

Step 7: (g) Fill the octahedral orbitals for five d electrons (i) If $\Delta_o > P$, placing an electron in e_g costs more energy than pairing it in t_{2g}. After the first three electrons occupy the three lower orbitals singly, the fourth and fifth pair in them. The low-spin configuration is

$$\boxed{t_{2g}^5 e_g^0},$$

with one unpaired electron.

(ii) If $\Delta_o < P$, promotion to e_g costs less energy than pairing. Each of the five d orbitals is occupied singly before any pairing occurs. The high-spin configuration is

$$\boxed{t_{2g}^3 e_g^2},$$

with five unpaired electrons.

Step 8: Conclusion (a) Aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion; (b) all tetrahedral positions and ligand-pair arrangements are equivalent; (c) $[CoF_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$ in Δ_o; (d) sp^3, diamagnetic; (e) more stable: $[Co(C_2O_4)_3]^{3-}$, high spin: $[CoF_6]^{3-}$; (f) alternative single donor versus two simultaneous donors; (g) $t_{2g}^5 e_g^0$ for $\Delta_o > P$, and $t_{2g}^3 e_g^2$ for $\Delta_o < P$.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons. For octahedral filling, compare Δ_o with P: a larger splitting favours pairing in t_{2g}, while a smaller splitting favours occupation of e_g.

32(a). (i) Calculate emf of the following cell at 25°C :

Zn (s) | Zn^{2+} (0.001 M) || Cd^{2+} (0.1 M) | Cd (s)

Given : $E^\circ_{Zn^{2+}/Zn} = -0.76\,V$, $E^\circ_{Cd^{2+}/Cd} = -0.40\,V$ **[log 10 = 1]**

(ii) State Faraday's second law of electrolysis. How will the pH of aqueous NaCl solution be affected when it is electrolysed ? [5 marks]

Solution:

Concept:

- Cell emf is the cathode reduction potential minus the anode reduction potential: $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$. Oxidation supplies electrons at the anode; reduction consumes them at the cathode.
- At 25°C, 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 per balanced cell reaction and Q is its reaction quotient; pure solids have unit activity.
- Faraday's second law relates masses liberated by the same charge to their chemical equivalent masses. During electrolysis of aqueous NaCl, formation of OH^- makes the solution alkaline.

Quick Tip to Solve: Write the balanced cell reaction before forming Q: here $Q = [Zn^{2+}]/[Cd^{2+}] = 10^{-2}$, so the Nernst correction must increase the emf. For aqueous NaCl, remember that water, rather than Na^+, is reduced at the cathode.

Step 1: (i) Identify the electrodes and balance the reaction The Cd^{2+}/Cd reduction potential is more positive than that of Zn^{2+}/Zn. Hence zinc is oxidised at the left-hand anode, while cadmium ions are reduced at the right-hand cathode:

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

The balanced reaction transfers $n = 2$ electrons. No stoichiometric coefficient is needed for either metal ion in the reaction quotient.

Step 2: Calculate the standard emf and reaction quotient Both tabulated values are reduction potentials, so subtract the zinc value from the cadmium value:

$$E^\circ_{\text{cell}} = (-0.40) - (-0.76) = 0.36\,\text{V}.$$

Omitting the pure solid metals and using the given molar concentrations,

$$Q = \frac{[Zn^{2+}]}{[Cd^{2+}]} = \frac{0.001}{0.1} = 10^{-2}, \qquad \log Q = -2.$$

The zinc-ion concentration belongs in the numerator because zinc ions are products of the cell reaction.

Step 3: Apply the Nernst equation at the stated temperature Substitute $n = 2$, $E^\circ_{\text{cell}} = 0.36\,\text{V}$ and $\log Q = -2$:

$$\begin{aligned}E_{\text{cell}} &= 0.36 - \frac{0.0591}{2}(-2)\\ &= 0.36 + 0.0591\,\text{V}.\end{aligned}$$

Since $Q < 1$, its logarithm is negative and the concentration correction raises the emf above the standard value. This is also a check on the sign in the calculation.

Step 4: (ii) State Faraday's second law When the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated at their electrodes are proportional to their chemical equivalent masses:

$$\frac{m_1}{m_2} = \frac{M_1/z_1}{M_2/z_2}.$$

Here m is the deposited or liberated mass, M is molar mass, and z is the number of electrons required per formula unit or atom of the electrode product. Thus M/z represents equivalent mass. The condition of equal charge, $q = It$, is essential to this comparison.

Step 5: Explain the change in pH during electrolysis In the electrolysis of aqueous $NaCl$, water is reduced at the cathode, producing hydrogen and hydroxide ions, while chloride ions give chlorine at the anode:

$$\begin{aligned}\text{Cathode: } & 2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq),\\ \text{Anode: } & 2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^-.\end{aligned}$$

Quick Tip to Solve: Write the balanced cell reaction before forming Q: here $Q = [Zn^{2+}]/[Cd^{2+}] = 10^{-2}$, so the Nernst correction must increase the emf. For aqueous $NaCl$, remember that water, rather than Na^+, is reduced at the cathode.

The Na^+ ions remain in solution with the generated OH^-, forming sodium hydroxide. The overall reaction is

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

Consequently the hydroxide-ion concentration increases, the hydrogen-ion concentration decreases, and the solution becomes alkaline.

Step 6: Conclusion (i) The cell emf is $\boxed{E_{cell} = 0.4191\,V \approx 0.42\,V}$. (ii) For equal charge, the masses deposited or liberated are proportional to their equivalent masses. The pH of aqueous $NaCl$ increases on electrolysis because OH^- is produced.

Quick Tip to Solve: Write the balanced cell reaction before forming Q: here $Q = [Zn^{2+}]/[Cd^{2+}] = 10^{-2}$, so the Nernst correction must increase the emf. For aqueous $NaCl$, remember that water, rather than Na^+, is reduced at the cathode.

OR

32(b). (i) Calculate the $\Delta_r G^\circ$ and $\log K_c$ for the following cell reaction :

$Fe\,(s) + Ag^+\,(aq) \rightleftharpoons Fe^{2+}\,(aq) + Ag\,(s)$

Given : $E^\circ_{Fe^{2+}/Fe} = -0.44\,V$, $E^\circ_{Ag^+/Ag} = +0.80\,V$, $1\,F = 96500\,C\,mol^{-1}$

(ii) Write any two advantages of the fuel cells over primary and secondary batteries ?

(iii) How many Faradays are required for the oxidation of 1 mole of H_2O to O_2 ? [5 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$, using both electrode values as reduction potentials.
- For a balanced cell reaction transferring n electrons, $\Delta_r G^\circ = -nFE^\circ_{cell} = -RT\ln K_c$. Here F is the Faraday constant, R the gas constant and T the absolute temperature.
- A fuel cell converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy. One Faraday is the charge carried by one mole of electrons.

Step 1: (i) Balance the electron transfer and find the cell potential Silver ions have the higher reduction potential, so they are reduced at the cathode, while iron is oxidised at the anode. The printed skeletal reaction must first be balanced for charge and atoms:

$$\begin{aligned} Fe\,(s) &\longrightarrow Fe^{2+}\,(aq) + 2\,e^-, \\ 2\,Ag^+\,(aq) + 2\,e^- &\longrightarrow 2\,Ag\,(s), \\ Fe\,(s) + 2\,Ag^+\,(aq) &\longrightarrow Fe^{2+}\,(aq) + 2\,Ag\,(s). \end{aligned}$$

Thus $n = 2$ per mole of the balanced reaction. Electrode potentials are intensive quantities, so the silver potential is not multiplied by two:

$$E^\circ_{cell} = 0.80 - (-0.44) = 1.24\,V.$$

Quick Tip to Solve: Balance the iron–silver reaction before choosing $n = 2$; never multiply an electrode potential by a stoichiometric coefficient. For water oxidation, count electrons per mole of water, not per mole of oxygen gas.

Step 2: (i) Calculate the standard Gibbs energy change Substitute the electron count for the balanced reaction and the given Faraday constant:

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\circ} &= -2 \times 96500 \times 1.24 \\ &= -239320\,\mathrm{J\ mol^{-1}} \\ &= -239.32\,\mathrm{kJ\ mol^{-1}}.\end{aligned}$$

The negative value is consistent with the positive cell potential: the forward reaction is spontaneous under standard conditions.

Step 3: (i) Relate the cell potential to the equilibrium constant Taking the conventional temperature of $298\,\mathrm{K}$ for these standard electrode data,

$$E^{\circ}_{\mathrm{cell}} = \frac{0.0591}{n} \log K_{\mathrm{c}}.$$

Therefore,

$$\log K_{\mathrm{c}} = \frac{2 \times 1.24}{0.0591} \approx 41.96.$$

This constant belongs to the balanced reaction, with the concentration quotient proportional to $[\mathrm{Fe}^{2+}]/[\mathrm{Ag}^{+}]^2$; pure solids have unit activity. The very large equilibrium constant agrees with the strongly favourable forward reaction.

Step 4: (ii) State two advantages of fuel cells First, a fuel cell can supply electrical energy continuously while fuel and oxidant are supplied; it does not require periodic replacement like a primary battery or external recharging like a secondary battery. Second, a hydrogen–oxygen fuel cell is clean in operation because its reaction product is water, avoiding the polluting battery waste associated with many conventional cells:

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)}.$$

Step 5: (iii) Count electrons released by water oxidation Write the balanced oxidation half-reaction:

$$2\,\mathrm{H_2O\,(l)} \longrightarrow \mathrm{O_2(g)} + 4\,\mathrm{H^{+}(aq)} + 4\,\mathrm{e^{-}}.$$

Two moles of water release four moles of electrons, so one mole of water releases two moles of electrons. Equivalently, each oxygen atom changes its oxidation number from -2 in water to 0 in oxygen. Thus the corresponding charge is $2F = 193000\,\mathrm{C}$.

Step 6: Conclusion (i) For the balanced cell reaction, $\Delta_{\mathrm{r}}G^{\circ} = -239.32\,\mathrm{kJ\ mol^{-1}}$ and $\log K_{\mathrm{c}} \approx 41.96$ at $298\,\mathrm{K}$. (ii) Fuel cells offer continuous operation with supplied reactants and clean operation for the hydrogen–oxygen cell. (iii) Oxidising one mole of water requires $\boxed{2\ \text{Faradays}}$.

Quick Tip to Solve: Balance the iron–silver reaction before choosing $n = 2$; never multiply an electrode potential by a stoichiometric coefficient. For water oxidation, count electrons per mole of water, not per mole of oxygen gas.

33(a). (i) Write the major product(s) in the following reactions:

(1) $C_6H_5CH_2CH_3 \xrightarrow[\text{b) } H^+]{\text{a) } KMnO_4, KOH}$ **?**

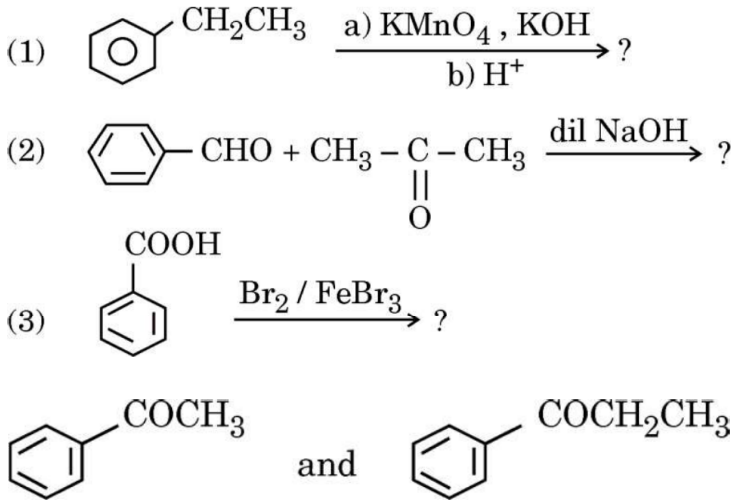
(2) $C_6H_5CHO + CH_3COCH_3 \xrightarrow{\text{dil. } NaOH}$ **?**

(3) $C_6H_5COOH \xrightarrow{Br_2/FeBr_3}$ **?**

(ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(1) $C_6H_5COCH_3$ **and** $C_6H_5COCH_2CH_3$

(2) Pentanal and Pentan-3-one [5 marks]



Solution:

Concept:

- Alkaline permanganate oxidises an alkyl side chain containing a benzylic hydrogen to a carboxylate; acidification gives the carboxylic acid.
- In crossed aldol condensation, an enolate from a carbonyl compound with an alpha hydrogen attacks another carbonyl compound. Dehydration gives a conjugated unsaturated carbonyl product.
- The $-COOH$ group withdraws electrons and directs electrophilic aromatic substitution mainly to the meta position.
- The iodoform test detects the methyl ketone group $-COCH_3$. Tollens' reagent distinguishes an aldehyde from an ordinary ketone by oxidation of the aldehyde and deposition of silver.

Step 1: (i)(1) Oxidise the ethyl side chain Ethylbenzene contains benzylic hydrogens, so alkaline $KMnO_4$ oxidises its side chain to potassium benzoate. Acid treatment then produces benzoic acid:

$$C_6H_5CH_2CH_3 \xrightarrow{KMnO_4, KOH} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.$$

The carbon originally attached to the ring becomes the carboxyl carbon. The ring remains intact; oxidation does not stop at an alcohol or an aldehyde under these conditions.

Step 2: (i)(2) Carry out the crossed aldol condensation Benzaldehyde has no alpha hydrogen, whereas acetone does. Dilute $NaOH$ generates the acetone enolate, which attacks benzaldehyde. Protonation gives the beta-hydroxy ketone $C_6H_5CH(OH)CH_2COCH_3$. Loss of water gives benzylideneacetone

Quick Tip to Solve: For the ketone pair, check whether the group beside the carbonyl is exactly CH_3, not CH_2CH_3. For the aldehyde/ketone pair, use Tollens' reagent and record the silver-mirror observation.

(4-phenylbut-3-en-2-one):

$$C_6H_5CHO + CH_3COCH_3 \longrightarrow C_6H_5CH{=}CHCOCH_3 + H_2O.$$

This conjugated enone is the mono-condensation product. Acetone has a second reactive methyl group, so with excess benzaldehyde a further condensation gives dibenzylideneacetone:

$$2\,C_6H_5CHO + CH_3COCH_3 \longrightarrow C_6H_5CH{=}CHCOCH{=}CHC_6H_5 + 2\,H_2O.$$

The extent of condensation depends on the reactant proportions; the second equation identifies the product of condensation at both ends of acetone.

Step 3: (i)(3) Apply the meta-directing effect In benzoic acid, the $-COOH$ group deactivates the ring and directs the incoming bromine to a meta position. Bromination with $Br_2/FeBr_3$ gives 3-bromobenzoic acid:

$$C_6H_5COOH + Br_2 \xrightarrow{FeBr_3} m{-}BrC_6H_4COOH + HBr.$$

The ortho and para intermediates are more strongly destabilised by the electron-withdrawing carboxyl group, explaining the meta orientation.

Step 4: (ii)(1) Use the iodoform test Warm separate samples with iodine and aqueous $NaOH$. Acetophenone, $C_6H_5COCH_3$, contains the methyl ketone group and gives a yellow precipitate of iodoform, CHI_3:

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

Propiophenone, $C_6H_5COCH_2CH_3$, lacks a methyl group directly attached to the carbonyl carbon and gives no yellow iodoform precipitate. Both are ketones, so Tollens' reagent would not distinguish this pair.

Step 5: (ii)(2) Use Tollens' reagent Warm separate samples gently with freshly prepared Tollens' reagent. Pentanal gives a silver mirror because its aldehyde group is oxidised to pentanoate while silver(I) is reduced:

$$CH_3CH_2CH_2CH_2CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \longrightarrow CH_3CH_2CH_2CH_2COO^- + 2\,Ag\downarrow + 4\,NH_3 + 2\,H_2O.$$

Pentan-3-one is an ordinary ketone and gives no silver mirror. Thus the positive observation identifies pentanal directly.

Step 6: Conclusion (i) The products are benzoic acid, benzylideneacetone (with further condensation giving dibenzylideneacetone when benzaldehyde is in excess), and 3-bromobenzoic acid. (ii) Acetophenone gives a yellow iodoform precipitate whereas propiophenone does not; pentanal gives a silver mirror with Tollens' reagent whereas pentan-3-one does not.

Quick Tip to Solve: For the ketone pair, check whether the group beside the carbonyl is exactly CH_3, not CH_2CH_3. For the aldehyde/ketone pair, use Tollens' reagent and record the silver-mirror observation.

OR

33(b). (i) Give reasons for the following :

(1) In semicarbazide, only one –NH_2 group is involved in the formation of semicarbazone.

(2) Acetaldehyde is more reactive than acetone towards addition of HCN.

(ii) (1) Arrange the following in decreasing order of their acidic strength : CH_3COOH, O_2N–CH_2–COOH, HCOOH

(2) Name the reagent in the following reaction : CH_3–CH=CH–CH_2–CN $\rightarrow$ CH_3–CH=CH–CH_2–CHO

(iii) Write the reaction involved in Hell-Volhard-Zelinsky reaction. [5 marks]

Solution:

Concept:

- A nitrogen atom acts as a nucleophile when its lone pair is available for donation. Resonance with an adjacent carbonyl group reduces this availability.
- Nucleophilic addition to a carbonyl group is favoured by greater positive character on the carbonyl carbon and less steric crowding around it.
- Electron-withdrawing groups stabilise a carboxylate ion and increase carboxylic acid strength; electron-donating groups have the opposite effect.
- Controlled reduction converts a nitrile into an aldehyde after hydrolysis. The Hell–Volhard–Zelinsky reaction replaces an alpha hydrogen of a carboxylic acid by a halogen.

Step 1: (i)(1) Locate the nucleophile Semicarbazide has the structure $H_2N{-}NH{-}C(=O){-}NH_2$. The lone pair on the nitrogen of the $-C(=O)-NH_2$ group is delocalised into the adjacent carbonyl group by resonance. This amide nitrogen is therefore a poor nucleophile. The terminal $H_2N{-}NH^-$ nitrogen has an available lone pair and attacks the carbonyl carbon of an aldehyde or ketone. Condensation followed by loss of water gives a semicarbazone:

$$R_2C{=}O + H_2N{-}NH{-}C(=O){-}NH_2 \longrightarrow R_2C{=}N{-}NH{-}C(=O){-}NH_2 + H_2O.$$

Thus, only the terminal amino group participates in semicarbazone formation.

Step 2: (i)(2) Compare the carbonyl compounds In the addition of HCN, the nucleophile CN^- attacks the electrophilic carbonyl carbon. Acetaldehyde, CH_3CHO, has one methyl group and one hydrogen attached to this carbon, whereas acetone, CH_3COCH_3, has two methyl groups. The additional methyl group in acetone donates electron density by the positive inductive effect, reducing the positive character of its carbonyl carbon. It also increases steric hindrance to the approaching nucleophile. Both electronic and steric factors therefore make acetaldehyde more reactive than acetone.

Step 3: (ii)(1) Compare conjugate-base stability The nitro group in $O_2N{-}CH_2{-}COOH$ exerts a strong negative inductive effect and stabilises the negative charge of the corresponding carboxylate ion. In CH_3COOH, the methyl group has a positive inductive effect and destabilises the carboxylate ion relative to formate. Formic acid has no electron-donating alkyl group. Consequently, the decreasing order of acidic strength is

$$O_2N{-}CH_2{-}COOH > HCOOH > CH_3COOH.$$

Quick Tip to Solve: For the nitrile conversion, preserve the carbon count and the double bond; choose DIBAL-H followed by hydrolysis. For the acid order, compare how each substituent stabilises the carboxylate ion.

Step 4: (ii)(2) Choose a selective reducing reagent Use diisobutylaluminium hydride (DIBAL-H), followed by hydrolysis. Controlled reduction at low temperature reduces the nitrile group to an intermediate that yields the aldehyde on hydrolysis, while retaining the carbon–carbon double bond:

$$\mathrm{CH_3{-}CH{=}CH{-}CH_2{-}CN} \xrightarrow[\text{2. hydrolysis}]{\text{1. DIBAL-H}} \mathrm{CH_3{-}CH{=}CH{-}CH_2{-}CHO}.$$

The nitrile carbon becomes the aldehyde carbon, so the carbon chain is unchanged.

Step 5: (iii) Write the alpha-halogenation reaction In the Hell–Volhard–Zelinsky reaction, a carboxylic acid containing at least one alpha hydrogen reacts with chlorine or bromine in the presence of a small amount of red phosphorus to give an alpha-halo carboxylic acid after hydrolysis. For bromination, the overall reaction is

$$\mathrm{R{-}CH_2{-}COOH + Br_2} \xrightarrow{\text{red P; then hydrolysis}} \mathrm{R{-}CHBr{-}COOH + HBr}.$$

Here, R denotes an alkyl group or hydrogen; the alpha carbon is the carbon immediately adjacent to the carboxyl group. For example, ethanoic acid gives bromoethanoic acid under these conditions.

Step 6: Conclusion The terminal amino group of semicarbazide is reactive because its lone pair is available. Acetaldehyde undergoes cyanide addition more readily because it is less electron-rich and less crowded than acetone. The acid order is $\mathrm{O_2N{-}CH_2{-}COOH} > \mathrm{HCOOH} > \mathrm{CH_3COOH}$. DIBAL-H followed by hydrolysis gives the required aldehyde, and the Hell–Volhard–Zelinsky reaction gives an alpha-halo acid using halogen and red phosphorus.

Quick Tip to Solve: For the nitrile conversion, preserve the carbon count and the double bond; choose DIBAL-H followed by hydrolysis. For the acid order, compare how each substituent stabilises the carboxylate ion.