CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-3-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

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

Section A (16 marks)

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

1. Which of the following does not show variable oxidation states ? [1 mark]

(A) Fe

(B) Cu

(C) Mn

(D) Sc

Correct Answer: (D) Sc

Solution:

Concept:

- Transition elements show variable oxidation states when both the outer ns and inner $(n-1)d$ electrons can participate in bonding.
- Scandium has configuration $[\mathrm{Ar}]3d^1 4s^2$; loss of these three electrons gives the stable Sc^{3+} ion.

Step 1: Examine scandium Scandium normally exhibits only the $+3$ oxidation state in its compounds. After losing its two $4s$ electrons and one $3d$ electron, it attains the argon noble-gas configuration. Further removal would involve a closed inner shell.

Step 2: Check the other choices Iron commonly exhibits $+2$ and $+3$; copper exhibits $+1$ and $+2$; manganese exhibits several oxidation states, including $+2$, $+4$ and $+7$. Thus all three satisfy variable oxidation states, while scandium does not.

Step 3: Conclusion Scandium does not normally show variable oxidation states. Hence, the correct option is (D).

Quick Tip to Solve: Remember Sc as the first 3d element: removing its three valence electrons gives only the stable $+3$ state.

2. The type of isomerism shown by the complex $[CoCl_2(en)_2]^+$ is : [1 mark]

(A) Ionisation isomerism

(B) Geometrical isomerism

(C) Linkage isomerism

(D) Coordination isomerism

Correct Answer: (B) Geometrical isomerism

Solution:

Concept:

- Ethylenediamine, en, is a bidentate ligand occupying two adjacent coordination sites.
- Two en ligands and two chloride ligands give coordination number six and an octahedral complex.

Step 1: Locate the chloride ligands In $[\mathrm{CoCl_2(en)_2}]^+$, the two chloride ligands can occupy adjacent

Quick Tip to Solve: For an octahedral complex with two identical monodentate ligands, first check whether they can be cis or trans.

positions, giving the cis isomer, or opposite positions, giving the trans isomer. The composition and connectivity remain the same, but the spatial arrangement differs.

Step 2: Distinguish the other isomerisms This change is geometrical isomerism. Ionisation isomerism requires interchange of a coordinated ligand and a counter-ion; linkage isomerism requires an ambidentate ligand bonding through different atoms; coordination isomerism requires ligand exchange between complex cations and anions. None describes the cis/trans arrangement here.

Step 3: Conclusion The complex shows geometrical isomerism. Hence, the correct option is (B).

Quick Tip to Solve: For an octahedral complex with two identical monodentate ligands, first check whether they can be cis or trans.

3. Which of the following is diamagnetic in nature ? [Atomic number : Co = 27] [1 mark]

(A) Co^{3+}, octahedral complex with strong field ligand

(B) Co^{3+}, octahedral complex with weak field ligand

(C) Co^{3+}, in a square planar complex

(D) Co^{3+}, in a tetrahedral complex

Correct Answer: (A) Co^{3+}, octahedral complex with strong field ligand

Solution:

Concept:

- A diamagnetic complex has no unpaired electrons; Co^{3+} has the $3d^6$ configuration.
- In an octahedral field, strong-field ligands produce a low-spin configuration when the splitting exceeds the electron-pairing energy.

Step 1: Fill the strong-field octahedral levels Neutral cobalt is $[Ar]3d^7 4s^2$. Removing three electrons gives Co^{3+} : $3d^6$. With strong-field octahedral ligands the six electrons pair in the three lower t_{2g} orbitals: $t_{2g}^6 e_g^0$. Every electron is paired, so this complex is diamagnetic.

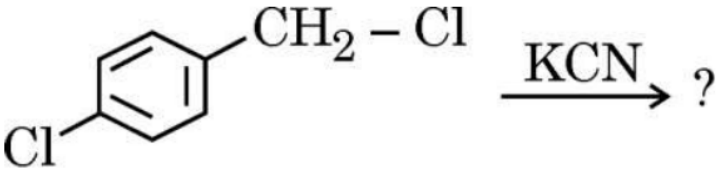
Step 2: Assess the remaining printed options Weak-field octahedral Co^{3+} is high-spin $t_{2g}^4 e_g^2$, with four unpaired electrons. Tetrahedral splitting is small, so a tetrahedral d^6 complex is also normally high-spin and paramagnetic. The square-planar option specifies geometry but no ligand strength or electron-pairing condition; it does not establish a unique spin state for d^6. The strong-field octahedral choice explicitly guarantees complete pairing.

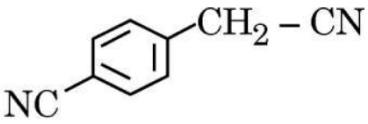
Step 3: Conclusion The explicitly established diamagnetic species is strong-field octahedral Co^{3+}, with $t_{2g}^6 e_g^0$. Hence, the correct option is (A).

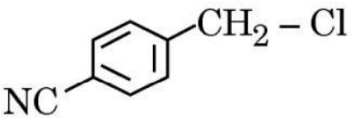
Quick Tip to Solve: Count d electrons after oxidation, then fill the split levels; diamagnetism requires every electron to be paired.

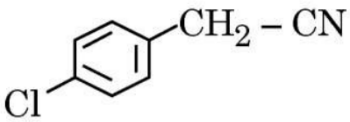
4. Consider the following reaction:

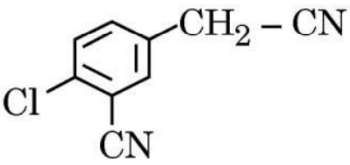
The major product of the reaction is : [1 mark]



(A) 

(B) 

(C) 

(D) 

(A) p-$NCC_6H_4CH_2CN$

(B) p-$NCC_6H_4CH_2Cl$

(C) p-$ClC_6H_4CH_2CN$

(D) 2-Cyano-4-chlorophenylacetonitrile

Correct Answer: (C) p-$ClC_6H_4CH_2CN$

Solution:

Concept:

- With ionic KCN, the carbon end of CN^- attacks an alkyl halide to form a nitrile, $R-CN$.
- A benzylic carbon-halogen bond undergoes nucleophilic substitution readily; an unactivated aryl carbon-halogen bond resists it.

Step 1: Identify the reacting chlorine The substrate has one chlorine directly bonded to the aromatic ring and another in the benzylic $-CH_2Cl$ group. Cyanide displaces the benzylic chloride; the chlorine bonded directly to the benzene ring remains unchanged.

Step 2: Write the product and compare the figures

$$p\text{-}ClC_6H_4CH_2Cl + KCN \longrightarrow p\text{-}ClC_6H_4CH_2CN + KCl.$$

Option (C) shows exactly this product. Option (A) also replaces the aryl chlorine, option (B) replaces only the aryl chlorine, and option (D) adds another ring cyano group. These changes are not produced

Quick Tip to Solve: With KCN, replace the chlorine on CH2Cl by CN; leave an unactivated ring chlorine untouched.

by ordinary substitution with KCN.

Step 3: Conclusion The major product is p-$ClC_6H_4CH_2CN$, as shown in option (C).

Quick Tip to Solve: With KCN, replace the chlorine on CH2Cl by CN; leave an unactivated ring chlorine untouched.

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

(A) p-Cresol

(B) p-Nitrophenol

(C) m-Nitrophenol

(D) 2,4,6-Trinitrophenol

Correct Answer: (D) 2,4,6-Trinitrophenol

Solution:

Concept:

- $pK_a = -\log K_a$; a lower pK_a means a stronger acid.
- Electron-withdrawing nitro groups stabilise a phenoxide conjugate base, whereas an electron-donating methyl group destabilises it.

Step 1: Compare substituent effects In p-cresol, the methyl group donates electron density and decreases acidity. A nitro group withdraws electron density by its inductive effect; at the para position it also stabilises phenoxide through resonance. Thus p-nitrophenol is more acidic than m-nitrophenol, whose nitro group does not provide the same resonance stabilisation.

Step 2: Identify the greatest conjugate-base stabilisation 2,4,6-Trinitrophenol, also called picric acid, has three strongly electron-withdrawing nitro groups, including groups at ortho and para positions. Their combined effects greatly stabilise the anion formed by loss of the phenolic proton. It therefore has the largest acid dissociation constant and the lowest pKa among the four compounds.

Step 3: Conclusion 2,4,6-Trinitrophenol has the lowest pK_a. Hence, the correct option is (D).

Quick Tip to Solve: For substituted phenols, look for the strongest stabilisation of phenoxide: multiple ortho/para nitro groups lower pKa.

6. $(CH_3)_2CH-O-CH_3$ when treated with HI gives : [1 mark]

(A) $(CH_3)_2CH-I + CH_3OH$

(B) $(CH_3)_2CH-OH + CH_3-I$

(C) $(CH_3)_2CH-I + CH_3-I$

(D) $(CH_3)_2CH-OH + CH_3OH$

Correct Answer: (B) $(CH_3)_2CH-OH + CH_3-I$

Solution:

Concept:

- HI protonates an ether oxygen, making cleavage of a carbon-oxygen bond possible.
- For a methyl-secondary ether, iodide attacks the less hindered methyl carbon by an S_N2 mechanism.

Step 1: Select the cleavage site The ether is methyl isopropyl ether. After protonation, I^- attacks the methyl group because its carbon is less hindered than the secondary isopropyl carbon. Breaking the methyl-oxygen bond leaves the oxygen attached to the isopropyl group.

Step 2: Write the cleavage products

$$(CH_3)_2CH - O - CH_3 + HI \longrightarrow (CH_3)_2CHOH + CH_3I.$$

Option (A) corresponds to cleavage at the more hindered carbon, and option (D) describes hydrolysis rather than reaction with HI. Option (C) can result from further reaction of the alcohol with excess hot HI, but the question gives no such further-treatment condition. The direct cleavage products are those in (B).

Step 3: Conclusion The products are isopropyl alcohol and methyl iodide. Hence, the correct option is (B).

Quick Tip to Solve: For HI cleavage of a methyl ether without a tertiary group, attach iodine to methyl and retain oxygen on the other group.

7. Which of the following compounds on treatment with benzene sulphonyl chloride forms an alkali-soluble precipitate ? [1 mark]

(A) CH_3CONH_2

(B) $(CH_3)_3N$

(C) $(CH_3)_2NH$

(D) $CH_3CH_2NH_2$

Correct Answer: (D) $CH_3CH_2NH_2$

Solution:

Concept:

- The Hinsberg reagent is benzene sulphonyl chloride, $C_6H_5SO_2Cl$.
- A primary amine forms a sulphonamide retaining an acidic N-H bond, so the product dissolves in alkali by salt formation.

Quick Tip to Solve: In the Hinsberg test, a primary amine gives a product with one N-H bond left; this explains its alkali solubility.

Step 1: Apply the primary-amine test Ethylamine, $CH_3CH_2NH_2$, is a primary amine. It reacts with benzene sulphonyl chloride to form $C_6H_5SO_2NHCH_2CH_3$. The remaining N-H proton is acidic because of the electron-withdrawing sulphonyl group; alkali removes it and forms a soluble salt.

Step 2: Eliminate the other compounds Dimethylamine is secondary and gives a sulphonamide with no N-H bond, making it insoluble in alkali. Trimethylamine is tertiary and has no N-H bond available for sulphonamide formation. Acetamide is an amide, whose nitrogen lone pair is delocalised into the carbonyl group; it does not behave as the primary aliphatic amine required in the Hinsberg test.

Step 3: Conclusion Ethylamine forms the alkali-soluble sulphonamide product. Hence, the correct option is (D).

Quick Tip to Solve: In the Hinsberg test, a primary amine gives a product with one N-H bond left; this explains its alkali solubility.

8. The order of increasing basicities of CH_3NH_2 (I), $(CH_3)_2NH$ (II), $(CH_3)_3N$ (III) and $C_6H_5NH_2$ (IV) in aqueous media is : [1 mark]

(A) IV $<$ III $<$ I $<$ II

(B) II $<$ I $<$ IV $<$ III

(C) I $<$ II $<$ III $<$ IV

(D) II $<$ III $<$ I $<$ IV

Correct Answer: (A) IV $<$ III $<$ I $<$ II

Solution:

Concept:

- Basicity measures the tendency of nitrogen to accept a proton using its lone pair.
- In aqueous solution, the inductive effect, solvation of the conjugate acid and steric hindrance together determine amine basicity.

Step 1: Compare aniline with alkylamines In aniline (IV), the nitrogen lone pair is delocalised into the benzene ring by resonance. It is therefore less available for protonation than the localised lone pair of an alkylamine. Hence IV is the weakest base; options (B), (C) and (D), which place aniline above an alkylamine, fail.

Step 2: Order the methylamines in water Methyl groups donate electron density to nitrogen, but hydration of the protonated amine must also be considered. Dimethylamine (II) has a favourable balance of electron donation and hydration. Methylamine (I) is better solvated than the more crowded trimethylamine (III). Thus the aqueous order is III $<$ I $<$ II; the gas-phase trend cannot be applied here.

Step 3: Conclusion The increasing basicity is $\boxed{\text{IV} < \text{III} < \text{I} < \text{II}}$. Hence, the correct option is (A).

Quick Tip to Solve: For aqueous methylamines, remember secondary $>$ primary $>$ tertiary; place aniline below all three.

9. The vitamin which plays an important role in coagulating blood is : [1 mark]

(A) Vitamin A

(B) Vitamin E

(C) Vitamin D

(D) Vitamin K

Correct Answer: (D) Vitamin K

Solution:

Concept:

- Vitamins are organic micronutrients required for normal physiological functions.
- Vitamin K is required for the formation of functional blood-clotting proteins, including prothrombin.

Step 1: Identify the clotting vitamin Coagulation involves a sequence of reactions in which clotting factors help form a fibrin clot. Vitamin K supports the synthesis and activation of several clotting factors in the liver. Its deficiency can impair clotting and cause excessive bleeding. Thus vitamin K is directly associated with the function named in the question.

Step 2: Check the other vitamins Vitamin A is chiefly associated with vision and maintenance of epithelial tissues. Vitamin E acts mainly as an antioxidant that protects cell membranes. Vitamin D helps regulate calcium and phosphate metabolism and supports bone mineralisation. These functions do not make A, E or D the vitamin specifically required for normal blood coagulation.

Step 3: Conclusion $\boxed{\text{Vitamin K}}$ plays an important role in coagulating blood. Hence, the correct option is (D).

Quick Tip to Solve: Link K with clotting; link A with vision and D with calcium and bones.

10. When a catalyst increases the rate of a chemical reaction, then the rate constant (k) : [1 mark]

(A) remains constant

(B) decreases

(C) increases

(D) may increase or decrease depending on the order of the reaction

Correct Answer: (C) increases

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, T is absolute temperature and R is the gas constant.
- A catalyst provides an alternative reaction pathway having a lower activation energy.

Step 1: Apply the effect of the catalyst At the same temperature, lowering the activation-energy barrier allows a larger fraction of reacting particles to make successful collisions. In the Arrhenius expression, a smaller E_a makes the exponential factor larger. The effective rate constant of the catalysed reaction therefore increases.

Quick Tip to Solve: At fixed temperature, follow the lower activation barrier to a higher effective rate constant.

Step 2: Reject the distractors For a given concentration of reactants, a larger effective rate constant produces a faster reaction. Thus a catalyst that increases the rate cannot leave the effective k unchanged or decrease it: (A) and (B) fail. The conclusion is not selected by whether the reaction is first or second order, so (D) also fails. A rate constant is constant for specified conditions, but changes when those conditions, such as catalysis, change.

Step 3: Conclusion The rate constant $\boxed{k \text{ increases}}$. Hence, the correct option is (C).

Quick Tip to Solve: At fixed temperature, follow the lower activation barrier to a higher effective rate constant.

11. 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 pressure at the same temperature.
- For a dilute nonelectrolyte solution, $\pi = CRT = (w/MV)RT$, where C is molarity, w is solute mass, M is molar mass and V is solution volume.

Step 1: Use a common solution volume A 1% solution contains $1\,\text{g}$ of X per $100\,\text{mL}$, while a 6% sucrose solution contains $6\,\text{g}$ per the same volume. Equal osmotic pressures at a common temperature imply equal molar concentrations. Since the volumes are equal, the numbers of moles of the two solutes must be equal.

Step 2: Calculate and check the molar mass Writing M_X for the molar mass of X gives

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

This value gives the same moles in each 100 mL portion. The values 34.2, 114 and 3.42 would give unequal molar concentrations and therefore do not satisfy the stated isotonic condition.

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

Quick Tip to Solve: For isotonic nonelectrolytes at the same temperature, equate mass concentration divided by molar mass.

12. During the electrolysis of aqueous NaCl, the cathodic reaction is : [1 mark]

(A) Oxidation of Cl^- ion

(B) Reduction of Na^+ ion

(C) Oxidation of H_2O

(D) Reduction of H_2O

Correct Answer: (D) Reduction of H_2O

Solution:

Concept:

- Reduction, the gain of electrons, occurs at the cathode during electrolysis.
- In aqueous sodium chloride, water is reduced preferentially to sodium ions, producing hydrogen gas and hydroxide ions.

Step 1: Identify the species discharged at the cathode The aqueous solution contains both Na^+ ions and water. Reduction of sodium ions to sodium metal is much more difficult than reduction of water under these conditions. Water therefore accepts electrons at the cathode; sodium ions remain in solution.

Step 2: Write the half-reaction and check the choices The cathodic half-reaction is

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq).$$

Both oxidation choices, (A) and (C), describe loss of electrons and cannot be cathodic reactions. Option (B) is incorrect for aqueous NaCl: sodium metal is obtained by electrolysis of molten sodium chloride, where water is absent. Thus only reduction of water matches the cathode in this question.

Step 3: Conclusion The cathodic process is $\boxed{\text{reduction of water}}$. Hence, the correct option is (D).

Quick Tip to Solve: Check whether NaCl is aqueous or molten before deciding which species is reduced at the cathode.

13. Assertion (A): Addition of ethylene glycol to water lowers its freezing point.

Reason (R): Ethylene glycol is insoluble in water due to lack of its ability to form hydrogen bonds with water molecules. [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:

- Freezing-point depression is a colligative property: $\Delta T_f = iK_f m$, with m the solute molality and K_f the solvent freezing-point constant.
- Ethylene glycol, $\mathrm{HOCH_2CH_2OH}$, has two hydroxyl groups capable of hydrogen bonding with water.

Step 1: Judge Assertion (A) Ethylene glycol is a soluble, nonvolatile solute. Adding it to water lowers the freezing point relative to pure water; $\Delta T_f = T_f^0 - T_f$ is positive. This is why ethylene glycol can be used as an antifreeze. Assertion (A) is true.

Step 2: Judge Reason (R) The two hydroxyl groups of ethylene glycol form hydrogen bonds with water molecules. Ethylene glycol is miscible with water, so both the claim of insolubility and the stated lack of hydrogen-bonding ability are false. Reason (R) is false.

Step 3: Test the explanatory link The lowering of the freezing point arises from the colligative effect of dissolved solute particles. The false reason cannot explain the true assertion. Options (A) and (B) wrongly make R true, while (D) wrongly makes A false.

Step 4: Conclusion The assertion is true, but the reason is false. Hence, the correct option is $\boxed{\text{(C)}}$.

Quick Tip to Solve: Look for the two OH groups in ethylene glycol before accepting a claim that it cannot hydrogen-bond.

14. Assertion (A): Order of reaction and molecularity are always same for complex reactions.

Reason (R): Order is determined experimentally and molecularity is applicable only for elementary reactions. [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:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- Molecularity counts reacting species in one elementary step; it is not assigned to an overall complex reaction.

Step 1: Judge Assertion (A) A complex reaction takes place through several elementary steps. Its observed rate law depends on the mechanism and may be governed by a slow step; its order cannot generally be read from the overall balanced equation. Molecularity is not defined for the overall complex reaction, so the assertion that order and molecularity are always the same is false.

Step 2: Judge Reason (R) Order is determined experimentally from the dependence of rate on concentrations. Molecularity refers only to the number of species involved in an elementary reaction step. Both statements in the reason are correct, so Reason (R) is true.

Step 3: Select the logical combination Since A is false, neither (A) nor (B), both of which require a true assertion, can be selected. Option (C) also incorrectly makes A true and R false. The observed combination is false assertion with true reason, as given in option (D).

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is $\boxed{\text{(D)}}$.

Quick Tip to Solve: For a multistep reaction, use its measured rate law for order; assign molecularity only to individual steps.

15. Assertion (A): The boiling point of ethanol is higher than that of dimethyl ether.

Reason (R): Ethanol molecules are associated through hydrogen bonding whereas in dimethyl ether, it is not possible. [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:

- Intermolecular hydrogen bonding requires hydrogen bonded directly to a highly electronegative atom such as oxygen.
- A higher boiling point indicates that more energy is required to overcome intermolecular attractions.

Step 1: Judge the assertion Ethanol and dimethyl ether are functional isomers with the same molecular formula, C_2H_6O. Ethanol has stronger intermolecular attraction and therefore a higher boiling point. Assertion (A) is true.

Step 2: Judge the reason Ethanol contains an $O-H$ group, allowing one molecule to hydrogen-bond to the oxygen of another. Pure dimethyl ether has oxygen but no $O-H$ bond, so its molecules cannot form such hydrogen bonds with one another. Reason (R) is true.

Step 3: Check the explanation and options Breaking the intermolecular hydrogen-bonded association in ethanol requires additional energy, directly explaining its higher boiling point. Option (B) incorrectly denies the explanatory connection, while (C) and (D) incorrectly classify one of the true statements as false.

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

Quick Tip to Solve: Compare the O-H groups of these isomers before comparing their molecular masses.

16. Assertion (A): Aniline does not undergo Friedel-Crafts reaction.

Reason (R): Friedel-Crafts reaction is an electrophilic substitution 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: (B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

Solution:

Concept:

- Friedel-Crafts alkylation and acylation are electrophilic aromatic substitution reactions using a Lewis acid catalyst such as $AlCl_3$.
- Aniline has a lone pair on nitrogen which interacts strongly with the Lewis acid catalyst.

Step 1: Judge the assertion Aniline does not undergo the usual Friedel-Crafts reaction. Its amino group reacts with the Lewis acid catalyst, producing a salt or complex in which the ring is strongly deactivated. Thus Assertion (A) is true.

Step 2: Judge the reason In a Friedel-Crafts reaction, an electrophile attacks the aromatic ring and replaces a ring hydrogen after aromaticity is restored. It is therefore an electrophilic substitution reaction, so Reason (R) is true.

Step 3: Check whether the reason explains the assertion The classification as electrophilic substitution does not explain the failure of aniline: aniline readily undergoes other electrophilic substitutions. The specific problem is the interaction of the amino group with the Lewis acid catalyst. Option (A) incorrectly claims an explanation; options (C) and (D) incorrectly reject a true statement.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence, the correct option is (B).

Quick Tip to Solve: For aniline in Friedel-Crafts reactions, check the amino group interaction with AlCl3.

Section B (10 marks)

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

Solution:

Concept:

- For a dilute solution of a non-electrolyte, freezing-point depression is $\Delta T_f = K_f m$, where m is molality.
- The cryoscopic constant K_f depends on the solvent, its freezing point and its molar enthalpy of fusion.

Quick Tip to Solve: Use kelvin for the freezing point and kg per mole for molar mass in this formula.

Step 1: Define the molal depression constant The molal depression constant, or cryoscopic constant, is the depression in the freezing point of a solvent when one mole of a non-volatile non-electrolyte is dissolved in one kilogram of that solvent, in the dilute-solution limit. Equivalently, $K_f = \Delta T_f / m$; it is the freezing-point depression corresponding to unit molality. Its unit is $\mathrm{K\,kg\,mol^{-1}}$.

Step 2: Relate it to the enthalpy of fusion The thermodynamic relation is

$$K_f = \frac{R(T_f^0)^2 M_1}{\Delta_{\text{fus}} H_m}.$$

Here R is the gas constant, T_f^0 is the freezing point of the pure solvent in kelvin, M_1 is its molar mass in $\mathrm{kg\,mol^{-1}}$, and $\Delta_{\text{fus}} H_m$ is its molar enthalpy of fusion in $\mathrm{J\,mol^{-1}}$. If the molar mass is expressed in $\mathrm{g\,mol^{-1}}$, the denominator must also contain a factor of 1000. For fixed freezing point and molar mass, a larger fusion enthalpy gives a smaller cryoscopic constant.

Step 3: Conclusion K_f is the freezing-point depression at unit molality, and $K_f = R(T_f^0)^2 M_1 / \Delta_{\text{fus}} H_m$ with M_1 in $\mathrm{kg\,mol^{-1}}$.

Quick Tip to Solve: Use kelvin for the freezing point and kg per mole for molar mass in this formula.

OR

17(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:

- Positive deviation from Raoult's law means the component vapour pressures exceed $p_i = x_i p_i^0$.
- Weaker unlike-molecule attractions allow molecules to escape more easily into the vapour phase.

Step 1: Identify the deviation and explain its origin Ethanol and acetone form a mixture showing positive deviation from Raoult's law. Pure ethanol molecules are associated by intermolecular hydrogen bonds. On adding acetone, this association is disrupted, and the resulting ethanol-acetone interactions are weaker overall than the original associations. Consequently the molecules escape more readily, raising each relevant partial vapour pressure and the total vapour pressure above the ideal-solution prediction.

Step 2: Identify the azeotrope A sufficiently large positive deviation produces a minimum-boiling azeotrope. The enhanced total vapour pressure means the mixture reaches the external pressure at a lower temperature. At the azeotropic composition the liquid and vapour have the same composition, so boiling occurs at constant composition and ordinary fractional distillation cannot separate the components beyond that composition.

Step 3: Conclusion The ethanol-acetone mixture shows positive deviation and forms a minimum-boiling azeotrope.

Quick Tip to Solve: Positive deviation raises vapour pressure, so remember that it lowers the boiling temperature.

18. (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:

- If other concentrations and temperature are fixed, a rate law $r = k[X]^n$ gives $r_2/r_1 = ([X]_2/[X]_1)^n$.
- A bimolecular reaction behaves as pseudo-first-order when one reactant is in large excess and its concentration remains practically constant.

Step 1: (a) Determine the order Let the order with respect to reactant X be n. Tripling its concentration gives

$$\frac{r_2}{r_1} = \left(\frac{3[X]}{[X]}\right)^n = 3^n = 27 = 3^3.$$

Thus the order with respect to X is three; for the stated reaction with rate governed by X, this is third order.

Step 2: (b) Give the condition and example For a bimolecular reaction with rate $r = k[A][B]$, take B in such large excess that its concentration changes negligibly during the reaction. Then $k_{\text{obs}} = k[B]$ is effectively constant and $r = k_{\text{obs}}[A]$, a first-order rate law. An example is the acid-catalysed hydrolysis of ethyl acetate in excess water:

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

At constant acid concentration, the effectively constant water concentration makes the measured rate proportional to the ester concentration.

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

Quick Tip to Solve: Write the ratio of rates first; for pseudo-first-order kinetics absorb the excess reactant into k.

19. Complete the following ionic equations :

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

(b) $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow$ [2 marks]

Solution:

Concept:

- In acidic medium, permanganate is reduced from manganese(VII) to $\mathrm{Mn^{2+}}$, while dichromate is reduced from chromium(VI) to $\mathrm{Cr^{3+}}$.
- An ionic redox equation must conserve both the number of atoms of every element and the total charge; the electrons lost by the reducing agent equal those gained by the oxidising agent.

Quick Tip to Solve: For acidic permanganate and dichromate equations, first write $\mathrm{Mn^{2+}}$ and $\mathrm{Cr^{3+}}$, then check atoms and total charge.

Step 1: Complete equation (a) Sulphite is oxidised to sulphate: sulphur changes from $+4$ to $+6$, losing two electrons per sulphite ion. Each permanganate ion gains five electrons, so two permanganate ions react with five sulphite ions:

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

The charge is -6 on each side, and oxygen and hydrogen are balanced by the three water molecules.

Step 2: Complete equation (b) The two chromium atoms together gain six electrons; six Fe^{2+} ions each lose one electron to form Fe^{3+}:

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

Both sides have charge $+24$; seven water molecules balance the seven oxygen atoms and fourteen hydrogen atoms.

Step 3: Conclusion The products are (a) $2Mn^{2+} + 5SO_4^{2-} + 3H_2O$ and (b) $2Cr^{3+} + 6Fe^{3+} + 7H_2O$.

Quick Tip to Solve: For acidic permanganate and dichromate equations, first write Mn^{2+} and Cr^{3+}, then check atoms and total charge.

20. (a) Which halogen compound in the following pair will react faster in S_N2 reactions and why ? CH_3-CH_2-I OR CH_3-CH_2-Br

(b) Why is chloroform stored in closed dark coloured bottles ? [2 marks]

Solution:

Concept:

- In an S_N2 reaction, the nucleophile attacks the carbon bonded to the halogen as the leaving group departs in the same step.
- For the same alkyl group, the weaker carbon–halogen bond and better leaving group favour faster substitution. Light and oxygen promote the oxidation of chloroform to poisonous phosgene.

Step 1: Compare the two ethyl halides Both compounds are primary ethyl halides and have the same steric hindrance. Thus their relative reactivity depends on the leaving group. The $C-I$ bond is weaker than the $C-Br$ bond, and I^- is a better leaving group than Br^-. Hence CH_3CH_2I undergoes S_N2 substitution faster than CH_3CH_2Br.

Step 2: Explain the storage of chloroform Chloroform is slowly oxidised by atmospheric oxygen in the presence of light to highly poisonous carbonyl chloride, called phosgene:

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl.$$

A closed bottle limits contact with air, while the dark coloured glass cuts off light. These measures suppress phosgene formation during storage.

Step 3: Conclusion (a) Ethyl iodide reacts faster because iodide is the better leaving group and the $C-I$ bond is weaker. (b) Closed dark coloured bottles suppress oxidation of chloroform to poisonous

Quick Tip to Solve: For identical alkyl groups, compare leaving groups; for chloroform storage, connect the closed cap with air and dark glass with light.

phosgene.

Quick Tip to Solve: For identical alkyl groups, compare leaving groups; for chloroform storage, connect the closed cap with air and dark glass with light.

21. Give reaction of glucose with the following :

(a) HCN

(b) Conc. HNO_3 [2 marks]

Solution:

Concept:

- The open-chain form of glucose is $CHO - (CHOH)_4 - CH_2OH$, containing an aldehyde group and a terminal primary alcohol group.
- HCN adds across a carbonyl group to form a cyanohydrin. Concentrated nitric acid oxidises both the aldehyde group and the terminal primary alcohol group to carboxylic acid groups.

Step 1: Reaction with HCN Hydrogen cyanide adds to the aldehyde group of the open-chain form. The carbonyl carbon acquires a cyano group and the carbonyl oxygen becomes a hydroxyl group:

$$CHO - (CHOH)_4 - CH_2OH + HCN \longrightarrow NC - CH(OH) - (CHOH)_4 - CH_2OH.$$

The product is glucose cyanohydrin. The original terminal CH_2OH group remains unchanged; the carbon of HCN adds one carbon to the chain.

Step 2: Reaction with concentrated nitric acid Concentrated HNO_3 is a strong oxidising agent. It converts the aldehyde end and the primary alcohol end into carboxyl groups:

$$CHO - (CHOH)_4 - CH_2OH + 3[O] \xrightarrow{\text{conc. } HNO_3} HOOC - (CHOH)_4 - COOH + H_2O.$$

The resulting dicarboxylic acid is saccharic acid (glucaric acid). The four interior secondary alcohol groups are retained in this standard glucose reaction.

Step 3: Conclusion Glucose forms glucose cyanohydrin with HCN and saccharic acid (glucaric acid) with concentrated HNO_3.

Quick Tip to Solve: Write glucose in its open-chain form: HCN changes only the aldehyde end, whereas concentrated nitric acid oxidises both terminal groups.

Section C (21 marks)

22. 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 a non-volatile solute, Raoult's law gives $p = x_1 p^\circ$, so the relative lowering is $(p^\circ - p)/p^\circ = x_2 = n_2/(n_1 + n_2)$. Here subscripts 1 and 2 denote water and solute.
- The amount of substance is $n = w/M$, where w is mass and M is molar mass. For a dilute solution, $n_2 \ll n_1$, giving the usual CBSE relation $(p^\circ - p)/p^\circ \simeq n_2/n_1$.

Step 1: Find the relative lowering The vapour pressure falls from $32\,\text{mm Hg}$ to $31.84\,\text{mm Hg}$ at the same temperature. Therefore,

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

Pressure units cancel in the ratio. This small mole fraction confirms that the solution is dilute.

Step 2: Use the dilute-solution relation Let the solute molar mass be M_2. Taking the molar mass of water as $18\,\text{g mol}^{-1}$,

$$0.005 \simeq \frac{w_2/M_2}{w_1/M_1} = \frac{5 \times 18}{200 M_2},$$

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

The non-volatile solute contributes no vapour pressure, so the lowering measures the solute particle fraction.

Step 3: Check the dilute approximation If the full mole-fraction expression is retained, then

$$0.005 = \frac{5/M_2}{200/18 + 5/M_2}, \qquad M_2 = \frac{5 \times 18(1 - 0.005)}{200 \times 0.005} = 89.55\,\text{g mol}^{-1}.$$

This differs by only 0.5% from the dilute calculation and rounds to approximately $90\,\text{g mol}^{-1}$. Thus neglecting solute moles in the total is consistent with the usual dilute-solution method.

Step 4: Conclusion The molar mass of the solute is approximately $\boxed{90\,\text{g mol}^{-1}}$ using the dilute-solution relation; retaining the exact mole fraction gives $89.55\,\text{g mol}^{-1}$.

Quick Tip to Solve: Use the lowering $32 - 31.84 = 0.16$, not the solution pressure itself, in the numerator of relative lowering of vapour pressure.

23. 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 the conductivity of the volume containing one mole of electrolyte. For conductivity κ in S cm^{-1} and concentration C in mol L^{-1}, $\Lambda_m = 1000\kappa/C$.
- Kohlrausch's law gives $\Lambda^0_m = \lambda^0_{K+} + \lambda^0_{Cl-}$ for KCl. The degree of dissociation requested is obtained from $\alpha = \Lambda_m/\Lambda^0_m$.

Step 1: Calculate molar conductivity The given concentration is $C = 0.2$ mol L^{-1} and the conductivity is $\kappa = 2.48 \times 10^{-2}$ S cm^{-1}. The factor 1000 converts litres to cubic centimetres, so the units of the result are S cm^2 mol^{-1}. Substituting,

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

Step 2: Calculate limiting molar conductivity and the ratio Each formula unit of KCl supplies one potassium ion and one chloride ion, so their limiting ionic conductivities are added with unit coefficients. Thus

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

Using the conductivity-ratio expression requested in the question,

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

The ratio is dimensionless because the numerator and denominator have identical units.

Step 3: Conclusion $\boxed{\Lambda_m = 124 \text{ S cm}^2 \text{ mol}^{-1}}$ and $\boxed{\alpha \approx 0.827\ (82.7\%)}$.

Quick Tip to Solve: Use the factor 1000 only when concentration is in mol per litre and conductivity is in S per centimetre; add both limiting ionic values before taking the ratio.

24. 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, $k = (2.303/t)\log([A]_0/[A]_t)$, where $[A]_0$ is the initial reactant concentration and $[A]_t$ is the concentration remaining after time t.
- If the fraction reacted is f, the fraction remaining is $1 - f$. First-order k has units of inverse time, and $t = (2.303/k)\log(1/(1-f))$.

Quick Tip to Solve: Convert each completion percentage to the percentage remaining first: use 75 for the initial calculation and 20 for the final calculation.

Step 1: Find the rate constant from 25 percent completion After 40 minutes, 25 percent of the reactant has reacted and 75 percent remains. Hence $[A]_0/[A]_{40} = 100/75 = 4/3$. Using the supplied logarithms,

$$\begin{aligned} k &= \frac{2.303}{40}\log\frac{4}{3} \\ &= \frac{2.303}{40}(0.60 - 0.48) \\ &= 6.909 \times 10^{-3}\,\text{min}^{-1}. \end{aligned}$$

It is the remaining concentration, rather than the reacted fraction, that enters the integrated rate equation.

Step 2: Find the time for 80 percent completion At 80 percent completion, only 20 percent remains, so $[A]_0/[A]_t = 100/20 = 5$. Using $\log 5 = 0.69$,

$$\begin{aligned} t &= \frac{2.303}{6.909 \times 10^{-3}}\log 5 \\ &= \frac{2.303 \times 0.69}{6.909 \times 10^{-3}} \\ &= 230\,\text{min}. \end{aligned}$$

This is the total time measured from the start of the reaction. The same result follows directly by taking the ratio $t/40 = 0.69/0.12$, which cancels the common rate constant.

Step 3: Conclusion $\boxed{k = 6.909 \times 10^{-3}\,\text{min}^{-1}}$; the reaction is 80 percent complete after $\boxed{230\,\text{min}}$.

Quick Tip to Solve: Convert each completion percentage to the percentage remaining first: use 75 for the initial calculation and 20 for the final calculation.

25. (a) What type of nucleophilic substitution (S_N1 or S_N2) occurs in the hydrolysis of 2-Bromobutane to form (±)-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:

- An S_N1 reaction proceeds through a carbocation. Its positively charged carbon is sp^2-hybridised and planar, permitting nucleophilic attack from either face.
- A racemic product, denoted $(\pm)$, contains both enantiomers. A single S_N2 displacement instead gives backside attack and inversion at the reacting stereocentre.
- The Wurtz–Fittig reaction couples an aryl halide with an alkyl halide using sodium metal in dry ether to form an alkylbenzene.

Step 1: Identify the hydrolysis mechanism in part (a) The formation of $(\pm)$-butan-2-ol indicates racemisation and therefore an S_N1 mechanism. First, the C–Br bond undergoes heterolytic cleavage,

Quick Tip to Solve: Connect the racemic symbol to a planar intermediate; for Wurtz–Fittig, join the aryl and alkyl groups and balance two sodium halide units.

producing the secondary carbocation

$$CH_3CH(Br)CH_2CH_3 \longrightarrow CH_3CH^+CH_2CH_3 + Br^-.$$

The carbocation centre is planar. Water attacks from either side of this plane; after loss of a proton, both enantiomers of butan-2-ol are obtained. This explains the racemic product. In contrast, an S_N2 step involves attack from only the side opposite the leaving group, so inversion alone does not explain formation of the stated racemate.

Step 2: Write the coupling reaction in part (b) Chlorobenzene and methyl chloride undergo the Wurtz–Fittig reaction with sodium in dry ether. The phenyl group and methyl group couple to give toluene (methylbenzene). The balanced equation is

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

Two sodium atoms are required because two chlorine atoms are removed as two formula units of sodium chloride.

Step 3: Conclusion (a) S_N1, because a planar carbocation permits attack from both faces and gives racemisation. (b) Toluene is formed by the Wurtz–Fittig reaction.

Quick Tip to Solve: Connect the racemic symbol to a planar intermediate; for Wurtz–Fittig, join the aryl and alkyl groups and balance two sodium halide units.

26. (a) Write the equations of 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:

- Phenol activates its aromatic ring toward electrophilic substitution at the ortho and para positions.
- Reimer–Tiemann formylation introduces a $-CHO$ group, whereas Kolbe carboxylation introduces a $-COOH$ group into the phenol ring.

Step 1: (a)(i) Reimer–Tiemann reaction Heat phenol with chloroform and aqueous sodium hydroxide, then acidify. The major product is ortho-hydroxybenzaldehyde (salicylaldehyde). The net equation after work-up is

$$C_6H_5OH + CHCl_3 + 3NaOH$$
$$\xrightarrow{\Delta} \text{o–}\ HOC_6H_4CHO + 3NaCl + 2H_2O.$$

The reactive electrophile is dichlorocarbene, formed from chloroform in alkaline medium. Formylation occurs mainly ortho to the hydroxyl group; the para isomer is a minor product.

Step 2: (a)(ii) Kolbe reaction First convert phenol to sodium phenoxide. Treat this salt with carbon

Quick Tip to Solve: Remember the group introduced: Reimer–Tiemann adds CHO, Kolbe adds COOH; bromine water substitutes all three activated positions.

dioxide at about $400\,\text{K}$ under pressure, then acidify the sodium salicylate formed:

$$\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O},$$

$$\text{C}_6\text{H}_5\text{ONa} + \text{CO}_2 \xrightarrow[\text{pressure}]{400\,\text{K}} \text{o}\text{–}\ \text{HOC}_6\text{H}_4\text{COONa},$$

$$\text{o}\text{–}\ \text{HOC}_6\text{H}_4\text{COONa} + \text{HCl} \longrightarrow \text{o}\text{–}\ \text{HOC}_6\text{H}_4\text{COOH} + \text{NaCl}.$$

The final product is salicylic acid (2-hydroxybenzoic acid).

Step 3: (b) Bromination reagent Use bromine water, $\text{Br}_2(\text{aq})$. Phenol decolourises it and gives a white precipitate of 2,4,6-tribromophenol:

$$\text{C}_6\text{H}_5\text{OH} + 3\text{Br}_2 \longrightarrow \text{C}_6\text{H}_2\text{Br}_3\text{OH} + 3\text{HBr}.$$

All three activated positions are substituted in aqueous medium.

Step 4: Conclusion Reimer–Tiemann reaction gives salicylaldehyde; Kolbe reaction gives salicylic acid. The reagent in (b) is bromine water.

Quick Tip to Solve: Remember the group introduced: Reimer–Tiemann adds CHO, Kolbe adds COOH; bromine water substitutes all three activated positions.

27. 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:

- Choose reagents that preserve the aromatic ring while changing the required functional group.
- Grignard reagents add a carbon group to an aldehyde, producing a secondary alcohol after hydrolysis; oxidation then gives a ketone.
- The haloform reaction cleaves a methyl ketone, RCOCH_3, to a carboxylate salt, which gives the acid on acidification.

Step 1: (a) Benzoic acid to benzaldehyde Convert the acid into benzoyl chloride with thionyl chloride. Carry out Rosenmund reduction using hydrogen and poisoned palladium supported on barium sulphate:

$$\text{C}_6\text{H}_5\text{COOH} \xrightarrow{\text{SOCl}_2} \text{C}_6\text{H}_5\text{COCl},$$

$$\text{C}_6\text{H}_5\text{COCl} + \text{H}_2 \xrightarrow{\text{Pd/BaSO}_4} \text{C}_6\text{H}_5\text{CHO} + \text{HCl}.$$

The poisoned catalyst limits reduction to the aldehyde stage.

Step 2: (b) Ethanal to propanone Add methylmagnesium bromide to ethanal in dry ether and hydrolyse the addition product to obtain propan-2-ol. Oxidise this secondary alcohol using acidified

Quick Tip to Solve: For a methyl ketone to acid conversion, use haloform cleavage; for one extra carbon before ketone formation, add a methyl Grignard reagent.

potassium dichromate:

$$\mathrm{CH_3CHO} \xrightarrow[\text{2. } \mathrm{H_3O^+}]{\text{1. } \mathrm{CH_3MgBr},\ \text{dry ether}} \mathrm{CH_3CH(OH)CH_3},$$

$$\mathrm{CH_3CH(OH)CH_3} + [\mathrm{O}] \xrightarrow{\mathrm{K_2Cr_2O_7/H^+}} \mathrm{CH_3COCH_3} + \mathrm{H_2O}.$$

The Grignard step increases the carbon chain from two carbons to three.

Step 3: (c) Acetophenone to benzoic acid Treat acetophenone with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate formed:

$$\mathrm{C_6H_5COCH_3} + 3\mathrm{I_2} + 4\mathrm{NaOH} \longrightarrow \mathrm{C_6H_5COONa} + \mathrm{CHI_3} + 3\mathrm{NaI} + 3\mathrm{H_2O},$$

$$\mathrm{C_6H_5COONa} + \mathrm{HCl} \longrightarrow \mathrm{C_6H_5COOH} + \mathrm{NaCl}.$$

This haloform reaction is possible because acetophenone contains the methyl ketone group.

Step 4: (d) Bromobenzene to 1-phenylethanol Prepare phenylmagnesium bromide from bromobenzene and magnesium in dry ether. Add ethanal and then hydrolyse:

$$\mathrm{C_6H_5Br} + \mathrm{Mg} \xrightarrow{\text{dry ether}} \mathrm{C_6H_5MgBr},$$

$$\mathrm{C_6H_5MgBr} + \mathrm{CH_3CHO} \longrightarrow \mathrm{C_6H_5CH(OMgBr)CH_3},$$

$$\mathrm{C_6H_5CH(OMgBr)CH_3} \xrightarrow{\mathrm{H_3O^+}} \mathrm{C_6H_5CH(OH)CH_3}.$$

Dry conditions prevent premature destruction of the Grignard reagent.

Step 5: Conclusion The required routes are Rosenmund reduction in (a), Grignard addition followed by oxidation in (b), haloform reaction followed by acidification in (c), and Grignard addition to ethanal in (d). Any three routes may be written.

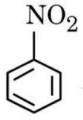
Quick Tip to Solve: For a methyl ketone to acid conversion, use haloform cleavage; for one extra carbon before ketone formation, add a methyl Grignard reagent.

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

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

(b) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273\,K]{NaNO_2+HCl} B \xrightarrow{C_6H_5OH} C$ [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:

- With ionic KCN, an alkyl halide gives a nitrile through carbon attack; this adds one carbon to the chain.
- $LiAlH_4$ reduces $-C \equiv N$ to $-CH_2NH_2$. Nitrous acid converts a primary aliphatic amine into the corresponding alcohol.
- Aromatic primary amines undergo diazotisation at 273–278 K; their diazonium salts couple with phenol to form an azo dye.

Step 1: (a) Identify A Chloroethane undergoes substitution with KCN to give propanenitrile:

$$CH_3CH_2Cl + KCN \longrightarrow CH_3CH_2C \equiv N + KCl.$$

Thus A is $CH_3CH_2C \equiv N$. It contains three carbon atoms, because the carbon of cyanide becomes part of the product skeleton.

Step 2: (a) Identify B and C Reduction of the nitrile gives propan-1-amine; reaction with nitrous acid at 0°C gives propan-1-ol:

$$CH_3CH_2CN + 4[H] \xrightarrow{LiAlH_4} CH_3CH_2CH_2NH_2,$$
$$CH_3CH_2CH_2NH_2 + HNO_2 \longrightarrow CH_3CH_2CH_2OH + N_2 + H_2O.$$

Hence B is $CH_3CH_2CH_2NH_2$, and C is $CH_3CH_2CH_2OH$. The unstable aliphatic diazonium intermediate loses nitrogen.

Step 3: (b) Identify A and B Fe/HCl reduces nitrobenzene to aniline (free amine after work-up). Aniline reacts with nitrous acid generated in situ from sodium nitrite and hydrochloric acid at 273 K:

$$C_6H_5NO_2 + 6[H] \xrightarrow{Fe/HCl} C_6H_5NH_2 + 2H_2O,$$
$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Thus A is aniline, $C_6H_5NH_2$, and B is benzenediazonium chloride, $C_6H_5 - N \equiv N^+\ Cl^-$.

Step 4: (b) Identify C Benzenediazonium chloride couples with phenol in mildly alkaline medium.

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), cold diazotisation preserves the diazonium salt for para coupling with phenol.

Coupling occurs mainly at the para position relative to OH:

$$C_6H_5N_2^+Cl^- + C_6H_5OH \longrightarrow p\text{–}\ HOC_6H_4 - N = N - C_6H_5 + HCl.$$

Thus C is p-hydroxyazobenzene, with structural formula $p\text{–}\ HO - C_6H_4 - N = N - C_6H_5$. The azo linkage joins the two aromatic rings.

Step 5: Conclusion (a) A: CH_3CH_2CN; B: $CH_3CH_2CH_2NH_2$; C: $CH_3CH_2CH_2OH$. (b) A: $C_6H_5NH_2$; B: $C_6H_5N_2^+Cl^-$; C: $p\text{–}\ HOC_6H_4 - N = N - C_6H_5$.

Quick Tip to Solve: Count the cyanide carbon in (a); in (b), cold diazotisation preserves the diazonium salt for para coupling with phenol.

Section D (8 marks)

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

29. 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.

[4 marks]

29(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.
- Transition metals can use variable oxidation states and available orbitals to form intermediate species with reactants.

Step 1: Explain intermediate formation Transition metals and their compounds can change oxidation state during a reaction. They can therefore accept electrons in one stage and donate them in another, forming intermediate compounds which subsequently decompose to give the products and regenerate the catalyst.

Step 2: Explain the surface contribution For a solid transition-metal catalyst, reactant molecules can adsorb on its surface through available orbitals. Adsorption brings reactants together and weakens their bonds, so the activation energy is lowered and the reaction proceeds faster.

Step 3: Conclusion Transition metals are good catalysts because of their variable oxidation states and ability to form intermediates; their surfaces also facilitate adsorption of reactants.

Quick Tip to Solve: Link variable oxidation states to intermediate formation, then explain how adsorption lowers activation energy.

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

Solution:

Concept:

- Shielding reduces the attraction of the nucleus for electrons outside a given shell.
- The $4f$ electrons shield the increasing nuclear charge poorly.

Step 1: Track the nuclear charge As atomic number increases along the lanthanoid series, each successive atom has one more proton, while the added electron enters the inner $4f$ subshell.

Step 2: Compare shielding with attraction The added $4f$ electrons do not effectively screen the increase in nuclear charge. The effective nuclear attraction on the outer electrons therefore rises, drawing the electron cloud inward and gradually decreasing atomic size.

Step 3: Conclusion Lanthanoid contraction is caused by the poor shielding of increasing nuclear charge by the $4f$ electrons.

Quick Tip to Solve: State poor shielding by 4f electrons and connect it to increasing effective nuclear charge and decreasing size.

29(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 the effective nuclear attraction and contracts the electron cloud.
- The third transition series follows the lanthanoids; its size is affected by this preceding contraction.

Step 1: Define the contraction Lanthanoid contraction is the regular, gradual decrease in atomic radii and in the radii of corresponding ions of the lanthanoids with increasing atomic number. Across the series, the increase in nuclear charge is not adequately screened by the electrons added to the $4f$ subshell, so the outer electrons experience greater attraction.

Step 2: Apply it to the transition series Ordinarily, atoms in a lower period are larger because they have an additional electron shell. However, the lanthanoid contraction reduces the sizes of the elements of the third, $5d$, transition series. It largely offsets the size increase due to the extra shell, so corresponding members of the second, $4d$, and third, $5d$, transition series have nearly equal atomic radii. A characteristic example is zirconium and hafnium, whose atomic radii are very similar.

Step 3: Conclusion Lanthanoid contraction is the progressive decrease in lanthanoid atomic and ionic radii. It makes corresponding elements of the second and third transition series nearly equal in atomic radius, as illustrated by Zr and Hf.

Quick Tip to Solve: For the consequence, compare corresponding 4d and 5d elements and use Zr-Hf as the standard example.

OR

29(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; the stronger reducing agent is oxidised more readily.
- For the metal-ion couples, a more negative standard reduction potential indicates that the lower oxidation state is a stronger reducing agent under standard conditions.
- A d^3 configuration has special stability in an octahedral environment, whereas d^5 is half-filled.

Step 1: Compare the aqueous electrode potentials The relevant standard reduction potentials are approximately

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

The more negative potential for the chromium couple means that Cr^{2+} has a greater tendency to lose an electron and form Cr^{3+}. Thus it donates electrons more readily than Fe^{2+}.

Step 2: Explain using electronic configurations Chromium(II) has a $3d^4$ configuration and is readily oxidised to chromium(III), with the more stable $3d^3$ configuration. Iron(II), $3d^6$, can also be oxidised to iron(III), $3d^5$, but the aqueous electrode potentials show that this oxidation is much less favourable. Although the half-filled iron(III) configuration is stable, it does not make iron(II) the stronger reducing agent; the comparison must account for the aqueous ions.

Step 3: Conclusion Cr^{2+} is the stronger reducing agent in aqueous media because it is more readily oxidised from $3d^4$ to the stable $3d^3$ configuration of Cr^{3+}, consistent with its more negative reduction potential.

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

30. 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. [4 marks]

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

Solution:

Concept:

- Amino acids are the building units of proteins; each contains amino and carboxyl functional groups.
- Essential amino acids must be supplied through food because the human body cannot synthesise them.

Step 1: Identify the meaning of essential The term essential refers to the inability of the body to make an amino acid, rather than to whether that amino acid occurs in a protein. Thus, the dietary source is necessary even though proteins contain both essential and non-essential amino acids.

Step 2: Connect the definition to diet For example, valine and lysine are essential amino acids. They must be obtained from dietary proteins, which are digested to release their constituent amino acids for use by the body.

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

Quick Tip to Solve: Use the phrase cannot be synthesised by the body; essential does not simply mean present in proteins.

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

Solution:

Concept:

- An amino acid contains an acidic carboxyl group and a basic amino group.
- An internal transfer of a proton can produce opposite charges on different groups in the same molecule.

Step 1: Account for proton transfer The carboxyl group donates a proton to the amino group. Consequently, the amino group becomes $-NH_3^+$, while the carboxyl group becomes $-COO^-$.

Step 2: Write the dipolar species The zwitter ionic form of a general α-amino acid is

$$^+H_3N - CH(R) - COO^-.$$

Quick Tip to Solve: Show both charges on the same molecule and distinguish zero net charge from the absence of charged groups.

It has both a positive and a negative charge within the same molecule, but their sum is zero; therefore it is electrically neutral overall. This dipolar form helps explain why amino acids can react with both acids and bases.

Step 3: Conclusion The zwitter ionic form is the dipolar, overall neutral form $^{+}H_3N - CH(R) - COO^{-}$, containing both positively charged amino and negatively charged carboxylate groups.

Quick Tip to Solve: Show both charges on the same molecule and distinguish zero net charge from the absence of charged groups.

30(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 have elongated structures, whereas globular proteins are folded into compact shapes.
- Proteins are polymers of amino acids linked through peptide bonds formed by condensation.

Step 1: (i) Give examples of the two protein classes Keratin, present in hair and wool, is a fibrous protein: its chains are arranged to produce an elongated structural material. Insulin is a globular protein: its polypeptide chains fold into a compact structure. These examples associate the requested molecular shapes with familiar proteins.

Step 2: (ii) Identify the linkage between monomers The carboxyl group of one amino acid reacts with the amino group of another with elimination of water. The resulting amide linkage, $-CO - NH-$, is called a peptide linkage. Repetition of this condensation links amino acid residues into the polypeptide chain. The peptide bond is the covalent connection along the primary chain; hydrogen bonding instead helps stabilise higher levels of protein structure.

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

Quick Tip to Solve: For the linkage question write the actual group -CO-NH-; hydrogen bonds stabilise folding but do not join consecutive amino acid residues.

OR

30(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 can furnish a free aldehyde or ketone group in its open-chain form.

Quick Tip to Solve: Check whether an anomeric centre can open; then remember that phosphate is the extra component in a nucleotide.

- A nucleoside contains a nitrogenous base and a pentose sugar; addition of phosphate produces a nucleotide.

Step 1: (i) Identify the reducing structural feature A reducing sugar has a free anomeric centre capable of opening the ring to give a free aldehydic or ketonic group. In the usual CBSE description, the presence of a free aldehyde or ketone group characterises a reducing sugar. Glucose gives an aldehyde in its open-chain form; fructose, a ketose, also behaves as a reducing sugar in alkaline tests through conversion to aldoses. If all anomeric centres are locked in glycosidic bonds, as in sucrose, the sugar is non-reducing.

Step 2: (ii) Compare the components A nucleoside consists of a nitrogenous base joined to a pentose sugar, which may be ribose or deoxyribose. A nucleotide contains these same two components together with a phosphate group attached to the sugar. Thus, phosphorylation of a nucleoside gives a nucleotide; the distinguishing additional structural component is phosphate.

Step 3: Conclusion (i) A free aldehydic or ketonic group, available through ring opening at a free anomeric centre, characterises a reducing sugar. (ii) Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.

Quick Tip to Solve: Check whether an anomeric centre can open; then remember that phosphate is the extra component in a nucleotide.

Section E (15 marks)

31(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:

- The electrode with the higher reduction potential is the cathode. The standard emf is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$.
- At 25°C, $E = E^{\circ} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- For equal electric charge, masses liberated are proportional to equivalent masses. Water reduction during aqueous NaCl electrolysis generates hydroxide ions.

Step 1: (i) Obtain the cell reaction and standard emf Cadmium has the higher reduction potential, so cadmium ions are reduced and zinc is oxidised. The half-reactions are

$$\text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{e}^{-}$$
$$\text{Cd}^{2+}\text{(aq)} + 2\text{e}^{-} \rightarrow \text{Cd(s)}.$$

Quick Tip to Solve: Write the cell reaction first: zinc ions are products, so Q is [Zn2+]/[Cd2+], and the electron number in the Nernst equation is 2.

Adding them gives $\mathrm{Zn(s) + Cd^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cd(s)}$, with $n = 2$. Both given values are reduction potentials, hence

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

The negative anode reduction potential must be subtracted as supplied.

Step 2: (i) Substitute the concentrations in the Nernst equation Zinc ions are products and cadmium ions are reactants. The pure zinc and cadmium solids are excluded from the quotient:

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

Therefore,

$$\begin{aligned} E_{\text{cell}} &= 0.36 - \frac{0.0591}{2}\log(10^{-2}) \\ &= 0.36 - \frac{0.0591}{2}(-2) \\ &= 0.4191\,\text{V}. \end{aligned}$$

The negative logarithm increases the emf above its standard value. This agrees with the relatively small concentration of product zinc ions, which favours the forward reaction.

Step 3: (ii) State Faraday's second law of electrolysis When the same quantity of electricity passes through different electrolytes, the masses of substances deposited or liberated at the electrodes are directly proportional to their chemical equivalent masses:

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

Here m is the mass liberated, M is molar mass and z is the number of electrons transferred per formula unit in the electrode reaction. The equivalent mass is M/z. Equal charge is essential when comparing the two masses using this law.

Step 4: (ii) Explain the change in pH During aqueous sodium chloride electrolysis, water is reduced at the cathode in preference to sodium ions:

$$\mathrm{2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)}.$$

Chloride ions are oxidised at the anode:

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

The hydroxide ions remain with sodium ions in solution, forming sodium hydroxide. Thus the solution becomes more alkaline and its pH increases. The usual brine electrolysis process is represented by

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

It is hydroxide-ion formation, rather than deposition of metallic sodium, that explains the rise in pH in an aqueous electrolyte.

Step 5: Conclusion (i) $\boxed{E_{\text{cell}} = 0.4191\,\text{V} \approx 0.42\,\text{V}}$. (ii) For equal charge, masses liberated are

Quick Tip to Solve: Write the cell reaction first: zinc ions are products, so Q is [Zn2+]/[Cd2+], and the electron number in the Nernst equation is 2.

proportional to equivalent masses; the pH of aqueous NaCl increases as NaOH forms.

Quick Tip to Solve: Write the cell reaction first: zinc ions are products, so Q is [Zn2+]/[Cd2+], and the electron number in the Nernst equation is 2.

OR

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

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

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

(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 $\mathrm{H_2O}$ to $\mathrm{O_2}$? [5 marks]

Solution:

Concept:

- Standard cell potential is $E^\circ_{\mathrm{cell}} = E^\circ_{\mathrm{cathode}} - E^\circ_{\mathrm{anode}}$, using reduction potentials for both electrodes.
- $\Delta_r G^\circ = -nFE^\circ_{\mathrm{cell}}$ and $\Delta_r G^\circ = -RT\ln K_c$. Here n is the number of electrons exchanged in the balanced cell reaction and F is the Faraday constant.
- At $298\,\mathrm{K}$, $E^\circ_{\mathrm{cell}} = (0.0591/n)\log K_c$. In electrolysis, one Faraday is the charge carried by one mole of electrons.

Step 1: (i) Balance the electron transfer and find the cell potential Iron is oxidised and silver ions are reduced. The corresponding half-reactions are

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

Thus, for the thermodynamic calculation the balanced cell reaction is

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

and $n = 2$. The cell potential is

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

Electrode potentials are not multiplied by the stoichiometric coefficients, because potential is an intensive quantity.

Step 2: (i) Calculate the standard Gibbs energy change and equilibrium constant Substitution gives

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

Quick Tip to Solve: Balance the iron–silver reaction before selecting n: iron transfers two electrons, and two water molecules transfer four electrons.

Using the usual room-temperature relation at 298 K,

$$\log K_c = \frac{nE^\circ_{cell}}{0.0591} = \frac{2 \times 1.24}{0.0591} \simeq 41.96.$$

The negative Gibbs energy change and large equilibrium constant both show that the balanced forward reaction is strongly favoured under standard conditions.

Step 3: (ii) State two advantages of fuel cells First, a fuel cell can supply electricity continuously as long as fuel and oxidant are supplied externally; it does not require periodic recharging like a secondary battery or replacement after its stored reactants are exhausted like a primary battery. Second, a hydrogen–oxygen fuel cell produces water as its reaction product, making it a clean source of electricity with minimal pollution during operation.

Step 4: (iii) Find the charge needed to oxidise water The oxidation half-reaction is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-.$$

Two moles of water release four moles of electrons. Therefore one mole of water releases $4/2 = 2$ moles of electrons and requires a charge of $2F = 193000$ C. The four-electron count belongs to two moles of water, not to one mole.

Step 5: Conclusion (i) $\Delta_r G^\circ = -239.32$ kJ mol^{-1} and $\log K_c \simeq 41.96$ at 298 K, for the balanced reaction. (ii) Fuel cells permit continuous operation with an external reactant supply, and hydrogen–oxygen fuel cells produce clean water. (iii) Oxidation of one mole of water requires 2 Faradays.

Quick Tip to Solve: Balance the iron–silver reaction before selecting n: iron transfers two electrons, and two water molecules transfer four electrons.

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

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

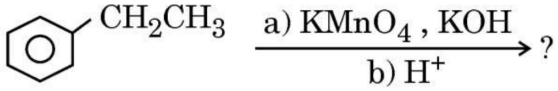
(2) $C_6H_5CHO + CH_3COCH_3 \xrightarrow{\text{dil. NaOH}}$ **?**

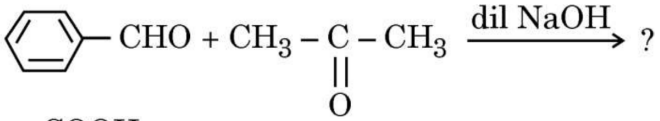
(3) Benzoic acid $C_6H_5COOH \xrightarrow{Br_2/FeBr_3}$ **?**

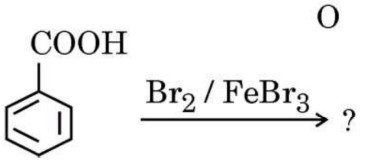
(ii) Give simple chemical tests to distinguish between the following pairs of compounds :

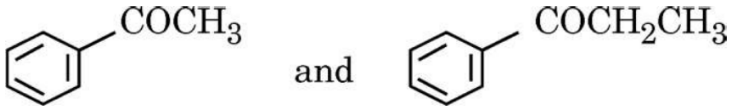
(1) $C_6H_5COCH_3$ **and** $C_6H_5COCH_2CH_3$

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

(1) 

(2) 

(3) 



Solution:

Concept:

- Strong alkaline permanganate oxidises an alkylbenzene containing a benzylic hydrogen to a benzoate salt; acidification produces benzoic acid.
- In a crossed aldol condensation, acetone supplies an enolate because it has alpha-hydrogens. Benzaldehyde has no alpha-hydrogen and acts as the electrophile.
- The electron-withdrawing $-\mathrm{COOH}$ group is a meta-directing group in electrophilic aromatic substitution.
- The iodoform test detects the methyl ketone group $-\mathrm{COCH_3}$. Tollens' reagent oxidises aldehydes but ordinarily does not oxidise ketones.

Step 1: (i)(1) Oxidation of ethylbenzene Ethylbenzene has benzylic hydrogens on the carbon directly attached to the ring. Alkaline $\mathrm{KMnO_4}$ oxidises its side chain to potassium benzoate, regardless of the original side-chain length. Subsequent acidification converts the salt into benzoic acid:

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

The required organic product is therefore benzoic acid.

Step 2: (i)(2) Crossed aldol condensation Dilute sodium hydroxide removes an alpha-hydrogen from acetone. The resulting enolate attacks benzaldehyde, giving the beta-hydroxy ketone $\mathrm{C_6H_5CH(OH)CH_2COCH_3}$. Dehydration gives the conjugated condensation product, benzylideneacetone (benzalacetone):

$$\mathrm{C_6H_5CHO + CH_3COCH_3} \xrightarrow{\text{dil. NaOH}} \mathrm{C_6H_5CH{=}CHCOCH_3 + H_2O}.$$

Its systematic name is 4-phenylbut-3-en-2-one. Benzaldehyde cannot undergo self-aldol addition because it has no alpha-hydrogen.

Step 3: (i)(3) Bromination of benzoic acid In the presence of $\mathrm{FeBr_3}$, bromine undergoes electrophilic aromatic substitution. The $-\mathrm{COOH}$ group deactivates the ring and directs the incoming bromine to the meta position:

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

The major product is 3-bromobenzoic acid (meta-bromobenzoic acid).

Step 4: (ii)(1) Distinguish acetophenone and propiophenone Warm each compound separately with iodine and aqueous sodium hydroxide. Acetophenone, $\mathrm{C_6H_5COCH_3}$, gives a yellow precipitate of iodoform, $\mathrm{CHI_3}$, because it contains a methyl ketone group:

$$\begin{aligned}&\mathrm{C_6H_5COCH_3 + 3I_2 + 4NaOH}\\ &\longrightarrow \mathrm{C_6H_5COONa + CHI_3\downarrow + 3NaI + 3H_2O}.\end{aligned}$$

Propiophenone, $\mathrm{C_6H_5COCH_2CH_3}$, contains an ethyl group next to the carbonyl instead of $\mathrm{COCH_3}$, so it does not give the yellow precipitate.

Step 5: (ii)(2) Distinguish pentanal and pentan-3-one Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Pentanal gives a silver mirror on the test-tube wall

Quick Tip to Solve: Check for the exact group $-\mathrm{COCH_3}$ before choosing the iodoform test; for an aldehyde versus an ordinary ketone, use Tollens' reagent.

as its aldehyde group is oxidised to a carboxylate ion:

$$CH_3(CH_2)_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3(CH_2)_3COO^- + 2Ag \downarrow + 4NH_3 + 2H_2O.$$

Pentan-3-one is a ketone and does not give a silver mirror with Tollens' reagent. The positive aldehyde test therefore identifies pentanal.

Step 6: Conclusion (i) The products are (1) benzoic acid, (2) benzylideneacetone, $C_6H_5CH{=}CHCOCH_3$, and (3) 3-bromobenzoic acid. (ii) Acetophenone gives yellow iodoform whereas propiophenone does not; pentanal gives a silver mirror with Tollens' reagent whereas pentan-3-one does not.

Quick Tip to Solve: Check for the exact group $-COCH_3$ before choosing the iodoform test; for an aldehyde versus an ordinary ketone, use Tollens' reagent.

OR

32(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:

- Carbonyl addition requires a nucleophile with an available lone pair; resonance delocalisation reduces the availability of that pair.
- Alkyl groups donate electron density and increase crowding around a carbonyl carbon, reducing its reactivity towards nucleophilic addition.
- Electron-withdrawing groups stabilise a carboxylate ion and increase acidity, whereas electron-donating groups decrease acidity.
- Controlled reduction converts a nitrile to an aldehyde; the Hell-Volhard-Zelinsky reaction halogenates the alpha carbon of a carboxylic acid containing an alpha hydrogen.

Step 1: (i)(1) Identify the reactive amino group in semicarbazide 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, so this amino group is much less nucleophilic. The terminal H_2N-NH- group has an available lone pair and attacks the carbonyl carbon of an aldehyde or ketone. Condensation eliminates water and gives

$$R^1R^2C=O + H_2N-NH-CO-NH_2 \longrightarrow R^1R^2C=N-NH-CO-NH_2 + H_2O.$$

Quick Tip to Solve: Locate the nitrogen next to C=O, compare alkyl donation at the carbonyl, and identify the alpha hydrogen before choosing the reaction.

Thus only the terminal amino group forms the semicarbazone; the amide amino group remains intact.

Step 2: (i)(2) Compare acetaldehyde and acetone In HCN addition, CN^- attacks the electrophilic carbonyl carbon. Acetaldehyde, CH_3CHO, has one methyl group and one hydrogen attached to that carbon, whereas acetone, $(CH_3)_2CO$, has two methyl groups. The two methyl groups of acetone exert a greater electron-donating inductive effect, decreasing the positive character of its carbonyl carbon. They also offer greater steric hindrance to the approaching cyanide ion. Both electronic and steric effects therefore make acetaldehyde more reactive towards HCN addition.

Step 3: (ii)(1) Compare the stability of the conjugate bases The nitro group in $O_2N - CH_2 - COOH$ has a strong electron-withdrawing inductive effect. It stabilises the carboxylate ion formed on loss of H^+, so nitroacetic acid is the strongest of the three. Formic acid has no electron-donating alkyl group. In acetic acid, the methyl group's electron-donating inductive effect destabilises the carboxylate relative to formate, making acetic acid weaker. The decreasing order is

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

Step 4: (ii)(2) Select a reagent for controlled nitrile reduction Use diisobutylaluminium hydride (DIBAL-H), followed by hydrolysis. Controlled reduction of the nitrile gives an intermediate that yields the aldehyde on hydrolysis, while the carbon-carbon double bond is retained:

$$CH_3CH = CHCH_2CN \xrightarrow[\text{then } H_2O]{\text{DIBAL-H}} CH_3CH = CHCH_2CHO.$$

The nitrile carbon becomes the aldehyde carbon; the carbon skeleton therefore does not change.

Step 5: (iii) Write the Hell-Volhard-Zelinsky reaction A carboxylic acid containing at least one alpha hydrogen reacts with chlorine or bromine in the presence of red phosphorus to form an alpha-halo carboxylic acid. For bromination, the general reaction is

$$RCH_2COOH + Br_2 \xrightarrow{\text{red phosphorus}} RCHBrCOOH + HBr.$$

Here the alpha carbon is the carbon directly adjacent to the carboxyl group. For example, acetic acid gives bromoacetic acid, $CH_2BrCOOH$. Halogen substitution occurs at the alpha carbon, and the carboxyl group is retained after hydrolysis of the reaction intermediate.

Step 6: Conclusion Only the terminal amino group of semicarbazide reacts because the amide nitrogen's lone pair is delocalised. Acetaldehyde is more reactive than acetone because it has less electron donation and steric hindrance. The acidity order is $O_2NCH_2COOH > HCOOH > CH_3COOH$. DIBAL-H followed by hydrolysis gives the required aldehyde; the HVZ reaction gives an alpha-halo acid using halogen and red phosphorus.

Quick Tip to Solve: Locate the nitrogen next to C=O, compare alkyl donation at the carbonyl, and identify the alpha hydrogen before choosing the reaction.

33. 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:

- Name ligands alphabetically and determine the metal oxidation state from the total charge; neutral aqua and ethane-1,2-diamine do not contribute to the charge.
- Ligand field strength determines octahedral splitting: $F^- < NH_3 < CN^-$. Compare splitting energy Δ_o with pairing energy P to predict electron occupation.
- Chelating ligands bind through multiple donor atoms and enhance complex stability. Magnetic character depends on the presence or absence of unpaired electrons.

Step 1: (a) Determine the oxidation state and name Let the oxidation state of cobalt be x. Water and each en ligand are neutral, whereas cyanido has charge -1. Hence $x - 1 = +2$, giving $x = +3$. The ligands are named in alphabetical order as aqua, cyanido and ethane-1,2-diamine; the two en ligands take the prefix bis. Since the coordination entity is a cation, the metal name is cobalt. The IUPAC name is **aquacyanidobis(ethane-1,2-diamine)cobalt(III) ion**.

Step 2: (b) Examine tetrahedral positions All four vertices of a tetrahedron are equivalent, and the angle between any two metal-ligand bonds is approximately $109.5°$. There are no opposite positions to distinguish a trans arrangement from a cis arrangement. With two types of unidentate ligands, apparent different placements can be superimposed by rotation, so geometrical isomerism is not possible.

Step 3: (c) Compare the octahedral splitting energies In all three complexes cobalt is in the $+3$ oxidation state and the coordination geometry is octahedral. Therefore compare the ligand strengths directly using the spectrochemical series: fluoride is weaker than ammonia, and cyanide is stronger than ammonia. The increasing order is

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

Step 4: (d) Apply valence bond theory to nickel carbonyl Carbon monoxide is neutral, so nickel has oxidation state zero. Free nickel has configuration $[Ar]3d^8 4s^2$. In the presence of CO, its electrons rearrange to give a filled $3d^{10}$ subshell. The vacant $4s$ and three $4p$ orbitals form four sp^3 hybrid

Quick Tip to Solve: First determine the metal oxidation state; then use ligand strength for spin and donor count for chelation. For d-five, decide whether the remaining two electrons pair or enter the upper level.

orbitals which accept lone pairs from four CO ligands. Thus $[Ni(CO)_4]$ is tetrahedral with sp^3 hybridization and is **diamagnetic**, since all electrons are paired.

Step 5: (e) Compare stability and spin (i) $[Co(C_2O_4)_3]^{3-}$ is more stable: each oxalate ligand is bidentate and forms a chelate ring, giving the chelate effect compared with unidentate fluoride ligands.
(ii) $[CoF_6]^{3-}$ is the high spin complex. Cobalt(III) is d^6, and weak field fluoride produces $\Delta_o < P$, giving $t_{2g}^4 e_g^2$ with four unpaired electrons.

Step 6: (f) Distinguish the donor modes An **ambidentate ligand** has two alternative donor atoms but coordinates through only one of them at a time; for example, NO_2^- can bind through N or O. A **bidentate ligand** coordinates to the same metal through two donor atoms simultaneously; for example, ethane-1,2-diamine binds through both nitrogen atoms. Thus alternative single-atom attachment differs from simultaneous two-atom attachment.

Step 7: (g) Fill the orbitals for an octahedral d-five ion The three t_{2g} orbitals lie below the two e_g orbitals. The first three electrons occupy separate t_{2g} orbitals.
(i) If $\Delta_o > P$, pairing costs less energy than promotion, so the next two electrons pair in t_{2g}: $\boxed{t_{2g}^5 e_g^0}$, the low spin configuration.
(ii) If $\Delta_o < P$, promotion costs less energy than pairing, so the next two electrons enter separate orbitals in e_g: $\boxed{t_{2g}^3 e_g^2}$, the high spin configuration.

Step 8: Conclusion All seven alternatives are answered above; attempt any five as instructed. The key results are cobalt(III) in (a), no tetrahedral geometrical isomerism in (b), increasing splitting $F^- < NH_3 < CN^-$ in (c), and sp^3, diamagnetic nickel carbonyl in (d). Oxalate gives greater stability, fluoride gives high spin, and the d^5 occupations are $t_{2g}^5 e_g^0$ or $t_{2g}^3 e_g^2$ according to Δ_o/P.

Quick Tip to Solve: First determine the metal oxidation state; then use ligand strength for spin and donor count for chelation. For d-five, decide whether the remaining two electrons pair or enter the upper level.