UP Board Class 12 Chemistry - 347 (KB) - 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) The concentration of solute in a solution is 3.5 ppm. By which of the following it may be expressed?

(A) 3.5 g/L

(B) 3.5 mol/L

(C) 3.5 mg/L

(D) 3.5 mol/kg

Correct Answer: (C) 3.5 mg/L

Solution:

Step 1: Define ppm in terms of mass units.

The unit ”ppm” stands for ”parts per million” and represents a mass ratio. A concentration of 1 ppm is equivalent to 1 mg of solute per kg of solution.

$$1\,\text{ppm} = 1\,\text{mg/kg}$$

Step 2: Relate mass of solution to volume.

For dilute aqueous solutions, the density can be approximated to that of pure water, which is about 1 kg per litre (1 kg/L).

Step 3: Convert the units.

Given a concentration of 3.5 ppm, we can write it as 3.5 mg/kg.

$$3.5\,\text{ppm} = \frac{3.5\,\text{mg solute}}{1\,\text{kg solution}}$$

Using the density approximation from Step 2, we can replace 1 kg of solution with 1 L of solution.

$$\frac{3.5\,\text{mg solute}}{1\,\text{kg solution}} \approx \frac{3.5\,\text{mg solute}}{1\,\text{L solution}} = 3.5\,\text{mg/L}$$

Step 4: Match with the given options.

The calculated expression 3.5 mg/L corresponds to option (C).

$$\boxed{3.5\,\text{mg/L}}$$

Quick Tip

Remember: In aqueous solutions, ppm is numerically equal to mg/L. This shortcut is very useful for environmental chemistry and water analysis problems.

(b) The most common oxidation states of Mn are –

(A) +2, +4

(B) +2, +5

(C) +2, +6

(D) +2, +7

Correct Answer: (A) +2, +4

Solution:

Step 1: Analyze the stability of the +2 oxidation state.

Manganese (Mn) has the electron configuration [Ar] $3d^5 4s^2$. By losing its two 4s electrons, it forms the Mn^{2+} ion with an electron configuration of [Ar] $3d^5$. This half-filled d-subshell is a state of special stability, making the +2 oxidation state very common and readily formed.

Step 2: Analyze the stability of the +4 oxidation state.

The +4 oxidation state of manganese is found in the compound manganese dioxide, MnO_2. This compound is very stable and is the main component of the mineral pyrolusite, which is the chief ore of manganese. The natural abundance and stability of MnO_2 make +4 a very common oxidation state for manganese.

Step 3: Compare with other oxidation states.

While manganese can exhibit other oxidation states such as +3, +6, and +7 (e.g., in $KMnO_4$), they are generally less stable. The +7 state, for example, is a powerful oxidizing agent, meaning it is readily reduced to a more stable state. The +2 state is stable due to its electron configuration, and the +4 state is common due to the high stability of its oxide.

Step 4: Final Conclusion.

Therefore, the combination of electronic stability (for +2) and the existence of a highly stable and abundant oxide (for +4) makes +2 and +4 the most common oxidation states of

manganese.

$$\boxed{+2, +4}$$

Quick Tip

Transition metals often exhibit multiple oxidation states, but the most common ones are usually those that give stable compounds. For Mn, +2 (simple salts) and +4 (MnO_2) are most frequent.

(c) The co-ordination number of Cu in $[Cu(CN)_4]^{3-}$ ion is:

(A) 2

(B) 3

(C) 4

(D) None of them

Correct Answer: (C) 4

Solution:

Step 1: Identify the components of the complex ion.

In the formula $[Cu(CN)_4]^{3-}$, Cu is the central metal atom, and CN^- (cyanide) is the ligand.

Step 2: Define coordination number.

The coordination number represents the number of ligand atoms that are directly bonded to the central metal atom. It essentially counts the number of coordinate bonds formed by the ligands with the metal.

Step 3: Determine the number and type of ligands.

The subscript '4' next to the CN ligand indicates that there are four cyanide ligands in the complex. The cyanide ion is a monodentate ligand, meaning each ligand forms only one bond to the central metal atom.

Step 4: Calculate the coordination number.

Since there are four monodentate ligands, each forming one bond, the total number of bonds to the central Cu atom is 4.

$$\text{Coordination Number} = 4 \times 1 = 4$$

Therefore, the coordination number of Cu is 4.

$\boxed{4}$

Quick Tip

The coordination number depends on the number of ligand donor atoms bonded, not on the charge of the ion. For example, $[Cu(NH_3)_4]^{2+}$ and $[Cu(CN)_4]^{3-}$ both have a coordination number of 4.

(d) Which of the following is obtained by Wolff Kishner reduction?

(A) $>CH_2$ group

(B) $-NO_3$ group

(C) –OH group

(D) >C=O group

Correct Answer: (A) $>CH_2$ group

Solution:

Step 1: Identify the reactant functional group.

The Wolff–Kishner reduction is a specific reaction for the carbonyl group (>C=O), which is found in aldehydes and ketones. This is the starting functional group for the reaction.

Step 2: Describe the chemical transformation.

This reaction uses hydrazine (NH_2NH_2) and a strong base (such as KOH) under high temperatures. The overall process is a deoxygenation that completely removes the oxygen atom of the carbonyl group.

Step 3: Identify the product functional group.

The oxygen atom is replaced by two hydrogen atoms. This transforms the carbonyl group (>C=O) into a methylene group ($>CH_2$).

$$R - C(=O) - R' \xrightarrow{NH_2NH_2, KOH, \Delta} R - CH_2 - R'$$

Step 4: Conclude the answer from the options.

The question asks what functional group is *obtained* as the product. As shown, the carbonyl group is converted into a methylene group (>CH_2). Therefore, option (A) is the correct answer.

$$\boxed{> CH_2 \text{ group}}$$

Quick Tip

Remember: Wolff–Kishner reduction and Clemmensen reduction both convert carbonyl groups to methylene groups. Wolff–Kishner is done under strongly basic conditions, while Clemmensen uses acidic conditions with Zn–Hg/HCl.

(e) Which of the following amine does not give carbylamine reaction?

(A) CH_3–CH_2–NH_2

(B) CH_3–NH_2

(C) CH_3–NH–CH_3

(D) C_6H_5–NH_2

Correct Answer: (C) CH_3–NH–CH_3

Solution:

Step 1: Recall the carbylamine reaction.

The carbylamine reaction is a test for primary amines (aliphatic or aromatic). In this reaction, a primary amine reacts with chloroform ($CHCl_3$) and alcoholic KOH to form isocyanides (carbylamines), which have a very unpleasant odor.

General reaction:

$$R\text{–}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{–}NC + 3KCl + 3H_2O$$

Step 2: Check each option.

- (A) CH_3–CH_2–NH_2: This is a primary aliphatic amine. It gives the carbylamine test.
- (B) CH_3–NH_2: This is also a primary aliphatic amine, so it gives the carbylamine test.
- (C) CH_3–NH–CH_3: This is a secondary amine. Secondary (and tertiary) amines do **not** give the carbylamine reaction.

- (D) C_6H_5–NH_2: Aniline is a primary aromatic amine. It also gives the carbylamine test.

Step 3: Final Answer.

Thus, the amine which does not give the carbylamine reaction is the secondary amine, CH_3–NH–CH_3.

$$\boxed{CH_3–NH–CH_3 \text{ (secondary amine)}}$$

Quick Tip

Only **primary amines** (aliphatic and aromatic) give the carbylamine reaction. Secondary and tertiary amines do not.

(f) Which of the following test is not given by aldehydic group present in glucose?

(A) Tollen's test

(B) Schiff's test

(C) Fehling test

(D) None of them

Correct Answer: (B) Schiff's test

Solution:

Step 1: Recall the nature of glucose.

Glucose is an aldohexose (contains an aldehyde group at C-1). However, in aqueous solution, glucose predominantly exists in cyclic hemiacetal form (pyranose or furanose), in which the aldehyde group is not free but can open to show reducing properties.

Step 2: Tests for aldehyde group.

- **Tollen's test:** Glucose gives Tollen's test (silver mirror test) because it is a reducing sugar.
- **Fehling's test:** Glucose also gives Fehling's test, producing a red precipitate of Cu_2O.
- **Schiff's test:** This test is generally not given by glucose. Schiff's reagent detects free aldehydes that immediately react to give a magenta colour. Since glucose mainly exists in cyclic form and its aldehyde group is not freely available, it gives only a very weak or negative Schiff's test.

Step 3: Conclusion.

Thus, among the given options, glucose does not give Schiff's test effectively.

$$\boxed{\text{Schiff's test (B)}}$$

> Quick Tip
>
> Glucose is a reducing sugar and gives Tollen's and Fehling's tests due to its ability to revert to the open-chain form, but Schiff's test requires a readily free aldehyde group, which glucose does not provide effectively.

2.(a) Explain molarity and molality by example.

Solution:

Molarity (M):

Molarity is defined as the number of moles of solute present in 1 litre of solution.

$$M = \frac{\text{moles of solute}}{\text{volume of solution in litres}}$$

Example:

If 58.5 g of NaCl (molar mass = 58.5 g/mol) is dissolved in water to make 1 litre of solution, then:

$$M = \frac{1}{1} = 1 \text{ M solution of NaCl}$$

—

Molality (m):

Molality is defined as the number of moles of solute present in 1 kg of solvent.

$$m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

Example:

5.0 g of ethanoic acid (CH_3COOH, molar mass = 60 g/mol) is dissolved in 150 g (0.150 kg) of benzene:

$$n = \frac{5.0}{60} = 0.0833\,\text{mol}$$

$$m = \frac{0.0833}{0.150} = 0.5567\,\text{mol/kg}$$

So, the molality is $0.557\,m$.

> **Quick Tip**
>
> Molarity depends on the **volume of solution**, hence changes with temperature.
>
> Molality depends on the **mass of solvent**, hence remains constant with temperature.

(b) Explain the following:

(i) Lanthanoid contraction

(ii) Oxidation states in Lanthanoids and Actinoids

Solution:

(i) Lanthanoid Contraction:

As we move from La (Z=57) to Lu (Z=71) in the lanthanoid series, the electrons are added to the 4f orbitals.

The 4f electrons have very poor shielding effect, so the increasing nuclear charge pulls the outer 5d and 6s orbitals closer to the nucleus.

This results in a steady decrease in atomic and ionic radii, known as **lanthanoid contraction**.

Consequences:

- Similarity of size between elements of second and third transition series.
- Difficulty in separation of lanthanoids.
- Greater basicity differences in lanthanoid hydroxides.

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(ii) Oxidation States in Lanthanoids and Actinoids:

Lanthanoids:

The most common oxidation state is $+3$.

However, $+2$ and $+4$ oxidation states are also shown in some compounds (e.g., Eu^{2+}, Ce^{4+}) due to stability of half-filled or empty f-orbitals.

Actinoids:

Actinoids exhibit a much wider range of oxidation states, from $+3$ to $+6$ and beyond.

For example, U shows $+3, +4, +5, +6$, while Np and Pu show multiple states.

This is because 5f, 6d, and 7s orbitals have comparable energies and all can participate in bonding.

> Quick Tip
>
> Lanthanoids: mostly $+3$.
>
> Actinoids: variable oxidation states due to availability of 5f, 6d, and 7s electrons.

(c) Explain valence bond theory in coordination compounds.

Solution:

Step 1: Basic idea.

According to Valence Bond Theory (VBT), the central metal ion in a coordination compound makes available a certain number of vacant orbitals (hybrid orbitals) for the formation of coordinate covalent bonds with ligands.

The ligands donate lone pairs of electrons into these vacant orbitals.

Step 2: Hybridisation concept.

- The type of hybridisation depends on the coordination number of the complex.
- For example:
- Coordination number 6 $\Rightarrow$ *octahedral complexes* $\Rightarrow d^2sp^3$ (inner orbital) or sp^3d^2 (outer orbital).
- Coordination number 4 $\Rightarrow$ *tetrahedral complexes* $\Rightarrow sp^3$.
- Coordination number 4 $\Rightarrow$ *square planar complexes* $\Rightarrow dsp^2$.

Step 3: Example.

$[Co(NH_3)_6]^{3+}$: Cobalt in +3 oxidation state has $3d^6$.

Pairing occurs to give empty d-orbitals.

Hybridisation is d^2sp^3, leading to an octahedral geometry.

VBT explains geometry, magnetic properties and bonding in coordination complexes.

Quick Tip

Always determine the metal oxidation state, then electronic configuration, then see whether pairing of d-electrons occurs.

This predicts the hybridisation and geometry of the coordination compound.

(d) Explain Wurtz and Fittig reactions by examples.

Solution:

Wurtz Reaction:

This reaction involves the coupling of alkyl halides in presence of sodium metal in dry ether to form higher alkanes.

$$2\,R{-}X + 2\,Na \xrightarrow[\text{dry ether}]{} R{-}R + 2\,NaX$$

Example:

$$2\,CH_3Cl + 2\,Na \longrightarrow C_2H_6 + 2\,NaCl$$

Product: ethane.

Fittig Reaction:

This is a similar reaction but with aryl halides.

Two aryl halide molecules react with sodium in dry ether to give biaryl compounds.

$$2\,Ar{-}X + 2\,Na \xrightarrow[\text{dry ether}]{} Ar{-}Ar + 2\,NaX$$

Example:

$$2\,C_6H_5Cl + 2\,Na \longrightarrow C_6H_5{-}C_6H_5 + 2\,NaCl$$

Product: biphenyl.

Note:

A combination of Wurtz and Fittig (Wurtz–Fittig reaction) allows coupling between aryl halides and alkyl halides to form alkylbenzenes.

> Quick Tip
>
> Wurtz $\Rightarrow$ alkane formation (from alkyl halides).
>
> Fittig $\Rightarrow$ biaryl formation (from aryl halides).
>
> Wurtz–Fittig $\Rightarrow$ alkylbenzene formation (from alkyl + aryl halides).

3.(a) 28 g KOH (molar mass = 56) is dissolved in 500 mL solution. Calculate the molarity of the solution.

Solution:

Step 1: Calculate number of moles of KOH.

$$n = \frac{\text{Mass of solute}}{\text{Molar mass}} = \frac{28}{56} = 0.5\,\text{mol}$$

Step 2: Convert volume of solution into litres.

$$V = 500\,\text{mL} = 0.500\,\text{L}$$

Step 3: Apply molarity formula.

$$M = \frac{n}{V} = \frac{0.5}{0.500} = 1.0\,M$$

$$\boxed{\text{Molarity of the solution = 1.0 M}}$$

> Quick Tip
>
> Always convert volume into litres before applying the molarity formula.

(b) Write chemical equation and the method of preparation of ethanol from molasses.

Solution:

Step 1: Raw material.

Molasses, a by-product of sugar industry, contains about 30–40% sucrose.

Step 2: Fermentation process.

Molasses is diluted with water and yeast (*Saccharomyces cerevisiae*) is added.

The enzyme invertase converts sucrose into glucose and fructose.

Then the enzyme zymase converts glucose/fructose into ethanol and carbon dioxide.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{invertase}} C_6H_{12}O_6 \ + \ C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH \ + \ 2CO_2$$

Step 3: Distillation.

The fermented solution is distilled to obtain ethanol of higher purity.

Thus, ethanol is prepared from molasses by fermentation followed by distillation.

Quick Tip

In fermentation, temperature must be maintained around 30–35°C; at higher temperature yeast dies and at lower temperature fermentation becomes slow.

(c) Explain the nature of carbonyl group and carboxylic group.

Solution:

Carbonyl group (C=O):

- The carbonyl group consists of a carbon atom double-bonded to an oxygen atom.
- The C=O bond is polar because oxygen is more electronegative than carbon.
- The carbon atom has a partial positive charge (δ^+) and oxygen a partial negative charge (δ^-).

- This polarity makes the carbonyl carbon susceptible to nucleophilic attack and the oxygen capable of hydrogen bonding.
- Hence, aldehydes and ketones (which contain the carbonyl group) undergo nucleophilic addition reactions.

Carboxylic group (–COOH):

- The carboxyl group is composed of a carbonyl group (C=O) and a hydroxyl group (–OH) attached to the same carbon.
- Due to resonance, the carboxyl group exists as a hybrid of two structures, making the C–O bonds equivalent.
- The O–H bond is highly polar, so carboxylic acids are acidic in nature and readily donate a proton (H^+).
- They form dimers through strong intermolecular hydrogen bonding, giving them higher boiling points.

> Quick Tip
>
> Carbonyl groups are mainly reactive towards nucleophiles (nucleophilic addition), while carboxylic groups show acidic character and hydrogen bonding due to –COOH functionality.

(d) Write chemical equation of two chemical properties of glucose.

Solution:

Property 1: Reduction of Fehling's solution.

Glucose is an aldohexose containing an –CHO group. It reduces Fehling's solution (alkaline Cu^{2+} ions) to red cuprous oxide (Cu_2O).

$$\mathrm{R{-}CHO} + 2\,\mathrm{Cu^{2+}} + 5\,\mathrm{OH^-} \longrightarrow \mathrm{R{-}COO^-} + \mathrm{Cu_2O} \downarrow + 3\,\mathrm{H_2O}$$

Property 2: Reduction of Tollens' reagent.

Glucose reduces Tollens' reagent (ammoniacal silver nitrate) to metallic silver (silver mirror).

$$\mathrm{R{-}CHO} + 2\,[\mathrm{Ag(NH_3)_2}]^{+} + 3\,\mathrm{OH^-} \longrightarrow \mathrm{R{-}COO^-} + 2\,\mathrm{Ag}\downarrow + 4\,\mathrm{NH_3} + 2\,\mathrm{H_2O}$$

Note:

These reactions confirm that glucose contains a free aldehyde (–CHO) group in its open-chain structure.

> **Quick Tip**
>
> Both Fehling's and Tollens' tests are classical tests for aldehydes. Glucose, despite existing mostly in cyclic form, gives these reactions due to the presence of a small amount of open-chain aldehyde structure in equilibrium.

4.(a) The vapour pressure of pure benzene at any temperature is 0.850 bar. 0.5 g non-volatile non-electrolytic solid is dissolved in 39.0 g benzene (molar mass 78 g mol^{-1}). The vapour pressure of the solution is 0.845 bar. Calculate the molar mass of the solid.

Solution:

For a non–volatile solute, Raoult's law gives relative lowering of vapour pressure:

$$\frac{\Delta P}{P^\circ} = X_{\text{solute}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Given:

$P^\circ = 0.850$ bar, $P = 0.845$ bar $\Rightarrow \Delta P = 0.005$ bar.

Mass of benzene $= 39.0$ g, $M_{\text{benzene}} = 78$ g mol^{-1} $\Rightarrow n_{\text{solvent}} = \frac{39.0}{78} = 0.50$ mol.

Mass of solute $= 0.50$ g, molar mass $= M \Rightarrow n_{\text{solute}} = \frac{0.50}{M}$ mol.

Step 1: Compute relative lowering.

$$\frac{\Delta P}{P^\circ} = \frac{0.005}{0.850} = 0.005882\ (\approx 5.882 \times 10^{-3})$$

Step 2: Apply Raoult's relation.

$$0.005882 = \frac{\frac{0.50}{M}}{\frac{0.50}{M} + 0.50}$$

Multiply numerator and denominator by M:

$$0.005882 = \frac{0.50}{0.50 + 0.50M}$$

$$0.005882(0.50 + 0.50M) = 0.50$$

$$0.002941 + 0.002941\,M = 0.50 \Rightarrow 0.002941\,M = 0.497059$$

$$M = \frac{0.497059}{0.002941} \approx 169 \text{ g mol}^{-1}$$

$$\boxed{\text{Molar mass of the solid } \approx 1.69 \times 10^2 \text{ g mol}^{-1}}$$

Quick Tip

For non-volatile solutes, use $\frac{\Delta P}{P^\circ} = X_{\text{solute}}$.
If the solute amount is very small, $X_{\text{solute}} \approx \frac{n_{\text{solute}}}{n_{\text{solvent}}}$ is a quick approximation; here we used the exact expression.

(b) Define standard electrode potential. Calculate the standard electrode potential of the following cell:

Zn / Zn^{2+} || Cu^{2+} / Cu when

$E^0_{(Zn^{2+}/Zn)} = -0.76\,V$ and $E^0_{(Cu^{2+}/Cu)} = +0.34\,V$.

Solution:

Definition:

The **standard electrode potential** of an electrode is the potential difference developed between the electrode and the standard hydrogen electrode (SHE) when the electrode is in contact with its ions at unit concentration (1 M), at 1 atm pressure, and 298 K.

Step 1: Write the given cell.

The cell is:

$$\mathrm{Zn} \mid \mathrm{Zn}^{2+}(1\mathrm{M}) \;||\; \mathrm{Cu}^{2+}(1\mathrm{M}) \mid \mathrm{Cu}$$

Step 2: Identify anode and cathode.

- For Zn^{2+}/Zn: $E^0 = -0.76\,V$ (more negative, so Zn acts as anode).
- For Cu^{2+}/Cu: $E^0 = +0.34\,V$ (more positive, so Cu acts as cathode).

Step 3: Formula for standard cell potential.

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

Step 4: Substitute values.

$$E^0_{\text{cell}} = \big(+0.34\,V\big) - \big(-0.76\,V\big)$$

$$E^0_{\text{cell}} = +0.34 + 0.76 = +1.10\,V$$

$$\boxed{E^0_{\text{cell}} = +1.10\,V}$$

> **Quick Tip**
>
> Always identify the cathode (higher E^0) and anode (lower E^0) correctly before applying the formula $E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$.

(c) Define order of reaction. How will you find out the order of reaction of the reaction nA + mB $\rightarrow$ xC + yD?

Solution:

Definition of order of reaction:

The order of a reaction is the sum of the powers of the concentrations of the reactants in the rate law expression of the reaction.

It indicates how the rate of reaction depends on the concentration of the reactants.

General reaction:

$$nA + mB \longrightarrow xC + yD$$

The rate law for this reaction can be written as:

$$r = k[A]^{\alpha}[B]^{\beta}$$

Where:

- k = rate constant,
- α = order of reaction with respect to A,
- β = order of reaction with respect to B.

Overall order of reaction:

$$\text{Order} = \alpha + \beta$$

Experimental determination:

The values of α and β are not necessarily equal to the stoichiometric coefficients n and m. They are determined experimentally using methods such as:

1. **Initial rate method:** By measuring the rate of reaction for different initial concentrations of A and B, the powers α and β are calculated.
2. **Integrated rate equations:** By analyzing the concentration of reactants as a function of time, the order of reaction can be established.

Thus, the order of reaction of $nA + mB \rightarrow xC + yD$ is given by the sum of experimentally determined powers $\alpha + \beta$.

$$\boxed{\text{Order of reaction} = \alpha + \beta}$$

Quick Tip

Remember that the order of a reaction is always determined experimentally. It may or may not be the same as the stoichiometric coefficients of the balanced chemical equation.

(d) What happens when—

(i) Chromite ore reacts with potassium carbonate in presence of air.

(ii) Potassium dichromate reacts with ferrous sulphate in presence of sulphuric acid.

(iii) Potassium permanganate is heated up to 513 K.

Solution:

(i) Oxidative roasting of chromite with K_2CO_3 (air):

Chromite ($FeCr_2O_4$) is oxidised to potassium chromate; iron becomes Fe_2O_3.

$$\boxed{4\,FeCr_2O_4 + 8\,K_2CO_3 + 7\,O_2 \longrightarrow 8\,K_2CrO_4 + 2\,Fe_2O_3 + 8\,CO_2}$$

(ii) $K_2Cr_2O_7$ + $FeSO_4$ in acidic medium:

Dichromate oxidises Fe^{2+} to Fe^{3+} and is reduced to Cr^{3+}.

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

In terms of salts:

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O$$

(iii) Heating $KMnO_4$ to $\sim 513\,K$:

Permanganate disproportionates giving manganate, manganese dioxide and oxygen.

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

> **Quick Tip**
>
> Remember: (i) Roasting chromite with alkali in air yields yellow chromate; (ii) $Cr_2O_7^{2-}$ is a strong oxidant in acid, converting $Fe^{2+} \rightarrow Fe^{3+}$; (iii) On heating, $KMnO_4$ releases oxygen—useful for lab O_2 prep.

5.(a) Explain molar conductivity. The resistance of a cell filled with 0.02 mol L^{-1} KCl solution is 480 Ω. Calculate the molar conductivity of the solution. (Cell constant = 1.29 cm^{-1}).

Solution:

Definition:

Molar conductivity (Λ_m) is the conductance of all the ions produced by 1 mole of electrolyte placed between two electrodes 1 cm apart, with the solution having unit cross-sectional area. It is given by $\Lambda_m = \kappa \dfrac{1000}{c}$, where κ is conductivity (S cm^{-1}) and c is concentration in mol L^{-1}.

Step 1: Find conductivity κ.

Conductance $G = \dfrac{1}{R} = \dfrac{1}{480}$ S $= 2.0833 \times 10^{-3}$ S.

$\kappa =$ (cell constant) $\times\, G = 1.29$ cm$^{-1} \times 2.0833 \times 10^{-3}$ S $= 2.6875 \times 10^{-3}$ S cm^{-1}.

Step 2: Calculate molar conductivity.

$c = 0.02$ mol L^{-1}.

$$\Lambda_m = \kappa \frac{1000}{c} = 2.6875 \times 10^{-3}\ \frac{1000}{0.02} = 2.6875 \times 10^{-3} \times 5.0 \times 10^{4} = 1.34375 \times 10^{2}\ \text{S cm}^2\ \text{mol}^{-1}.$$

$$\boxed{\Lambda_m \approx 1.34 \times 10^{2}\ \text{S cm}^2\ \text{mol}^{-1}}$$

> **Quick Tip**
>
> $\kappa =$ (cell constant) $\times\, G$ with cell constant in cm^{-1} and G in S.
> Use $\Lambda_m = \kappa \dfrac{1000}{c}$ (with c in mol L^{-1}) to get S cm^2 mol^{-1}.

(b) Write unit of first order reaction. The initial concentration of N_2O_5 at 318 K was 0.60×10^{-2} mol L^{-1} in the first order reaction, which became 0.20×10^{-2} mol L^{-1} after 60 min. Calculate the velocity constant at 318 K. (log 3 = 0.4771).

Solution:

Unit of a first-order rate constant:

Time^{-1} (e.g., s^{-1} or min^{-1}).

Data:

$a = 0.60 \times 10^{-2} = 6.0 \times 10^{-3}$ mol L^{-1}.

$a_t = 0.20 \times 10^{-2} = 2.0 \times 10^{-3}$ mol L^{-1}.

$t = 60$ min.

First-order relation:

$k = \dfrac{2.303}{t} \log\left(\dfrac{a}{a_t}\right) = \dfrac{2.303}{60} \log(3).$

Given $\log 3 = 0.4771$:

$k = \dfrac{2.303 \times 0.4771}{60} = \dfrac{1.099}{60} = 1.831 \times 10^{-2}$ min^{-1}.

In s^{-1}: $k = \dfrac{1.831 \times 10^{-2}}{60} = 3.05 \times 10^{-4}$ s^{-1}.

$$\boxed{k \approx 1.83 \times 10^{-2} \text{ min}^{-1} \ (= \ 3.05 \times 10^{-4} \text{ s}^{-1} \ )}$$

Quick Tip

For first order, plot or use $k = \dfrac{2.303}{t} \log\left(\dfrac{a}{a_t}\right)$.

When concentration drops by a factor of 3 in time t, simply use $\log 3$.

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

(i) Hexa aqua chromium (III) chloride

(ii) Dichlorido diammin e platinum (II)

(iii) Hexa ammine platinum (IV) chloride

(iv) Sodium penta cyano nitrosyl ferrate (II)

Solution:

(i) Hexa aqua chromium(III) chloride $\Rightarrow \boxed{[Cr(H_2O)_6]Cl_3}$

(Complex cation charge $+3$ balanced by 3 chloride ions.)

(ii) Dichlorido diammin e platinum(II) $\Rightarrow \boxed{[Pt(NH_3)_2Cl_2]}$

(Neutral complex: Pt^{2+} with two neutral ammine and two chlorido ligands.)

(iii) Hexa ammine platinum(IV) chloride $\Rightarrow \boxed{[Pt(NH_3)_6]Cl_4}$

(Pt^{4+} with six neutral ammine ligands gives a $4+$ complex cation, balanced by 4 Cl^-.)

(iv) Sodium penta cyano nitrosyl ferrate(II) $\Rightarrow \boxed{Na_2[Fe(CN)_5NO]}$

(Anion charge -2 since Fe^{2+}, five CN^- and NO^+; hence 2 Na^+ counterions.)

Quick Tip

While writing formulae: put the coordination entity in square brackets, list ligands alphabetically inside the bracket, compute the complex charge from metal oxidation state and ligand charges, then add the appropriate counter-ions outside the bracket.

(d) Explain primary, secondary, tertiary and quaternary structures of protein in detail.

Solution:

Proteins are large biomolecules made of amino acids linked by peptide bonds.

The function and properties of proteins depend on the arrangement of amino acids and their folding into higher structures.

Protein structure can be described at four different levels:

1. Primary Structure:

- The primary structure refers to the linear sequence of amino acids in a polypeptide chain.
- This sequence is determined by the genetic code (DNA).
- Even a small change in the sequence (mutation) can drastically alter the protein's function.

2. Secondary Structure:

- The secondary structure is the regular folding or coiling of the polypeptide chain due to hydrogen bonding between the carbonyl oxygen and the amide hydrogen of the peptide backbone.
- The two most common patterns are:

(a) α-helix (coiled structure)

(b) β-pleated sheet (zig-zag structure).

3. Tertiary Structure:

- The tertiary structure refers to the overall three-dimensional folding of a polypeptide chain.
- This folding occurs due to interactions among side chains (R-groups), such as:
- Hydrogen bonds
- Ionic interactions
- Hydrophobic interactions
- Disulfide bonds (covalent).

- The tertiary structure determines the biological activity of the protein (e.g., enzyme active site).

4. Quaternary Structure:

- The quaternary structure arises when two or more polypeptide chains (subunits) associate together to form a functional protein.
- Examples include hemoglobin (composed of four polypeptide subunits).
- This structure is stabilized by the same interactions as tertiary structure but involves multiple polypeptide chains.

Thus, proteins exhibit a hierarchical structure: primary $\rightarrow$ secondary $\rightarrow$ tertiary $\rightarrow$ quaternary, each level being essential for their stability and biological function.

> Quick Tip
>
> Remember: The primary structure is about amino acid sequence, secondary is local folding (-helix, -sheet), tertiary is overall 3D folding, and quaternary is association of multiple chains.

6.(a) Explain the mechanism of substitution reactions of Haloalkane.

Solution:

Haloalkanes undergo nucleophilic substitution reactions because the carbon atom attached to the halogen is electron-deficient (due to the electronegativity of halogen). The C–X bond is polarized ($C^{\delta+}$ – $X^{\delta-}$), making carbon susceptible to attack by nucleophiles.

There are two main mechanisms:

1. S_N1 **mechanism (Unimolecular Nucleophilic Substitution):**

- Two-step process.
- Step 1: Slow ionization of haloalkane to form carbocation (rate-determining).

$$R{-}X \longrightarrow R^+ + X^-$$

- Step 2: Fast attack of nucleophile on carbocation.

$$R^+ + Nu^- \longrightarrow R{-}Nu$$

- Rate depends only on haloalkane concentration: Rate = k[R–X].

- Favoured in tertiary haloalkanes (stable carbocation).

2. S_N2 **mechanism (Bimolecular Nucleophilic Substitution):**

- One-step, concerted process.

- Nucleophile attacks carbon from the side opposite to the leaving group (backside attack).

- Transition state has partial bonds to both nucleophile and leaving group.

$$R{-}X + Nu^- \longrightarrow [R{-}(Nu)(X)]^{\ddagger} \longrightarrow R{-}Nu + X^-$$

- Rate depends on both haloalkane and nucleophile concentrations: Rate = k[R–X][Nu$^-$].

- Favoured in primary haloalkanes (less steric hindrance).

> Quick Tip
>
> Tertiary haloalkanes follow S_N1, primary haloalkanes follow S_N2, and secondary haloalkanes may follow either depending on conditions.

OR

Explain optical activity, chirality, retention, inversion and racemisation in Haloalkane.

Solution:

Optical activity:

A compound is said to be optically active if it can rotate the plane of plane-polarized light. Haloalkanes with a chiral carbon show optical activity.

Chirality:

A carbon atom bonded to four different groups is called a chiral carbon (asymmetric carbon). Such molecules exist in two non-superimposable mirror image forms (enantiomers).

Retention:

If during a reaction the spatial arrangement around the chiral carbon remains unchanged, the configuration is retained — this is called **retention of configuration**.

Inversion:

In S_N2 mechanism, the nucleophile attacks from the backside, opposite to the leaving group. This flips the configuration at the chiral carbon, called **Walden inversion**.

Racemisation:

In S_N1 mechanism, the planar carbocation formed can be attacked by the nucleophile from either side with equal probability. This gives a mixture of enantiomers (50:50), which is optically inactive due to mutual cancellation. This process is called **racemisation**.

> Quick Tip
>
> - $S_N2 \Rightarrow$ inversion of configuration.
> - $S_N1 \Rightarrow$ racemisation (mixture of retention + inversion).
> - Optical activity arises only when a molecule has chirality (no plane of symmetry).

(b) Write chemical equations of dehydration reactions of primary, secondary and tertiary alcohols and also write mechanism of dehydration reaction of primary alcohol.

Solution:

Dehydration reaction: Alcohols on heating with concentrated H_2SO_4 or H_3PO_4 undergo dehydration to give alkenes.

(i) Primary alcohol:

Example: Ethanol

$$CH_3CH_2OH \xrightarrow[\Delta]{conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

(ii) Secondary alcohol:

Example: 2-propanol

$$CH_3{-}CHOH{-}CH_3 \xrightarrow[\Delta]{conc.\ H_2SO_4} CH_3{-}CH{=}CH_2 + H_2O$$

(iii) Tertiary alcohol:

Example: tert-butanol

$$(CH_3)_3COH \xrightarrow[\Delta]{conc.\ H_2SO_4} (CH_3)_2C{=}CH_2 + H_2O$$

Mechanism of dehydration of primary alcohol (Ethanol):

Step 1: Protonation of alcohol.

$$CH_3CH_2OH + H^+ \longrightarrow CH_3CH_2OH_2^+$$

Step 2: Formation of carbocation (slow step).

$$CH_3CH_2OH_2^+ \longrightarrow CH_3CH_2^+ + H_2O$$

Step 3: Deprotonation to form alkene.

$$CH_3CH_2^+ \longrightarrow CH_2{=}CH_2 + H^+$$

Thus, the product is ethene.

Primary alcohols undergo dehydration via E1 (or E2 under strong conditions), giving alkenes.

Quick Tip

The ease of dehydration of alcohols follows the order: tertiary $>$ secondary $>$ primary, due to increasing carbocation stability. Always use concentrated H_2SO_4 or H_3PO_4 and heat.

OR

Q. Write chemical equations for obtaining the following from phenol:

(i) 4-Nitrophenol

(ii) Picric acid

(iii) 4-Bromophenol

(iv) Salicylaldehyde

(v) Benzoquinone

Solution:

(i) Preparation of 4-Nitrophenol:

Phenol undergoes nitration with dilute HNO_3 at room temperature.

$$C_6H_5OH + HNO_3 \longrightarrow o\text{-nitrophenol} + p\text{-nitrophenol}$$

Para product (4-nitrophenol) is the major one due to steric effects.

(ii) Preparation of Picric acid (2,4,6-trinitrophenol):

On treatment with concentrated HNO_3 in presence of concentrated H_2SO_4, phenol gives picric acid.

$$C_6H_5OH \xrightarrow[conc.\ H_2SO_4]{conc.\ HNO_3} 2,4,6\text{-trinitrophenol (picric acid)}$$

(iii) Preparation of 4-Bromophenol:

Phenol reacts with bromine water to give 2,4,6-tribromophenol. But to obtain monobromo derivative, phenol is treated with bromine in CS_2 at low temperature.

$$C_6H_5OH + Br_2 \xrightarrow[CS_2]{273K} 4\text{-bromophenol}$$

(iv) Preparation of Salicylaldehyde:

This is obtained by the Reimer–Tiemann reaction. Phenol is treated with chloroform ($CHCl_3$) and alkali (KOH/NaOH).

$$C_6H_5OH + CHCl_3 + 3NaOH \longrightarrow o\text{-HO–C}_6H_4\text{–}CHO + 3NaCl + 2H_2O$$

(Main product is salicylaldehyde at ortho-position.)

(v) Preparation of Benzoquinone:

Phenol is oxidised by strong oxidising agents like $Na_2Cr_2O_7/H_2SO_4$.

$$C_6H_5OH \xrightarrow[oxidation]{} p\text{-benzoquinone}$$

Thus, phenol can yield nitrophenols, bromophenols, aldehydes, and quinones via suitable reactions.

Quick Tip

Phenol is highly reactive towards electrophilic substitution due to the activating effect of –OH group. By controlling the conditions (dilute vs. concentrated reagents, catalysts, solvents), selective products such as mono-, tri-nitro, halo, or formyl-substituted phenols can be obtained.

7.(a) Write chemical equation for five methods of preparation of Ketones.

Solution:

1. Oxidation of secondary alcohols:

$$R{-}CH(OH){-}R' \xrightarrow{[O]} R{-}C(=O){-}R' + H_2O$$

2. Ozonolysis of alkenes:

$$RCH{=}CHR' \xrightarrow{O_3/Zn,H_2O} R{-}C(=O){-}R'$$

3. Friedel–Crafts acylation of aromatic compounds:

$$C_6H_6 + RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

4. From calcium salts of carboxylic acids (dry distillation):

$$(COO)_2Ca \xrightarrow{\Delta} R{-}C(=O){-}R + CaCO_3$$

5. From nitriles (using dialkyl cadmium):

$$RCN + R'_2Cd \longrightarrow R{-}C(=O){-}R'$$

Thus, ketones can be prepared by oxidation, ozonolysis, acylation, dry distillation, and nitrile methods.

Quick Tip

Secondary alcohols $\rightarrow$ ketones by oxidation; alkenes $\rightarrow$ ketones by ozonolysis; benzene + acyl chloride $\rightarrow$ aryl ketone.

OR

Write chemical equation for two methods of preparation and three chemical properties of carboxylic acid.

Solution:

Methods of Preparation:

1. Oxidation of primary alcohols/aldehydes:

$$RCH_2OH \xrightarrow{[O]} RCOOH \quad ; \quad RCHO \xrightarrow{[O]} RCOOH$$

2. Hydrolysis of nitriles:

$$RCN + 2H_2O \xrightarrow{H^+/OH^-} RCOOH + NH_3$$

—

Chemical Properties:

1. Acidic nature:

$$RCOOH \rightleftharpoons RCOO^- + H^+$$

2. Reaction with alcohols (esterification):

$$RCOOH + R'OH \xrightarrow{H^+} RCOOR' + H_2O$$

3. Decarboxylation:

$$RCOONa + NaOH \xrightarrow{CaO,\Delta} RH + Na_2CO_3$$

Thus, carboxylic acids are prepared by oxidation and hydrolysis, and show acidic, esterification, and decarboxylation reactions.

Quick Tip

Carboxylic acids are weak acids but stronger than alcohols; they easily form esters and undergo decarboxylation on heating with soda lime.

(b) Write chemical equation of five chemical properties of amines.

OR,

Write chemical equations of three methods of preparation of amine and also write the mechanism of ammonolysis of alkyl halides.

Solution:

Part–I: Five chemical properties of amines (with equations)

1) Basic character (salt formation):

$$\mathrm{RNH_2 + HCl \rightarrow RNH_3^+Cl^-}$$

2) Acylation (Schotten–Baumann):

$$\mathrm{RNH_2 + R'COCl \xrightarrow{NaOH} R'CONHR + HCl}$$

3) Alkylation (Hofmann exhaustive alkylation):

$$\mathrm{RNH_2 + R'X \xrightarrow{EtOH} R_2NH \xrightarrow{R'X} R_3N \xrightarrow{CH_3I,\, Ag_2O,\, \Delta}} \text{ quaternary ammonium hydroxide}$$

4) Carbylamine reaction (test for 1° amines):

$$\mathrm{RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O}$$

5) Diazotization / coupling (aromatic 1° amines):

$$\mathrm{C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{0-5^\circ C} C_6H_5N_2^+Cl^- + 2H_2O + NaCl}$$

$$\mathrm{C_6H_5N_2^+Cl^- + C_6H_5OH \xrightarrow{NaOH}} \text{ azo dye}$$

OR

Part–II: Three methods of preparation of amines + mechanism of ammonolysis

(A) Three preparations (with equations)

1) Reduction of nitro compounds:

$$\mathrm{ArNO_2} \xrightarrow{\mathrm{Sn/HCl\ or\ H_2/Ni}} \mathrm{ArNH_2 + H_2O}$$

2) Gabriel phthalimide synthesis (only 1° alkyl amines):

$$\mathrm{Phth{-}NH} \xrightarrow{\mathrm{KOH}} \mathrm{Phth{-}N^-K^+} \xrightarrow{\mathrm{R{-}X}} \mathrm{Phth{-}NR} \xrightarrow{\mathrm{H_2N{-}NH_2}} \mathrm{RNH_2} + \text{phthalylhydrazide}$$

3) Hofmann bromamide degradation (1 carbon less):

$$\mathrm{RCONH_2} \xrightarrow{\mathrm{Br_2/NaOH}} \mathrm{RNH_2 + CO_2}$$

(B) Mechanism of ammonolysis of alkyl halides (formation of amines)

Overall reaction (primary example):

$$\mathrm{R{-}X + NH_3} \xrightarrow{\mathrm{EtOH,\ sealed\ tube}} \mathrm{RNH_2 + HX}$$

Step 1: S_N2 backside attack (rate = k[R–X][NH_3]).

$$\mathrm{R{-}X{+} : NH_3} \rightarrow [\mathrm{R \cdots NH_3 \cdots X}]^{\ddagger} \rightarrow \mathrm{R{-}NH_3^+ + X^-}$$

Step 2: Base deprotonation.

$$\mathrm{R{-}NH_3^+ + NH_3} \rightarrow \mathrm{R{-}NH_2 + NH_4^+}$$

Side reactions (over-alkylation):

$$\mathrm{R{-}NH_2 + R{-}X} \rightarrow \mathrm{R_2NH} \rightarrow \mathrm{R_3N} \rightarrow [\mathrm{R_4N}]^+\mathrm{X^-}$$

Hence, to maximize 1° amine, use $\mathrm{NH_3}$ in excess and primary halides (less steric hindrance). Tertiary halides undergo elimination rather than S_N2.

Quick Tip

Amines are basic and nucleophilic: remember **acylation**, **alkylation**, **carbylamine** (only 1°), and **diazotization** (aromatic 1°).

Ammonolysis of $\mathrm{R}{-}\mathrm{X}$ is S_N2; use excess ammonia to limit over-alkylation and prefer primary halides for best yield.
