UP Board Class 12 Chemistry - 347 (KA) - 2025 Question Paper with Solutions

Time Allowed :3 Hours	**Maximum Marks :**100	**Total questions :**7

General Instructions

1. All questions are compulsory.
2. This question paper has five sections: Section A, Section B, Section C, Section D and Section E.
3. Section A is of multiple choice type and each question carries 1 mark.
4. Section B is of very short answer type and each question carries 1 mark.
5. Section C is of short answer type-I and carries 2 marks each.
6. Section D is of short answer type-II and carries 3 marks each.
7. Section E is of long answer type. Each question carries 5 marks. In all four questions of this section with internal choices have been given. You have to do only one question from the choices given in the question.
8. The symbols used in the question paper have usual meaning.

Section - A

1.(a) Example of gaseous solution is

(A) Solution of camphor in nitrogen.

(B) Solution of hydrogen in palladium.

(C) Amalgam of mercury with sodium.

(D) Oxygen dissolved in water.

Correct Answer: (A) Solution of camphor in nitrogen.

Solution:

Step 1: Defining the Type of Solution

The type of a solution (whether it is solid, liquid, or gaseous) is determined by the physical state of the **solvent**, which is the component present in the largest amount. A ”gaseous solution” is a homogeneous mixture where the solvent is a gas.

Step 2: Analyzing the Options based on the Solvent’s Phase

Let’s identify the solvent and its physical state for each of the given options.

- **(A) Solution of camphor in nitrogen:** Camphor is a solid that sublimes into a vapor (gas), which then mixes with nitrogen gas. The solvent here is nitrogen, which is a **gas**. Therefore, this is a gaseous solution.
- **(B) Solution of hydrogen in palladium:** Hydrogen gas (the solute) is absorbed into palladium, which is a **solid**. The solvent is the solid palladium. This is a solid solution.
- **(C) Amalgam of mercury with sodium:** Sodium (a solid solute) is dissolved in mercury, which is a **liquid**. The solvent is the liquid mercury. This is a liquid solution.
- **(D) Oxygen dissolved in water:** Oxygen gas (the solute) is dissolved in water, which is a **liquid**. The solvent is the liquid water. This is a liquid solution.

Step 3: Final Conclusion

The only mixture where the solvent is a gas is the solution of camphor in nitrogen.

Therefore, it is the only example of a gaseous solution among the choices.

Hence, the correct answer is option (A).

Quick Tip

In gaseous solutions, the solvent is always a gas. Common examples include mixtures of gases (like air) or solids dispersed in gases (like camphor in nitrogen).

(b) Compound of which transition metal ion is colourless?

(A) Cr^{3+}

(B) Co^{2+}

(C) Ni^{2+}

(D) Zn^{2+}

Correct Answer: (D) Zn^{2+}

Solution:

Step 1: The Principle of Color in Transition Metal Ions

The color of transition metal compounds is typically caused by d-d electronic transitions. This means an electron in a lower-energy d-orbital absorbs a photon of visible light and jumps to a higher-energy d-orbital. For this to happen, two conditions must be met:

1. The d-subshell must be **partially filled**. An electron needs a d-orbital to jump from.
2. There must be an empty or partially filled d-orbital at a higher energy level for the electron to jump **into**.

Therefore, ions with empty d-orbitals (d^0) or completely full d-orbitals (d^{10}) will be colorless, as d-d transitions are not possible.

Step 2: Determining the d-Electron Count for Each Ion

We will find the electronic configuration for each ion to check the state of its d-subshell.

- **(A) Cr^{3+}**: The atomic number of Chromium (Cr) is 24. Its neutral configuration is [Ar] $4s^1\ 3d^5$. To form Cr^{3+}, it loses three electrons (one from 4s, two from 3d), resulting in the configuration **[Ar] $3d^3$**. Since this is a partially filled d-subshell, Cr^{3+} compounds are colored (typically green or violet).

- **(B) Co^{2+}**: The atomic number of Cobalt (Co) is 27. Its neutral configuration is [Ar] $4s^2$ $3d^7$. To form Co^{2+}, it loses the two 4s electrons, resulting in the configuration **[Ar] $3d^7$**. This is a partially filled d-subshell, so Co^{2+} compounds are colored (typically pink or blue).
- **(C) Ni^{2+}**: The atomic number of Nickel (Ni) is 28. Its neutral configuration is [Ar] $4s^2$ $3d^8$. To form Ni^{2+}, it loses the two 4s electrons, resulting in the configuration **[Ar] $3d^8$**. This is a partially filled d-subshell, so Ni^{2+} compounds are colored (typically green).
- **(D) Zn^{2+}**: The atomic number of Zinc (Zn) is 30. Its neutral configuration is [Ar] $4s^2$ $3d^{10}$. To form Zn^{2+}, it loses the two 4s electrons, resulting in the configuration **[Ar] $3d^{10}$**.

Step 3: Conclusion

The Zn^{2+} ion has a completely filled d-subshell ($3d^{10}$). There are no vacant d-orbitals for an electron to jump into, so d-d transitions cannot occur. As a result, its compounds do not absorb light in the visible spectrum and are colorless.

Therefore, the correct answer is option (D).

Quick Tip

Compounds of transition metal ions are coloured only when the d-orbitals are partially filled, allowing d–d transitions. Fully filled (d^{10}) or empty (d^0) configurations generally give colourless compounds.

(c) Oxidation number of cobalt in $K[Co(CO)_4]$ is

(A) -1

(B) $+3$

(C) -1

(D) -3

Correct Answer: (A) -1

Solution:

Step 1: The Principle of Charge Neutrality for a Compound

The given formula, $K[Co(CO)_4]$, represents a neutral coordination compound. According to the rules of oxidation state assignment, the sum of the oxidation numbers of all atoms in a neutral compound must equal zero.

Step 2: Identify the Oxidation States of the Components

We can determine the oxidation states of the parts of the compound we know:

- **Potassium (K):** As an alkali metal (Group 1), potassium always has an oxidation state of $+1$ in its compounds.
- **Carbonyl Ligand (CO):** Carbon monoxide is a neutral molecule. When it acts as a ligand in a coordination complex, its oxidation state is 0. There are four such ligands.
- **Cobalt (Co):** This is the unknown oxidation state that we need to find. Let's call it x.

Step 3: Construct and Solve the Equation

We can now set up an algebraic equation where the sum of all the oxidation states equals zero:

$$(\text{Oxidation state of K}) + (\text{Oxidation state of Co}) + 4 \times (\text{Oxidation state of CO}) = 0$$

Substituting the known values:

$$(+1) + (x) + 4 \times (0) = 0$$

$$1 + x + 0 = 0$$

Solving for x:

$$x = -1$$

Step 4: Conclusion

The oxidation number of cobalt (Co) in the complex $K[Co(CO)_4]$ is -1. This is a rare but valid negative oxidation state for a transition metal, which occurs when bonded to strong π-acceptor ligands like CO.

Quick Tip

When finding oxidation numbers in coordination compounds, remember: neutral ligands like CO, NH_3, and H_2O contribute zero charge, while ionic ligands like Cl^- or OH^- contribute their usual charge.

(d) The correct order of increasing acid strength is

(A) Phenol $<$ Ethanol $<$ Chloroacetic acid $<$ Acetic acid

(B) Chloroacetic acid $<$ Acetic acid $<$ Ethanol $<$ Phenol

(C) Ethanol $<$ Phenol $<$ Acetic acid $<$ Chloroacetic acid

(D) Phenol $<$ Acetic acid $<$ Chloroacetic acid $<$ Ethanol

Correct Answer: (C) Ethanol $<$ Phenol $<$ Acetic acid $<$ Chloroacetic acid

Solution:

Step 1: The Principle of Acidity and Conjugate Base Stability

The strength of an acid is determined by the stability of its conjugate base formed after donating a proton (H^+). A more stable conjugate base corresponds to a stronger acid. We will analyze the stability of the conjugate base for each compound.

Step 2: Analysis of Each Compound's Conjugate Base

- **Ethanol (**CH_3CH_2OH**)**: Forms the ethoxide ion ($CH_3CH_2O^-$). The ethyl group ($-CH_2CH_3$) has an electron-donating inductive effect (+I effect), which intensifies the negative charge on the oxygen atom, making the ethoxide ion highly unstable. This makes ethanol the weakest acid.
- **Phenol (**C_6H_5OH**)**: Forms the phenoxide ion ($C_6H_5O^-$). The negative charge on the oxygen is delocalized over the benzene ring through resonance. This delocalization stabilizes the conjugate base, making phenol significantly more acidic than ethanol.
- **Acetic acid (**CH_3COOH**)**: Forms the acetate ion (CH_3COO^-). The negative charge is delocalized by resonance across two highly electronegative oxygen atoms. This is a much more effective stabilization than in the phenoxide ion (where the charge is shared

with less electronegative carbon atoms). Therefore, acetic acid is a stronger acid than phenol.

- **Chloroacetic acid (**$ClCH_2COOH$**)**: Forms the chloroacetate ion ($ClCH_2COO^-$). This ion has the same resonance stabilization as the acetate ion. However, the highly electronegative chlorine atom exerts a strong electron-withdrawing inductive effect (-I effect). This effect pulls electron density away from the carboxylate group, further dispersing and stabilizing the negative charge. This additional stabilization makes the chloroacetate ion more stable than the acetate ion.

Step 3: Arranging by Conjugate Base Stability

The order of stability of the conjugate bases is:

$$\text{Ethoxide} < \text{Phenoxide} < \text{Acetate} < \text{Chloroacetate}$$

Step 4: Determining the Final Order of Acid Strength

Since a more stable conjugate base means a stronger acid, the acid strength follows the same order:

$$\text{Ethanol} < \text{Phenol} < \text{Acetic acid} < \text{Chloroacetic acid}$$

This corresponds to option (C).

Quick Tip

Acid strength increases when the conjugate base is stabilized. Resonance and $-I$ effects (electron withdrawing groups) strongly enhance acidity.

(e) Which of the following gives a positive Fehling's solution test?

(A) Glucose

(B) Sucrose

(C) Fat

(D) Protein

Correct Answer: (A) Glucose

Solution:

Step 1: Recall what Fehling's test detects.

Fehling's solution test is used to detect reducing sugars. Reducing sugars have a free aldehyde group ($-CHO$) or a free ketone group ($-C=O$) that can be oxidized. On heating with Fehling's solution, such sugars reduce Cu^{2+} ions to Cu_2O, producing a red precipitate.

Step 2: Analyze each option.

- (A) Glucose: Glucose is an aldohexose and a reducing sugar. It contains a free aldehyde group that can reduce Fehling's solution, giving a positive test (red precipitate of Cu_2O).
- (B) Sucrose: Sucrose is a non-reducing sugar because the glycosidic bond involves the reducing groups of both glucose and fructose units, so it does not give a positive Fehling's test.
- (C) Fat: Fats are esters of glycerol and fatty acids; they do not have free aldehyde or ketone groups, so they do not respond to Fehling's test.
- (D) Protein: Proteins contain amino acids linked by peptide bonds; they do not act as reducing sugars, hence no reaction with Fehling's solution.

Step 3: Final Answer.

Only glucose gives a positive Fehling's solution test.

Correct Answer: Glucose (A)

Quick Tip

Remember: All monosaccharides like glucose and fructose (except those without free carbonyl groups) give a positive Fehling's test, while disaccharides like sucrose usually do not.

(f) Best method of preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is

(A) Hofmann bromide reaction

(B) Gabriel's phthalimide synthesis

(C) Sandmeyer reaction

(D) Reaction with NH_3

Correct Answer: (B) Gabriel's phthalimide synthesis

Solution:

Step 1: Recall the requirement.

The question asks for the preparation of primary amines from alkyl halides **without changing the number of carbon atoms in the chain**. This means the reaction must directly substitute the halogen with an $–NH_2$ group, giving a pure primary amine.

Step 2: Analyze each option.

- (A) Hofmann bromide reaction: This involves the conversion of amides to amines using Br_2 and NaOH. However, it reduces the carbon chain length by one (–CO group is removed). Hence, it is not suitable here.
- (B) Gabriel's phthalimide synthesis: In this method, phthalimide reacts with alkyl halide to form an N-alkyl phthalimide, which on hydrolysis gives a pure primary amine. This method introduces the $–NH_2$ group without changing the carbon skeleton. This is the correct choice.
- (C) Sandmeyer reaction: This is used to prepare aryl halides from aromatic amines via diazonium salts. It is not a method to prepare primary amines.
- (D) Reaction with NH_3: Direct reaction of alkyl halides with NH_3 gives amines but also produces secondary and tertiary amines due to multiple substitutions. Hence, it is not a selective method for pure primary amines.

Step 3: Final Answer.

Thus, the best method is Gabriel's phthalimide synthesis.

Gabriel's phthalimide synthesis (B)

Quick Tip

Gabriel's phthalimide synthesis is the most reliable method for preparing pure primary amines from alkyl halides, since it avoids the formation of secondary and tertiary amines.

2.(a) In a solution 30 mass percent of benzene is dissolved in carbon tetrachloride. Calculate mole fraction of benzene.

Solution:

We are given 30 mass percent benzene in the solution. This means:

- Mass of benzene = 30 g

- Mass of carbon tetrachloride (CCl_4) = 70 g

Molar masses:

- Molar mass of benzene (C_6H_6) = 78 g/mol

- Molar mass of carbon tetrachloride (CCl_4) = 154 g/mol

Step 1: Calculate moles of benzene.

$$n_{\text{benzene}} = \frac{30}{78} = 0.385\,\text{mol}$$

Step 2: Calculate moles of carbon tetrachloride.

$$n_{\text{CCl}_4} = \frac{70}{154} = 0.455\,\text{mol}$$

Step 3: Calculate mole fraction of benzene.

$$\chi_{\text{benzene}} = \frac{n_{\text{benzene}}}{n_{\text{benzene}} + n_{\text{CCl}_4}} = \frac{0.385}{0.385 + 0.455} = \frac{0.385}{0.840} = 0.458$$

$$\boxed{\chi_{\text{benzene}} = 0.458}$$

Thus, the mole fraction of benzene is 0.458.

> Quick Tip
>
> Always convert mass percent composition into actual masses by assuming 100 g of solution. Then, calculate moles using molar masses before applying the mole fraction formula.

(b) Explain Raoult's Law.

Solution:

Raoult's Law states that the partial vapor pressure of a component in a liquid solution is directly proportional to its mole fraction in the solution.

$$p_A = \chi_A \cdot p_A^0$$

Where:

- p_A = partial vapor pressure of component A in solution,
- χ_A = mole fraction of component A in solution,
- p_A^0 = vapor pressure of pure component A.

For a binary solution (components A and B), the total vapor pressure is:

$$p_{\text{total}} = p_A + p_B = \chi_A p_A^0 + \chi_B p_B^0$$

Significance: - Raoult's Law helps in understanding colligative properties like relative lowering of vapor pressure, elevation of boiling point, depression of freezing point, and osmotic pressure.

- It is valid for ideal solutions where intermolecular interactions between unlike molecules are similar to those between like molecules.

Quick Tip

Raoult's Law is fundamental in studying solutions. Remember that it applies strictly to ideal solutions, while real solutions show positive or negative deviations depending on intermolecular forces.

(c) Transition metals and their maximum compounds are paramagnetic. Explain it.

Solution:

Paramagnetism arises from the presence of **unpaired electrons**. Transition elements have their valence electrons in the $(n-1)d$ and ns subshells. Because the d-subshell can accommodate ten electrons and is *partially filled* across the series, most transition-metal atoms and many of their ions retain one or more unpaired d-electrons.

$\Rightarrow$ These unpaired electrons give a net magnetic moment ($\mu \propto \sqrt{n(n+2)}$, where n is the number of unpaired electrons), hence **paramagnetism**.

Further, transition metals exhibit **variable oxidation states**; during oxidation or complex formation, electrons are removed from ns and $(n-1)d$ levels, often leaving unpaired d-electrons in the cations/complexes.

Notes/Exceptions: Closed-shell cases like $\mathrm{Zn}^{2+}(\mathrm{d}^{10})$, $\mathrm{Cd}^{2+}(\mathrm{d}^{10})$, $\mathrm{Hg}^{2+}(\mathrm{d}^{10})$ are **diamagnetic**. Some strong-field, low-spin complexes can also become diamagnetic if all electrons pair.

> Quick Tip
>
> Count unpaired d-electrons in the metal ion/complex to predict magnetism: any $n > 0 \Rightarrow$ paramagnetic; $n = 0 \Rightarrow$ diamagnetic.

(d) The spin-only magnetic moment value of $[\mathrm{MnBr_4}]^{2-}$ is $5.9\,\mathrm{BM}$. What will be the geometry of the complex ion?

Solution:

Step 1: Find number of unpaired electrons from μ_{so}.

Spin-only formula: $\mu_{\mathrm{so}} = \sqrt{n(n+2)}\,\mathrm{BM}$. Given $5.9\,\mathrm{BM} \Rightarrow n(n+2) \approx (5.9)^2 \approx 34.8$. The nearest integer solution is $n = 5$ (since $\sqrt{5(5+2)} = \sqrt{35} = 5.92\,\mathrm{BM}$).

Step 2: Determine metal oxidation state and d-count.

Let oxidation state of Mn be x: $x + 4(-1) = -2 \Rightarrow x = +2$. Thus Mn^{2+} is d^5.

Step 3: Decide geometry.

Br^- is a **weak-field** ligand, so pairing is unfavorable; a d^5 ion remains **high spin** with 5 unpaired electrons—consistent with the observed μ. Four-coordinate Mn^{2+} with weak-field ligands prefers **tetrahedral** over square planar (which is typical for d^8 ions and would require strong-field stabilization).

Geometry of $[\mathrm{MnBr_4}]^{2-}$ is tetrahedral.

Quick Tip

Use $\mu_{\text{so}} = \sqrt{n(n+2)}$ to get n. For four-coordinate complexes: weak-field ligands (e.g., Br^-, I^-) $\Rightarrow$ usually **tetrahedral**; strong-field cases and d^8 metals $\Rightarrow$ often **square planar**.

3.(a) Write the uses of carbon tetrachloride and chloroform.

Solution:

Uses of Carbon Tetrachloride (CCl_4):

- Used as a cleaning agent for degreasing metals and machinery.
- Acts as a solvent for oils, fats, and varnishes.
- Earlier used in fire extinguishers (though avoided now due to toxicity).
- Plays a role in the manufacture of refrigerants and propellants.

Uses of Chloroform ($CHCl_3$):

- Widely used as a solvent in laboratories and industries.
- Employed in the preparation of chlorofluorocarbons (CFCs).
- Historically used as an anesthetic, though not common now due to harmful effects.
- Helps in extraction and purification of alkaloids and other organic compounds.

Quick Tip

Carbon tetrachloride and chloroform are useful industrial solvents but both are toxic to health. Hence, their use has been restricted or replaced by safer alternatives.

(b) Boiling point of propanol is greater than butane. Explain.

Solution:

Step 1: Nature of forces in butane.

Butane (C_4H_{10}) is a hydrocarbon and non-polar in nature. The only intermolecular forces present in butane are weak Van der Waals (London dispersion) forces. These forces require relatively little energy to overcome, so butane has a low boiling point.

Step 2: Nature of forces in propanol.

Propanol (C_3H_7OH) is an alcohol containing an –OH group. The hydroxyl group allows molecules of propanol to form intermolecular hydrogen bonds. Hydrogen bonds are much stronger than Van der Waals forces. Breaking these bonds requires more energy, which raises the boiling point of propanol significantly.

Step 3: Comparison.

Because propanol forms hydrogen bonds while butane does not, the boiling point of propanol is much greater than that of butane.

Propanol has a higher boiling point due to hydrogen bonding.

Quick Tip

Always compare the type of intermolecular forces when explaining differences in boiling points: hydrogen bonding $>$ dipole–dipole interactions $>$ Van der Waals forces.

(c) Explain Cannizzaro reaction with chemical equation.

Solution:

The Cannizzaro reaction is a redox (disproportionation) reaction that occurs when an aldehyde without an α-hydrogen atom (such as formaldehyde, benzaldehyde) is treated with a concentrated alkali.

In this reaction:

- One molecule of the aldehyde is oxidized to a carboxylate ion, and
- Another molecule of the same aldehyde is reduced to a primary alcohol.

General reaction:

$$2\,R{-}CHO \xrightarrow[\text{conc. NaOH/KOH}]{} R{-}CH_2OH \;+\; R{-}COONa$$

Example with formaldehyde:

$$2\,HCHO \xrightarrow[\text{conc. NaOH}]{} CH_3OH \;+\; HCOONa$$

Thus, the Cannizzaro reaction simultaneously produces an alcohol and a carboxylate salt.

> Quick Tip
>
> Remember: The Cannizzaro reaction takes place only with aldehydes that lack α-hydrogen atoms (like formaldehyde and benzaldehyde). If α-hydrogens are present, aldol condensation occurs instead.

(d) What is nucleic acid? Write two important properties of them.

Solution:

Nucleic acids are complex biomolecules that store and transmit genetic information in living organisms.

They are polymers of nucleotides, which consist of a nitrogenous base, a pentose sugar, and a phosphate group.

The two main types of nucleic acids are:

- DNA (Deoxyribonucleic acid)
- RNA (Ribonucleic acid)

Two important properties:

1. **Genetic Information Storage:** DNA carries hereditary information that controls the development, functioning, and reproduction of all living organisms.
2. **Self-Replication and Protein Synthesis:** Nucleic acids can replicate themselves and guide protein synthesis through transcription (DNA $\rightarrow$ RNA) and translation (RNA $\rightarrow$ protein).

Thus, nucleic acids are essential molecules of life.

Quick Tip

Nucleic acids are often called the "blueprint of life" because they not only store genetic information but also ensure its transfer across generations.

4.(a) A cell in which the following reaction occurs:

$$\text{Zn}_{(s)} + \text{Cu}^{2+}_{(aq)} \rightarrow \text{Zn}^{2+}_{(aq)} + \text{Cu}_{(s)}$$

has standard electrode potential $E^\circ_{\text{cell}} = 1.1$ V **at** 298 K. **Calculate the standard Gibbs energy and the equilibrium constant of the cell reaction.**

Solution:

For a galvanic cell at standard state, $\Delta G^\circ = -nFE^\circ_{\text{cell}}$ and $\Delta G^\circ = -RT\ln K$. Hence, $K = \exp\left(\dfrac{nFE^\circ_{\text{cell}}}{RT}\right)$.

Given: $E^\circ_{\text{cell}} = 1.1$ V, $T = 298$ K, $F = 96485$ C mol^{-1}, $R = 8.314$ J mol^{-1}K^{-1}.

Overall reaction involves transfer of $n = 2$ electrons.

Step 1: Calculate standard Gibbs energy change.

$$\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2)(96485)(1.1)\text{ J mol}^{-1} = -2.12267\times10^5\text{ J mol}^{-1} = \boxed{-2.12\times10^5\text{ J mol}^{-1}\ (= -2.12}$$

Step 2: Calculate equilibrium constant.

$$K = \exp\left(\frac{nFE^\circ_{\text{cell}}}{RT}\right) = \exp\left(\frac{(2)(96485)(1.1)}{(8.314)(298)}\right) = \exp(85.65)$$

$$\Rightarrow\ \log_{10} K = \frac{85.65}{2.3026} = 37.20\ \Rightarrow\ \boxed{K \approx 1.6\times10^{37}}$$

Answer: $\boxed{\Delta G^\circ \approx -2.12\times10^5\text{ J mol}^{-1} = -212\text{ kJ mol}^{-1},\quad K \approx 1.6\times10^{37}}$.

Quick Tip

Use $\Delta G^\circ = -nFE^\circ$ first to find the energy change, then connect to the equilibrium constant via $\Delta G^\circ = -RT\ln K$. For quick order-of-magnitude checks, convert to base-10 using $\log_{10} K = \dfrac{nFE^\circ}{2.303\,RT}$.

(b) How do the following factors affect the velocity of reaction?

(i) Concentration

(ii) Temperature

(iii) Catalyst

Solution:

(i) Concentration:

According to the **law of mass action**, the rate of a chemical reaction is directly proportional to the concentration of reactants. Higher concentration $\Rightarrow$ more molecules per unit volume $\Rightarrow$ greater frequency of effective collisions $\Rightarrow$ higher reaction rate. For example, doubling the concentration of reactant in a first-order reaction doubles the rate.

(ii) Temperature:

Raising temperature increases the kinetic energy of molecules. This leads to: - More frequent collisions, and - A higher fraction of molecules possessing energy greater than the **activation energy**.

As per the **Arrhenius equation**, $k = Ae^{-E_a/RT}$, the rate constant k increases exponentially with temperature. Roughly, a $10^{\circ}C$ rise in temperature nearly doubles the rate of many reactions.

(iii) Catalyst:

A catalyst provides an alternate reaction pathway with lower activation energy (E_a). This does not affect the equilibrium position but significantly increases the rate at which equilibrium is achieved. Both homogeneous and heterogeneous catalysts enhance the velocity by lowering the energy barrier for effective collisions.

Thus, concentration, temperature, and catalyst all increase the velocity of a reaction.

Quick Tip

Remember: - Concentration affects **collision frequency**. - Temperature affects both **collision frequency** and the **fraction of molecules with energy** $\geq E_a$. - Catalysts lower the **activation energy**, making reactions faster without being consumed.

(c) Describe the method of preparation of potassium permanganate. How does *acidic* potassium permanganate react with the following? Give ionic equations: (i) H_2S (ii) Fe (iii) iodide ion.

Solution:

Preparation of Potassium Permanganate ($KMnO_4$):

Step 1 (Oxidative fusion): Natural MnO_2 (pyrolusite) is fused with KOH in air / with an oxidiser (e.g., KNO_3) to form potassium manganate.

$$\boxed{2\,\mathrm{MnO_2} + 4\,\mathrm{KOH} + \mathrm{O_2} \longrightarrow 2\,\mathrm{K_2MnO_4} + 2\,\mathrm{H_2O}}$$

Step 2 (Conversion to permanganate): The green manganate ($\mathrm{MnO_4^{2-}}$) is oxidised to the purple permanganate ($\mathrm{MnO_4^-}$) by chlorine/ozone or by electrolysis. One convenient route is:

$$\boxed{2\,\mathrm{K_2MnO_4} + \mathrm{Cl_2} \longrightarrow 2\,\mathrm{KMnO_4} + 2\,\mathrm{KCl}}$$

(Alternatively, $\mathrm{MnO_4^{2-}}$ disproportionates in neutral/acidic medium:
$3\,\mathrm{MnO_4^{2-}} + 2\,\mathrm{H_2O} \rightarrow 2\,\mathrm{MnO_4^-} + \mathrm{MnO_2} + 4\,\mathrm{OH^-}$.)

Reactions of acidic $KMnO_4$ (strong oxidant; Mn(VII) $\rightarrow$ Mn^{2+}):

Overall reduction half-equation in acid: $\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O}$.

(i) With H_2S (to sulfur):

$$\boxed{2\,\mathrm{MnO_4^-} + 6\,\mathrm{H^+} + 5\,\mathrm{H_2S} \longrightarrow 2\,\mathrm{Mn^{2+}} + 8\,\mathrm{H_2O} + 5\,\mathrm{S}\downarrow}$$

(ii) With Fe^{2+} (to Fe^{3+}):

$$\boxed{\mathrm{MnO_4^-} + 5\,\mathrm{Fe^{2+}} + 8\,\mathrm{H^+} \longrightarrow \mathrm{Mn^{2+}} + 5\,\mathrm{Fe^{3+}} + 4\,\mathrm{H_2O}}$$

(iii) With iodide ion, I^- (to iodine):

$$\boxed{2\,MnO_4^- + 10\,I^- + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 5\,I_2 + 8\,H_2O}$$

> **Quick Tip**
>
> In acidic medium, MnO_4^- is a very strong oxidising agent and is *always* reduced to Mn^{2+}. Balance such redox equations by combining the standard permanganate reduction half-reaction with the appropriate oxidation half-reaction of the substrate.

(d) What is elevation of boiling point? A liquid has boiling point 353.23 K. The boiling point of solution becomes 354.11 K after dissolving 1.8 g non-volatile solute of molar mass 58 g mol^{-1} to 90 g liquid. Calculate boiling point elevation constant for the liquid.

Solution:

The elevation in boiling point is given by the formula:

$$\Delta T_b = K_b \times m$$

Where:

- ΔT_b = elevation in boiling point
- K_b = molal elevation constant
- m = molality of the solution

Step 1: Calculate elevation in boiling point.

$$\Delta T_b = 354.11 - 353.23 = 0.88\,K$$

Step 2: Calculate number of moles of solute.

Mass of solute $= 1.8\,g$

Molar mass of solute $= 58\,g\,mol^{-1}$

$$n = \frac{\text{mass}}{\text{molar mass}} = \frac{1.8}{58} = 0.0310\,mol$$

Step 3: Calculate mass of solvent in kilograms.

Mass of solvent $= 90\,g = 0.090\,kg$

Step 4: Calculate molality of solution.

$$m = \frac{0.0310}{0.090} = 0.344\,mol\,kg^{-1}$$

Step 5: Calculate boiling point elevation constant.

$$K_b = \frac{\Delta T_b}{m} = \frac{0.88}{0.344} = 2.56\,K\,kg\,mol^{-1}$$

$$\boxed{K_b = 2.56\,K\,kg\,mol^{-1}}$$

Thus, the boiling point elevation constant for the liquid is $2.56\,K\,kg\,mol^{-1}$.

> Quick Tip
>
> Always convert the solvent mass to kilograms when calculating molality. Remember that elevation of boiling point depends only on the number of solute particles, not their nature.

5.(a) Explain in brief the Faraday's laws of Electrolysis. $CuSO_4$ solution was electrolysed for 20 minutes with 2.0 ampere current. What will be the mass of precipitated copper at cathode?

Solution:

Faraday's First Law: The mass of a substance liberated (or deposited) at an electrode is directly proportional to the total electric charge passed through the electrolyte.

$$m \propto Q \quad \Rightarrow \quad m = Z\,Q$$

where m is mass deposited, $Q = It$ is charge, and Z is the electrochemical equivalent.

Faraday's Second Law: When the same quantity of electricity is passed through different electrolytes, the masses of substances deposited are proportional to their chemical (equivalent) weights.

Numerical Part: In $CuSO_4$ electrolysis, copper is deposited by

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$

For a metal ion requiring n electrons,

$$m = \frac{It\,M}{nF}$$

where $I = 2.0\,\text{A}$, $t = 20\,\text{min} = 1200\,\text{s}$, $M(\text{Cu}) = 63.5\,\text{g mol}^{-1}$, $n = 2$, $F = 9.65 \times 10^4\,\text{C mol}^{-1}$.

$$m = \frac{(2.0)(1200) \times 63.5}{(2)(9.65 \times 10^4)} = \frac{2400 \times 63.5}{1.93 \times 10^5} \approx 0.79\,\text{g}$$

$$\boxed{m_{\text{Cu deposited}} \approx 0.79\ \text{g}}$$

> **Quick Tip**
>
> Always match n to the electrons in the half-reaction. For Cu^{2+}, $n = 2$. Use t in seconds and F in C mol^{-1} for consistent units.

(b) A first order reaction completes 20% in 10 minutes. Calculate the time taken for 75% completion.

Solution:

For a first-order reaction:

$$k = \frac{1}{t} \ln\left(\frac{[A]_0}{[A]}\right)$$

After 10 min, 20% is complete $\Rightarrow$ 80% remains: $[A]/[A]_0 = 0.80$. Hence

$$k = \frac{1}{10} \ln\left(\frac{1}{0.80}\right) = \frac{1}{10} \ln(1.25) \approx 0.0223\ \text{min}^{-1}.$$

For 75% completion, 25% remains: $[A]/[A]_0 = 0.25$. Time required:

$$t = \frac{1}{k} \ln\left(\frac{1}{0.25}\right) = \frac{1}{k} \ln(4) = \frac{1.3863}{0.0223} \approx 6.21 \times 10^1\ \text{min}$$

$$\boxed{t \approx 62\ \text{minutes}}$$

Quick Tip

For first-order kinetics, times for given $\%$ completion depend only on the fraction remaining, not on initial concentration. Use $t = \frac{1}{k} \ln\left(\frac{1}{\text{fraction remaining}}\right)$.

(c)(i) Write formula of the following coordination compounds:

(x) Tetraammine diaqua cobalt (III) chloride

(y) Potassium trioxalato chromate (III)

Solution:

(x) Tetraammine diaqua cobalt (III) chloride

Ligands: 4 ammine (NH_3; neutral) and 2 aqua (H_2O; neutral). Central metal: Co(III) $\Rightarrow$ complex cation charge $= +3$. Chloride is the counter anion (-1 each), hence three Cl^- are required.

$$\boxed{[Co(NH_3)_4(H_2O)_2]Cl_3}$$

(y) Potassium trioxalato chromate (III)

Oxalato (oxalate) ligand = $C_2O_4^{2-}$ (bidentate). Three such ligands: total charge $= -6$.
Central metal: Cr(III) $\Rightarrow$ complex-anion charge $= (+3) + (-6) = -3$. Balance with three K^+.

$$\boxed{K_3[Cr(C_2O_4)_3]}$$

Quick Tip

Name $\Rightarrow$ formula: determine ligand charges and count, assign oxidation state from the Roman numeral, find the net charge on the complex, then add the required counter-ions.

(c)(ii) The colour of dilute solutions of $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are different. Explain.

Solution:

Both complexes contain Fe(II) (d^6), but the ligands differ in field strength. CN^- is a *strong-field* ligand and produces a large octahedral splitting (Δ_o), giving a low-spin configuration $t_{2g}^6 e_g^0$, while H_2O is a *weak-field* ligand with smaller Δ_o, often giving higher-spin populations.

Because Δ_o is different, the energy of the $d \rightarrow d$ electronic transition (and thus the wavelength of light absorbed) differs for the two complexes. They therefore absorb different parts of the visible spectrum and appear different in colour (e.g., $[Fe(CN)_6]^{4-}$ is very pale/yellowish, while $[Fe(H_2O)_6]^{2+}$ is pale green). Hence, colour difference arises from differing crystal-field splitting due to ligand field strength.

> **Quick Tip**
>
> Colour in coordination compounds mainly comes from d–d transitions. Strong-field ligands (like CN^-) increase Δ_o (higher transition energy; shorter absorbed wavelength), while weak-field ligands (like H_2O) decrease it.

(d) Explain the following terms:

(i) Zwitter ion

(ii) Peptide bond

(iii) Primary structure of protein

(iv) Polysaccharides

Solution:

(i) Zwitter ion:

A zwitter ion is a dipolar ion that contains both a positive and a negative charge within the same molecule but is overall electrically neutral. Amino acids in aqueous solution commonly exist as zwitter ions, where the amino group ($-NH_2$) is protonated to $-NH_3^+$ and the carboxyl group ($-COOH$) is deprotonated to $-COO^-$.

$$H_2N{-}CH(R){-}COOH \rightleftharpoons {}^{+}H_3N{-}CH(R){-}COO^-$$

(ii) Peptide bond:

A peptide bond is a covalent bond formed between the $-\mathrm{COOH}$ group of one amino acid and the $-\mathrm{NH_2}$ group of another with the elimination of a water molecule (condensation reaction). It has partial double bond character due to resonance, making it rigid and planar.

(iii) Primary structure of protein:

The primary structure of a protein is the linear sequence of amino acids in a polypeptide chain, linked together by peptide bonds. This sequence determines the higher levels of protein structure and ultimately governs its biological function. Example: the exact order of amino acids in insulin.

(iv) Polysaccharides:

Polysaccharides are long-chain carbohydrates formed by the condensation of numerous monosaccharide units joined by glycosidic bonds. They can be storage polysaccharides (e.g., starch, glycogen) or structural polysaccharides (e.g., cellulose, chitin). They are usually insoluble in water and serve as energy reserves or structural materials in living organisms.

Quick Tip

Zwitter ions are typical of amino acids, peptide bonds link them, the primary structure is their order, and polysaccharides are analogous long chains of sugars. Remember: amino acids build proteins, and monosaccharides build polysaccharides.

6.(a) Write structures of the following compounds: (i) 2-Chloro-3-methylpentane

(ii) 1,4-dibromobut-2-ene

(iii) 1-Bromo-2,2-dimethylpropane

(iv) 1-Bromo-2-methylbut-2-ene

(v) 1-Chloro-2-methylbenzene

Solution:

(i) 2-Chloro-3-methylpentane

Condensed structure: $\mathrm{CH_3{-}CH(Cl){-}CH(CH_3){-}CH_2{-}CH_3}$

Main chain = pentane; Cl at C-2; methyl at C-3.

(ii) 1,4-Dibromobut-2-ene

Condensed structure: $\mathrm{Br{-}CH_2{-}CH{=}CH{-}CH_2{-}Br}$

But-2-ene backbone ($C_2{=}C_3$); Br at C-1 and C-4.

(iii) 1-Bromo-2,2-dimethylpropane (neopentyl bromide)

Condensed structure: $\mathrm{(CH_3)_3C{-}CH_2{-}Br}$

Choose the propane chain $\mathrm{CH_3{-}C(CH_3)_2{-}CH_2Br}$; Br at C-1; two $\mathrm{CH_3}$ groups at C-2.

(iv) 1-Bromo-2-methylbut-2-ene

Condensed structure: $\mathrm{Br{-}CH_2{-}C(CH_3){=}CH{-}CH_3}$

But-2-ene backbone ($C_2{=}C_3$); Br at C-1; methyl substituent at C-2.

(v) 1-Chloro-2-methylbenzene (o-chlorotoluene)

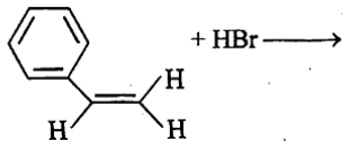
Aromatic structure: benzene ring with adjacent substituents Cl at C-1 and $\mathrm{CH_3}$ at C-2.

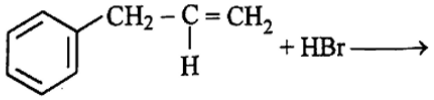
Condensed/SMILES: $\mathrm{Clc_1cccc(c_1)CH_3}$.

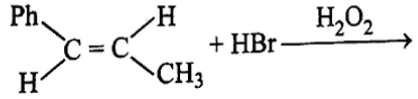
> Quick Tip
>
> When writing structures from IUPAC names: (1) pick the parent chain/ring, (2) place the multiple bond(s) at the specified locant(s), (3) add substituents at their locants, and (4) check valency at each carbon.

OR

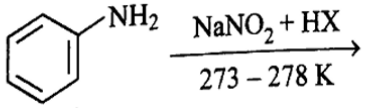
Write the products of the following reactions:

(i) 

(ii) 

(iii) 

(iv) $C_6H_5Br + 2Na + BrCH_2CH_2CH_2CH_3 \xrightarrow[\Delta]{\text{Dry ether}}$

(v) 

Solution:

(i) Addition of HBr to styrene (Markovnikov):

$$\mathrm{Ph{-}CH{=}CH_2} \xrightarrow{\mathrm{HBr}} \mathrm{Ph{-}CH(Br){-}CH_3}$$

Product: 1-bromo-1-phenylethane (Markovnikov addition via benzylic carbocation).

(ii) Addition of HBr to allylbenzene (Markovnikov):

$$\mathrm{Ph{-}CH_2{-}CH{=}CH_2} \xrightarrow{\mathrm{HBr}} \mathrm{Ph{-}CH_2{-}CH(Br){-}CH_3}$$

Product: 3-phenyl-2-bromopropane.

(iii) Addition of HBr to 1-phenylpropene in the presence of peroxides (anti-Markovnikov, radical):

$$\mathrm{Ph{-}CH{=}CH{-}CH_3} \xrightarrow[\mathrm{ROOR}]{\mathrm{HBr}} \mathrm{Ph{-}CH_2{-}CH_2{-}CH_2Br}$$

Product: 3-phenyl-1-bromopropane (Br adds to the less substituted end to form a benzylic radical intermediate).

(iv) Wurtz–Fittig coupling (dry ether):

$$\mathrm{C_6H_5Br + 2\,Na + Br{-}(CH_2)_4CH_3 \xrightarrow[\Delta]{\text{dry ether}} C_6H_5{-}(CH_2)_4CH_3 + 2\,NaBr}$$

Product: n-butylbenzene.

(v) Diazotisation of aniline at 273–278 K:

$$\mathrm{Ph{-}NH_2 \xrightarrow[273-278\,K]{NaNO_2/HX} Ph{-}N_2^+X^- + 2\,H_2O}$$

Product: benzenediazonium halide (X = Cl/Br, as per HX used).

> **Quick Tip**
>
> Remember: plain HBr follows Markovnikov's rule, whereas HBr with peroxides (ROOR) adds anti-Markovnikov via a radical pathway. Aryl + alkyl halides with Na in dry ether give Wurtz–Fittig coupling to an alkylbenzene. Aniline forms a stable diazonium salt only in cold acidic solution (273–278 K).

(b) What do you understand by dehydration reaction? Write the mechanism of dehydration reaction of alcohol.

Solution:

Dehydration reaction: A dehydration reaction is a chemical reaction in which a molecule of water (H_2O) is eliminated from the reacting molecule. In the case of alcohols, when heated with a strong acid catalyst (such as conc. H_2SO_4 or H_3PO_4), alcohols undergo dehydration to form alkenes.

$$R - CH_2 - CH_2 - OH \xrightarrow{\text{conc. } H_2SO_4,\ \text{heat}} R - CH = CH_2 + H_2O$$

This reaction follows the mechanism of *E1 elimination* for secondary and tertiary alcohols and *E2 elimination* for primary alcohols.

Mechanism of Dehydration of Alcohol (E1 for 2° or 3° alcohols):

Step 1: Protonation of alcohol.

The lone pair of electrons on the oxygen atom of the alcohol attacks a proton (H^+) from the acid catalyst, converting the hydroxyl group into a better leaving group (water).

$$R - CH(OH) - R' + H^+ \rightarrow R - CH(OH_2^+) - R'$$

Step 2: Formation of carbocation.

The protonated alcohol loses a water molecule, forming a carbocation intermediate.

$$R - CH(OH_2^+) - R' \rightarrow R - C^+ - R' + H_2O$$

Step 3: Elimination of proton.

A base (often HSO_4^-) abstracts a β-hydrogen atom from the carbon adjacent to the carbocation, leading to the formation of a double bond (alkene).

$$R - C^+ - CH_2 \rightarrow R - CH = CH_2 + H^+$$

Overall reaction:

$$\text{Alcohol} \xrightarrow{\text{conc. } H_2SO_4,\ 170^\circ C} \text{Alkene} + H_2O$$

> Quick Tip
>
> Dehydration of alcohols generally follows the Saytzeff's Rule: the more substituted alkene is the major product because it is more stable. Always check whether the mechanism proceeds via E1 (carbocation intermediate) or E2 (concerted elimination), depending on the nature of the alcohol.

OR

Explain the following reactions with examples:

(i) Kolbe reaction

(ii) Reimer–Tiemann reaction

(iii) Williamson Ether synthesis

Solution:

(i) Kolbe Reaction:

The Kolbe reaction involves the **electrolysis of sodium or potassium salts of carboxylic acids**, resulting in the decarboxylation and coupling of alkyl radicals to form alkanes.

$$2\,RCOONa \xrightarrow[\text{electrolysis}]{} R{-}R \;+\; 2\,CO_2 \;+\; H_2 \;+\; 2\,NaOH$$

Example:

Electrolysis of sodium acetate gives ethane:

$$2\,CH_3COONa \xrightarrow[\text{electrolysis}]{} C_2H_6 \;+\; 2\,CO_2 \;+\; H_2 \;+\; 2\,NaOH$$

(ii) Reimer–Tiemann Reaction:

The Reimer–Tiemann reaction introduces a formyl group ($-CHO$) into the aromatic ring of phenols, mainly at the **ortho position**, using chloroform ($CHCl_3$) and alkali (NaOH/KOH).

$$C_6H_5OH \;+\; CHCl_3 \;+\; 3NaOH \;\longrightarrow\; o{-}HO{-}C_6H_4{-}CHO \;+\; 3NaCl \;+\; 2H_2O$$

Example:

Phenol reacts with chloroform in alkaline medium to give salicylaldehyde (2-hydroxybenzaldehyde).

(iii) Williamson Ether Synthesis:

The Williamson ether synthesis involves the reaction of a **sodium alkoxide** with a **primary alkyl halide** to form ethers. It is a nucleophilic substitution (S_N2) reaction.

$$R{-}ONa \;+\; R'X \;\longrightarrow\; R{-}O{-}R' \;+\; NaX$$

Example:

Sodium ethoxide reacts with methyl iodide to give ethyl methyl ether:

$$C_2H_5ONa \;+\; CH_3I \;\longrightarrow\; C_2H_5{-}O{-}CH_3 \;+\; NaI$$

Quick Tip

Kolbe reaction forms alkanes by decarboxylation, Reimer–Tiemann introduces $-CHO$ into phenols (ortho position), and Williamson ether synthesis is the most common lab method to prepare ethers using S_N2.

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

(i) (ring with –CHO and adjacent $–CH_3$)

(ii) $(CH_3)_2CHCOCH(CH_3)_2$

(iii) $CH_3CH(OCH_3)CHO$

(iv) $HOOC–(CH_2)_4–COOH$

(v) (benzene–CH_2COOH)

Solution:

(i) 2-methylbenzaldehyde (*o*-methylbenzaldehyde).

(ii) 2,4-dimethylpentan-3-one.

(iii) 2-methoxypropanal.

(iv) hexane-1,6-dioic acid (hexanedioic acid, adipic acid).

(v) 2-phenylethanoic acid (phenylacetic acid).

Quick Tip

Prioritise the highest-ranking functional group (–CHO $>$ –CO– $>$ –COOH in naming context) and choose the parent chain to include it with the lowest possible locants; then place substituents (like methyl/methoxy/phenyl) with correct numbering.

OR

An organic compound (A) has molecular formula C_8H_8O. It gives an orange-red precipitate with 2,4-dinitrophenylhydrazine (2,4-DNP) and a yellow precipitate on heating with iodine in the presence of NaOH. It does not reduce Tollens' reagent or Fehling's solution and does not decolourise Br_2-water/Baeyer's reagent. On strong oxidation with chromic acid it forms a carboxylic acid (B) of formula $C_7H_6O_2$. Identify (A) and (B).

Solution:

Step 1: Functional group tests.

2,4-DNP test $(+) \Rightarrow$ (A) contains a carbonyl group (aldehyde/ketone).

Tollens/Fehling tests $(-) \Rightarrow$ not an aldehyde $\Rightarrow$ (A) is a **ketone**.

Iodoform test $(+)$ with I_2/NaOH $\Rightarrow$ **methyl ketone** fragment $-COCH_3$.

Step 2: Unsaturation test.

No decolourisation of Br_2-water/alkaline $KMnO_4 \Rightarrow$ no reactive $C = C$ in the side chain (an aromatic ring does not respond to these).

Step 3: Use formulas to infer the skeleton.

Given molecular formula C_8H_8O with a methyl-ketone group suggests $C_6H_5COCH_3$ (acetophenone, phenyl methyl ketone).

Step 4: Check with oxidation product.

Strong oxidation of an aryl side chain (including aryl methyl ketones) with chromic acid gives **benzoic acid**, $C_7H_6O_2$, which matches (B).

$$\underbrace{C_6H_5COCH_3}_{\text{(A) acetophenone}} \xrightarrow{CrO_3/H^+} \underbrace{C_6H_5COOH}_{\text{(B) benzoic acid}}$$

(Consistency check: iodoform reaction of (A): $C_6H_5COCH_3 \xrightarrow{I_2/NaOH} CHI_3 \downarrow + C_6H_5COO^-$)

$\boxed{\text{(A) } C_6H_5COCH_3 \text{ (acetophenone)}}$, $\boxed{\text{(B) } C_6H_5COOH \text{ (benzoic acid)}}$

> **Quick Tip**
>
> A positive 2,4-DNP plus iodoform test and negative Tollens/Fehling together pinpoint a *methyl ketone*. For aryl compounds, vigorous oxidation of any side chain (–CH_3, –CH_2R, –$COCH_3$) typically yields benzoic acid.

(b) Give the structures of A, B, and C in the following reaction sequences:

(i) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{HO^- \,/\, H_2O} B \xrightarrow[Br_2/NaOH]{} C$

(ii) $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_3O^+} B \xrightarrow[\Delta]{NH_3} C$

(iii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273\,K]{HNO_2} C$

Solution:

(i) From ethyl iodide via nitrile and amide (Hofmann bromamide):

$$\mathrm{CH_3CH_2I} \xrightarrow{\mathrm{NaCN}} \mathrm{CH_3CH_2CN\ (A)} \xrightarrow[\text{controlled}]{\mathrm{HO^-/H_2O}} \mathrm{CH_3CH_2CONH_2\ (B)} \xrightarrow{\mathrm{Br_2/NaOH}} \mathrm{CH_3CH_2NH_2\ (C)}$$

$$\boxed{A = \text{propanenitrile (propionitrile)}, \quad B = \text{propanamide}, \quad C = \text{ethylamine}}$$

(ii) Sandmeyer to nitrile, hydrolysis to acid, then ammonolysis:

$$\mathrm{C_6H_5N_2^+Cl^-} \xrightarrow{\mathrm{CuCN}} \mathrm{C_6H_5CN\ (A)} \xrightarrow{\mathrm{H_3O^+}} \mathrm{C_6H_5COOH\ (B)} \xrightarrow[\Delta]{\mathrm{NH_3}} \mathrm{C_6H_5CONH_2\ (C)}$$

$$\boxed{A = \text{benzonitrile}, \quad B = \text{benzoic acid}, \quad C = \text{benzamide}}$$

(iii) From bromoethane to nitrile, reduction to amine, then nitrous acid:

$$\mathrm{CH_3CH_2Br} \xrightarrow{\mathrm{KCN}} \mathrm{CH_3CH_2CN\ (A)} \xrightarrow{\mathrm{LiAlH_4}} \mathrm{CH_3CH_2CH_2NH_2\ (B)} \xrightarrow[273\,\mathrm{K}]{\mathrm{HNO_2}} \mathrm{CH_3CH_2CH_2OH\ (C)}$$

$$\boxed{A = \text{propanenitrile}, \quad B = \text{propylamine}, \quad C = \text{propan-1-ol}}$$

Quick Tip

Alkyl halide + $\mathrm{CN^-} \Rightarrow$ **nitrile** (adds one carbon).

Nitrile $\xrightarrow[\text{controlled}]{\text{hydrolysis}}$ **amide**; amide $\xrightarrow{Br_2/NaOH}$ **amine with one carbon less** (Hofmann).

$\mathrm{ArN_2^+} \xrightarrow{CuCN}$ **Ar–CN** (Sandmeyer); Ar–CN $\xrightarrow{H_3O^+}$ **Ar–COOH**; Ar–COOH $\xrightarrow{NH_3,\ \Delta}$ **amide**.

Primary aliphatic amine + HNO_2 at $0{-}5^\circ C \Rightarrow$ **alcohol** (deamination).

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oR

(i) Describe the method of identification of primary, secondary and tertiary amines. Write the chemical equations of these reactions also.

Solution:

The **Hinsberg's Test** is the standard method for distinguishing primary, secondary and tertiary amines. It uses benzenesulfonyl chloride ($\mathrm{C_6H_5SO_2Cl}$) in the presence of aqueous alkali (NaOH/KOH).

Step 1: Reaction with primary amine.

Primary amines react with benzenesulfonyl chloride to give sulfonamides which are soluble in alkali due to the presence of an acidic hydrogen atom.

$$RNH_2 + C_6H_5SO_2Cl \longrightarrow R{-}NH{-}SO_2C_6H_5$$

This product dissolves in alkali, forming a soluble salt.

Step 2: Reaction with secondary amine.

Secondary amines react to form sulfonamides which have no acidic hydrogen and hence remain insoluble in alkali.

$$R_2NH + C_6H_5SO_2Cl \longrightarrow R_2N{-}SO_2C_6H_5$$

The product is insoluble in alkali.

Step 3: Reaction with tertiary amine.

Tertiary amines do not react with benzenesulfonyl chloride under these conditions. They remain unreacted and can be recovered unchanged.

Conclusion:

- **Primary amines:** give soluble sulfonamide salts.
- **Secondary amines:** give insoluble sulfonamides.
- **Tertiary amines:** do not react.

> Quick Tip
>
> Hinsberg's test is a simple and reliable way to distinguish between primary, secondary, and tertiary amines. Always check solubility in alkali after reaction with benzenesulfonyl chloride.

(ii) The boiling points of amines are lower than their comparable alcohols and carboxylic acids. Explain.

Solution:

Step 1: Intermolecular forces in amines.

Amines can form intermolecular hydrogen bonds because of the presence of a nitrogen atom with a lone pair. However, N–H bonds are less polar than O–H bonds, and nitrogen is less electronegative than oxygen. Thus, the hydrogen bonding in amines is weaker compared to alcohols and carboxylic acids.

Step 2: Intermolecular forces in alcohols.

Alcohols have O–H bonds, which are more polar and form stronger hydrogen bonds than N–H bonds. Hence, alcohols have higher boiling points than corresponding amines.

Step 3: Intermolecular forces in carboxylic acids.

Carboxylic acids form very strong **dimeric hydrogen bonds** in which two molecules are linked via two O–H…O bonds. This gives them the highest boiling points among the three classes of compounds.

Conclusion:

Boiling point order for comparable molecular masses is:

$$\text{Carboxylic acids} > \text{Alcohols} > \text{Amines}$$

Quick Tip

Always compare hydrogen bonding capacity when reasoning about boiling points: stronger hydrogen bonding leads to higher boiling points. Oxygen forms stronger H-bonds than nitrogen, and carboxylic acids form dimers, making them especially high boiling.