CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 2 hours **Maximum Marks: 35**

General Instructions

(i) This question paper contains **12** questions. **All** questions are compulsory.

(ii) This question paper is divided into **three** Sections – **Section A, B and C**.

(iii) **Section - A** Q. Nos. **1** to **3** are very short answer type questions carrying **2** marks each.

(iv) **Section - B** Q. Nos. **4** to **11** are short answer type questions carrying **3** marks each.

(v) **Section - C** Q. No. **12** is case based question carrying **5** marks.

(vi) Use of log tables and calculators is NOT allowed.

Section A (6 marks)

1. Arrange the following compounds as directed: (any Two)

(i) In decreasing order of basic strength in aqueous solution: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$

(ii) In increasing order of solubility in water: $(C_2H_5)_2NH$, $C_2H_5NH_2$, $C_6H_5NH_2$

(iii) In decreasing order of their pKb values: $C_6H_5NH_2$, $C_2H_5NH_2$, NH_3 [2 marks]

Solution:

Concept:

- In aqueous solution, amine basicity depends on the electron-releasing effect of alkyl groups, solvation of the conjugate acid and steric hindrance.
- Water solubility reflects hydrogen bonding and the size of the hydrophobic hydrocarbon group. Also, $pK_b = -\log K_b$, so a weaker base has a larger pK_b.

Step 1: (i) Compare aqueous basic strength Ethyl groups increase electron density on nitrogen by their $+I$ effect, making its lone pair more available for protonation. In water, however, the protonated amine must also be stabilised by hydration. Combining the alkyl effect with solvation and steric effects gives the order for these ethylamines:

$$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2.$$

Thus, counting alkyl groups alone would give the wrong aqueous order: the secondary amine is the strongest of the three.

Step 2: (ii) Compare solubility in water Ethylamine and diethylamine can form hydrogen bonds with water, but the larger nonpolar part of diethylamine reduces its solubility relative to ethylamine. Aniline has a much larger hydrophobic phenyl group and is the least soluble. The increasing order is

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2.$$

Step 3: (iii) Reverse the basicity order to obtain the pKb order Aniline is weaker than ammonia because its nitrogen lone pair is delocalised into the benzene ring and is less available to accept a proton. Ethylamine is stronger than ammonia because the ethyl group's $+I$ effect increases electron density on nitrogen. Hence basic strength increases as aniline, ammonia, ethylamine. Since pK_b decreases as basic strength increases, the decreasing order is

$$pK_b(C_6H_5NH_2) > pK_b(NH_3) > pK_b(C_2H_5NH_2).$$

Step 4: Conclusion (i) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$. (ii) $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$. (iii) $pK_b(C_6H_5NH_2) > pK_b(NH_3) > pK_b(C_2H_5NH_2)$. Any two of these arrangements are required.

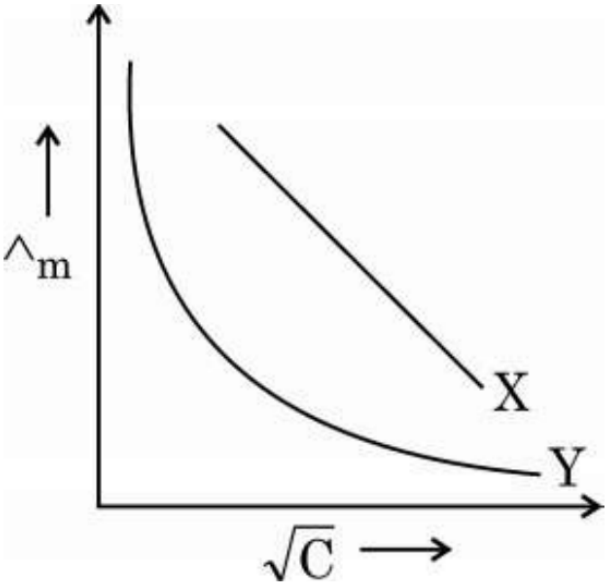
Quick Tip to Solve: For aqueous ethylamines use secondary > tertiary > primary; reverse the basicity order when the question asks for decreasing pKb.

2. In the plot of molar conductivity (Λ_m) Vs. square root of concentration ($\sqrt{C}$), following curves are obtained for two electrolytes X and Y:

Answer the following:

(i) Predict the nature of electrolyte X and Y.

(ii) What happens on extrapolation of Λ_m to concentration approaching zero for electrolytes X and Y? [2 marks]



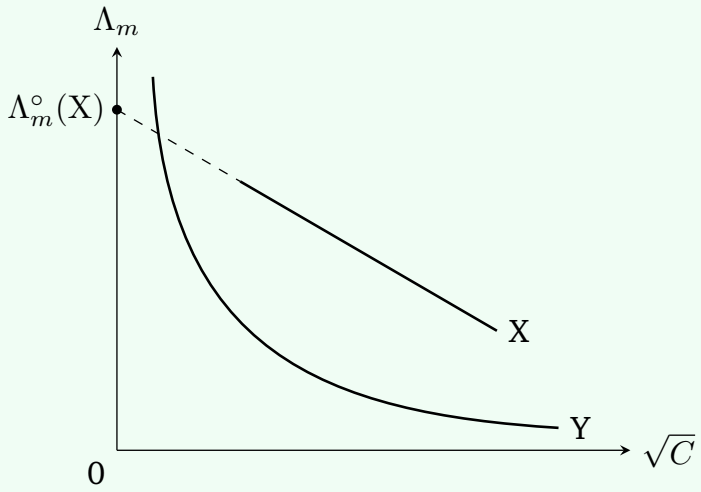
Solution:

Concept:

- Molar conductivity Λ_m is conductivity per molar concentration. On dilution, reduced interionic interactions increase Λ_m; a weak electrolyte also undergoes increased ionisation.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$, where C is concentration, A is a positive constant and Λ_m° is limiting molar conductivity.

Step 1: (i) Identify the electrolytes from the shapes of the curves Curve X is a straight line with a negative slope when Λ_m is plotted against $\sqrt{C}$. This behaviour characterises a strong electrolyte, which is essentially completely ionised in solution. Dilution mainly reduces interactions between its ions. Curve Y is strongly curved and rises steeply as concentration decreases. It represents a weak electrolyte: dilution increases its degree of ionisation, producing a large increase in molar conductivity.

Quick Tip to Solve: On a molar-conductivity versus square-root-concentration plot, identify the straight line as strong; only that line gives the limiting value by direct extrapolation.



Schematic conductivity curves; the dashed continuation of X gives its limiting intercept.

Step 2: (ii) Examine the limiting value at zero concentration For X, extend the straight line to $\sqrt{C} = 0$. Its intercept on the Λ_m-axis gives Λ_m° directly, because the concentration-dependent term in $\Lambda_m = \Lambda_m^\circ - A\sqrt{C}$ vanishes there. For Y, the non-linear curve cannot be reliably extrapolated to obtain Λ_m°. A limiting molar conductivity does exist, but its value is determined using Kohlrausch's law of independent migration of ions, by combining suitable strong-electrolyte limiting conductivities. The steep rise must not be interpreted as infinite limiting molar conductivity.

Step 3: Conclusion X is a strong electrolyte and Y is a weak electrolyte. Extrapolating the straight line for X to zero concentration gives Λ_m°; direct extrapolation of Y does not give a reliable value of Λ_m°, which is obtained using Kohlrausch's law.

Quick Tip to Solve: On a molar-conductivity versus square-root-concentration plot, identify the straight line as strong; only that line gives the limiting value by direct extrapolation.

3. What do you mean by complex reactions? Can we determine order and molecularity of a complex reaction? [2 marks]

Solution:

Concept:

- A complex reaction proceeds through two or more elementary steps, rather than a single elementary collision or event.
- The order is the sum of the powers of reactant concentrations in the experimentally determined rate law. Molecularity counts the reacting species participating in one elementary step.

Step 1: Define a complex reaction A reaction that takes place through a sequence of elementary reactions is called a complex reaction. The sequence constitutes its mechanism and may involve intermediates which are formed in one step and consumed in another. Its overall balanced equation gives the net chemical change, but does not show all these individual events.

Step 2: Determine the order from the rate law The order of a complex reaction can be determined

Quick Tip to Solve: For a multistep reaction, obtain order from the measured rate law and discuss molecularity only for an individual elementary step.

experimentally. For example, if experiments give the rate law $r = k[A]^m[B]^n$, its overall order is $m + n$. The exponents must come from the observed rate law; they cannot in general be read from the stoichiometric coefficients of the overall equation. The slow, rate-determining step and the rest of the mechanism govern the observed rate law.

Step 3: Explain the restriction on molecularity Molecularity is defined only for an elementary reaction, whose reacting species participate in one event. Therefore a complex reaction has no single overall molecularity. Each elementary step in its mechanism has its own molecularity, obtained by counting the reacting species in that step; adding the coefficients in the overall equation does not give a molecularity for the complex reaction.

Step 4: Conclusion Complex reactions occur in multiple elementary steps. Their order can be determined experimentally, but molecularity cannot be assigned to the overall complex reaction; it applies separately to each elementary step.

Quick Tip to Solve: For a multistep reaction, obtain order from the measured rate law and discuss molecularity only for an individual elementary step.

Section B (24 marks)

4(a). Write any three differences between physisorption and chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance, called the adsorbate, on the surface of another substance, called the adsorbent.
- Physisorption results from weak van der Waals forces; chemisorption involves the formation of chemical bonds between adsorbate and adsorbent.

Step 1: Difference 1: nature of the attractive forces In physisorption, the adsorbate is held on the adsorbent surface by weak van der Waals forces. No chemical bond is formed between them. In chemisorption, the adsorbate is attached by chemical bonds to the surface. These bonds are much stronger than van der Waals attractions, so the binding of adsorbate to the surface is stronger in chemisorption.

Step 2: Difference 2: enthalpy of adsorption Physisorption has a relatively low magnitude of adsorption enthalpy, usually about 20–$40\,\text{kJ mol}^{-1}$. Chemisorption has a much higher magnitude, usually about 80–$240\,\text{kJ mol}^{-1}$, because chemical bonds form. Both processes are generally exothermic: the quoted ranges are the magnitudes of heat released, while the actual adsorption enthalpy is negative.

Step 3: Difference 3: specificity Physisorption is not highly specific: van der Waals attractions can act between many different adsorbates and surfaces. Chemisorption is highly specific, because it occurs only when the adsorbate and the adsorbent can form suitable chemical bonds. For example, a gas may physically adsorb on many surfaces, but its chemisorption requires a surface with which it can chemically interact.

Step 4: Conclusion The three differences are: weak van der Waals forces versus chemical bonds;

Quick Tip to Solve: Compare the same property on both sides: forces, adsorption enthalpy and specificity give three distinct differences.

low versus high magnitude of adsorption enthalpy; and low specificity versus high specificity, for physisorption and chemisorption respectively.

Quick Tip to Solve: Compare the same property on both sides: forces, adsorption enthalpy and specificity give three distinct differences.

OR

4(b). Define the following terms with a suitable example in each:

(i) Lyophilic sol

(ii) Macromolecular colloid

(iii) Coagulation [3 marks]

Solution:

Concept:

- A colloid contains a dispersed phase distributed through a dispersion medium; the dispersed particles have dimensions in the colloidal range.
- Colloids are classified by the affinity of the dispersed phase for the medium and by the nature of their particles. Coagulation describes the loss of colloidal stability and aggregation of particles.

Step 1: (i) Lyophilic sol A lyophilic sol is a colloidal sol in which the particles of the dispersed phase have a strong affinity for the dispersion medium. The particles are extensively solvated, making these sols relatively stable. They can generally be prepared by directly mixing the substance with a suitable dispersion medium and are reversible: the separated dispersed phase can form the sol again when the medium is added. For example, starch in water is a lyophilic sol; water is the dispersion medium and hydrated starch is the dispersed phase.

Step 2: (ii) Macromolecular colloid A macromolecular colloid is formed when a substance having very large molecules is dissolved in a suitable medium and each individual molecule has a size in the colloidal range. Thus, a colloidal particle is a single macromolecule, rather than an aggregate of many small molecules. For example, a solution of a protein in water is a macromolecular colloid because individual protein molecules have colloidal dimensions. Starch and cellulose are other common macromolecular substances.

Step 3: (iii) Coagulation Coagulation is the process in which colloidal particles aggregate and separate out as a precipitate. For a charged lyophobic sol, adding a suitable electrolyte can neutralise the particle charge, reduce repulsion and allow the particles to come together. For example, adding sodium chloride solution to a negatively charged arsenic sulphide sol causes coagulation: the Na^+ ions neutralise the negative charge on the As_2S_3 particles, which aggregate and precipitate.

Step 4: Conclusion Lyophilic sol: strong affinity for the medium, as in starch in water. Macromolecular colloid: individual large molecules of colloidal size, as in proteins in water. Coagulation: aggregation and precipitation of colloidal particles, as when $NaCl$ is added to an As_2S_3 sol.

Quick Tip to Solve: Pair each term with its defining feature and one example: affinity, molecular size, or aggregation.

5(a). Illustrate the following reactions giving suitable example in each case:

(i) Gabriel phthalimide synthesis.

(ii) Carbylamine reaction.

(iii) Hoffmann bromamide degradation reaction. [3 marks]

Solution:

Concept:

- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylation of potassium phthalimide followed by hydrolysis of the substituted imide.
- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide on heating. Secondary and tertiary amines do not give this test.
- Hoffmann bromamide degradation converts a primary amide into a primary amine with one carbon atom fewer using bromine and aqueous alkali.

Step 1: (i) Gabriel phthalimide synthesis Phthalimide is treated with alcoholic KOH to form potassium phthalimide. This salt reacts with an alkyl halide to give an N-alkylphthalimide, which on hydrolysis releases a primary amine. Using bromoethane gives ethylamine. In the following equations, $C_6H_4(CO)_2NH$ denotes cyclic phthalimide:

$$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O,$$
$$C_6H_4(CO)_2NK + C_2H_5Br \longrightarrow C_6H_4(CO)_2NC_2H_5 + KBr,$$
$$C_6H_4(CO)_2NC_2H_5 + 2H_2O \xrightarrow{\text{hydrolysis}} C_6H_4(COOH)_2 + C_2H_5NH_2.$$

The products in the last line are phthalic acid and ethylamine.

Step 2: (ii) Carbylamine reaction A primary aliphatic or aromatic amine, when heated with chloroform and alcoholic potassium hydroxide, forms an isocyanide (carbylamine) having an offensive smell. For example, aniline gives phenyl isocyanide:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\Delta]{\text{alcoholic}} C_6H_5NC + 3KCl + 3H_2O.$$

The product contains the isocyanide linkage $-N \equiv C$, with the phenyl group bonded to nitrogen.

Step 3: (iii) Hoffmann bromamide degradation A primary amide is heated with bromine and aqueous sodium hydroxide to yield a primary amine with one carbon atom fewer than the amide. For example, ethanamide gives methanamine:

$$CH_3CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is removed from the organic product and appears in carbonate.

Step 4: Conclusion Suitable examples are Gabriel synthesis of ethylamine from phthalimide and bromoethane, carbylamine formation of phenyl isocyanide from aniline, and Hoffmann degradation of ethanamide to methanamine.

Quick Tip to Solve: Remember the distinguishing products: Gabriel gives a primary amine, carbylamine an isocyanide, and Hoffmann an amine with one fewer carbon atom.

OR

5(b). Write the structures of A, B and C in the following reactions:

(i) $CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[0\,^\circ C]{HNO_2} C$

(ii) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow[\textbf{(b)}\ H_2O]{\textbf{(a)}\ LiAlH_4} B \xrightarrow{C_6H_5SO_2Cl} C$ [3 marks]

Solution:

Concept:

- Cyanide ion in KCN substitutes halide through its carbon atom, forming an alkyl cyanide and adding one carbon to the chain.
- $LiAlH_4$ reduces nitriles and amides to primary amines: $R{-}CN \longrightarrow R{-}CH_2NH_2$ and $R{-}CONH_2 \longrightarrow R{-}CH_2NH_2$, where R is an alkyl group.
- An aliphatic primary amine reacts with nitrous acid to form an alcohol with evolution of nitrogen; a primary amine reacts with benzenesulphonyl chloride to form an N-substituted benzenesulphonamide.

Step 1: Follow the cyanide sequence in (i) Chloroethane undergoes nucleophilic substitution with KCN. The cyanide carbon joins the ethyl group, giving propanenitrile:

$$CH_3CH_2Cl + KCN \longrightarrow CH_3CH_2CN + KCl.$$

Thus A is $CH_3CH_2{-}C{\equiv}N$. Reduction of its nitrile group by $LiAlH_4$ gives B, propan-1-amine, $CH_3CH_2CH_2NH_2$. There is no loss of carbon during reduction. On treatment with HNO_2 at $0\,^\circ C$, this primary aliphatic amine forms propan-1-ol:

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

Hence C has the structure $CH_3CH_2CH_2OH$.

Step 2: Follow the amide sequence in (ii) Ethanoic acid first forms ammonium ethanoate with ammonia. Heating the salt eliminates water and gives A, ethanamide:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4, \qquad CH_3COONH_4 \xrightarrow{\Delta} CH_3CONH_2 + H_2O.$$

Reduction with $LiAlH_4$, followed by water, converts the carbonyl group into a methylene group while retaining the two-carbon skeleton. B is ethanamine, $CH_3CH_2NH_2$. It then undergoes the Hinsberg reaction with benzenesulphonyl chloride to form C:

$$CH_3CH_2NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHCH_2CH_3 + HCl.$$

The product is N-ethylbenzenesulphonamide; its nitrogen is bonded to the ethyl group, the sulphonyl group and one hydrogen.

Step 3: Conclusion (i) A = CH_3CH_2CN, B = $CH_3CH_2CH_2NH_2$, C = $CH_3CH_2CH_2OH$.
(ii) A = CH_3CONH_2, B = $CH_3CH_2NH_2$, C = $C_6H_5{-}S(=O)_2{-}NH{-}CH_2CH_3$.

Quick Tip to Solve: Count the carbons first: KCN adds one carbon, whereas reduction of an amide retains its carbon count. Then identify the final reagent as nitrous acid or the Hinsberg reagent.

6. An organic compound 'X' with the molecular formula $C_5H_{10}O$ forms 2,4-DNP derivative, does not reduce Tollens' reagent but gives positive iodoform test on heating with I_2 in the presence of NaOH. Compound 'X' gives ethanoic acid and propanoic acid on vigorous oxidation. Write the

(i) Structure of the compound 'X'.

(ii) Structure of the product obtained when compound 'X' reacts with 2,4-DNP reagent.

(iii) Structures of the products obtained when compound 'X' is heated with I_2 in the presence of NaOH. [3 marks]

Solution:

Concept:

- Formation of a 2,4-dinitrophenylhydrazone establishes a carbonyl group. An ordinary ketone does not reduce Tollens' reagent, whereas an aldehyde does.
- A methyl ketone, CH_3-CO-R, gives a positive iodoform test. Cleavage with alkaline iodine produces CHI_3 and the carboxylate $RCOO^-$, where R is the group on the other side of the carbonyl.

Step 1: Identify the structure of X The negative Tollens' test identifies the carbonyl compound as a ketone. Its positive iodoform test requires CH_3-CO-R. The formula $C_5H_{10}O$ leaves a three-carbon alkyl group. The straight-chain structure is

$$CH_3-C(=O)-CH_2-CH_2-CH_3.$$

Vigorous oxidation gives the stated ethanoic acid and propanoic acid. This acid pair selects pentan-2-one over the branched methyl ketone.

Step 2: Write the 2,4-DNP derivative Condensation with $H_2N-NH-C_6H_3(NO_2)_2$ replaces $C=O$ by $C=N-NH-C_6H_3(NO_2)_2$, eliminating water. Both alkyl groups stay attached to the imine carbon:

$$CH_3-C(=N-NH-C_6H_3(NO_2)_2)-CH_2-CH_2-CH_3.$$

The nitro groups occupy ring positions 2 and 4 relative to $-NH-$. This is pentan-2-one 2,4-dinitrophenylhydrazone.

Step 3: Write the alkaline iodine products The carbonyl-adjacent methyl gives CHI_3; the other four carbons form sodium butanoate. The balanced equation is

$$CH_3COCH_2CH_2CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + CH_3CH_2CH_2COONa + 3\,NaI + 3\,H_2O.$$

The structures are $H-C(I)_3$ and $CH_3CH_2CH_2-C(=O)O^-\,Na^+$. Alkaline conditions give the carboxylate salt; acidification is needed for free butanoic acid.

Step 4: Conclusion (i) X is pentan-2-one, $CH_3COCH_2CH_2CH_3$.

(ii) Its 2,4-DNP derivative is $CH_3C(=NNHC_6H_3(NO_2)_2)CH_2CH_2CH_3$, with nitro groups at ring positions 2 and 4.

(iii) The organic products are iodoform, CHI_3, and sodium butanoate, $CH_3CH_2CH_2COONa$.

Quick Tip to Solve: For a methyl ketone's iodoform products, detach the carbonyl-adjacent methyl as CHI3 and convert the remaining carbonyl fragment into the sodium carboxylate; check that all five carbons are accounted for.

7(a). (i) On the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$.
(ii) Using valence bond theory, predict the hybridization and magnetic character of $[Ni(CN)_4]^{2-}$. (Atomic number of Ni = 28)
(iii) Write the formula of the following complex using IUPAC norms: Dichloridobis(ethane-1,2-diamine)cobalt(III)

[3 marks]

Solution:

Concept:

- In an octahedral crystal field, the five d orbitals split into the lower-energy t_{2g} set and the higher-energy e_g set. Δ_o is the splitting energy and P is the electron-pairing energy.
- A strong-field ligand such as CN^- causes pairing in a d^8 nickel(II) ion, permitting dsp^2 hybridization. Magnetic character is decided by the number of unpaired electrons.
- In a complex formula, ligand charges and the metal oxidation state determine the charge outside the coordination brackets; ethane-1,2-diamine, abbreviated en, is neutral and bidentate.

Step 1: (i) Distribute the four d electrons Since $\Delta_o < P$, promotion of an electron to an e_g orbital costs less energy than pairing it in a t_{2g} orbital. The first three electrons occupy the three t_{2g} orbitals singly according to Hund's rule; the fourth occupies an e_g orbital. Thus the high-spin octahedral configuration is $t_{2g}^3 e_g^1$, with four unpaired electrons.

Step 2: (ii) Apply valence bond theory to the nickel complex Let the oxidation state of Ni be x. In $[Ni(CN)_4]^{2-}$, $x + 4(-1) = -2$, so $x = +2$. Neutral Ni has configuration $[Ar]3d^8 4s^2$; removal of the two 4s electrons gives Ni^{2+} : $[Ar]3d^8$. The strong-field cyanide ligands pair the eight 3d electrons in four 3d orbitals, leaving one 3d orbital vacant. This vacant orbital mixes with one 4s and two 4p orbitals to form four dsp^2 hybrid orbitals. They accept the four ligand lone pairs in a square-planar arrangement. All electrons are paired, so the complex is diamagnetic.

Step 3: (iii) Construct the coordination formula Dichlorido means two Cl^- ligands, while bis(ethane-1,2-diamine) means two neutral en ligands. The metal is cobalt(III), with charge $+3$. Therefore the complex charge is $+3 - 2 = +1$. Each en ligand binds through two nitrogen donor atoms; together with the two chlorido ligands, this gives six donor atoms around cobalt. The named coordination entity is written $[CoCl_2(en)_2]^+$. No counter-ion is specified in the name.

Step 4: Conclusion (i) $t_{2g}^3 e_g^1$; (ii) dsp^2 hybridization, square-planar and diamagnetic; (iii) $[CoCl_2(en)_2]^+$.

Quick Tip to Solve: Compare splitting with pairing energy first; for the named complex, count ligand charges separately from ligand donor atoms.

OR

7(b). When a co-ordination compound $NiCl_2 \cdot 6H_2O$ is mixed with $AgNO_3$, 2 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex.

(ii) Secondary valency of 'Ni' in the complex.

(iii) IUPAC name of the complex. [3 marks]

Solution:

Concept:

- Chloride ions outside the coordination sphere ionize in solution and react with Ag^+ to give insoluble $AgCl$. Chlorido ligands bound to the metal are not counted as freely ionizable chloride ions in this test.
- In Werner's theory, primary valency corresponds to oxidation state, while secondary valency is the coordination number: the number of donor atoms directly attached to the metal.
- Water is a neutral monodentate ligand named aqua. A positively charged coordination entity retains the metal's ordinary name, followed by its oxidation state in Roman numerals.

Step 1: (i) Locate the chloride ions and write the structural formula Each mole of the compound gives two moles of $AgCl$, so both chloride ions are freely ionizable and must lie outside the coordination sphere. All six water molecules therefore occupy the coordination sphere around nickel. The structural formula is $[Ni(H_2O)_6]Cl_2$, consisting of a $[Ni(H_2O)_6]^{2+}$ ion and two Cl^- counter-ions. Its dissociation and precipitation can be represented as

$$[Ni(H_2O)_6]Cl_2 \longrightarrow [Ni(H_2O)_6]^{2+} + 2Cl^-,$$
$$2Ag^+ + 2Cl^- \longrightarrow 2AgCl\downarrow .$$

Placing a chloride inside the brackets would leave fewer than two freely ionizable chlorides and would contradict the given precipitation result.

Step 2: (ii) Determine the secondary valency Six water molecules are directly coordinated to Ni, and each contributes one oxygen donor atom. Consequently the coordination number, or secondary valency, of nickel is 6. This is distinct from its primary valency 2: the two external chlorides balance a $+2$ complex ion, and neutral water does not alter the oxidation state of nickel.

Step 3: (iii) Name the complex according to IUPAC norms Name the cation first and then the anion. Six aqua ligands give the prefix hexaaqua. Since the complex is cationic, the metal is named nickel, and its oxidation state is indicated as (II). The counter-ion is chloride. Thus the complete name is hexaaquanickel(II) chloride; the nickelate form is reserved for anionic nickel complexes and is inappropriate here.

Step 4: Conclusion (i) $[Ni(H_2O)_6]Cl_2$; (ii) secondary valency $= 6$; (iii) hexaaquanickel(II) chloride.

Quick Tip to Solve: Use the moles of AgCl to count chloride ions outside the brackets, then count water donor atoms inside them for secondary valency.

8(a). Account for the following:

(i) Zr and Hf have almost similar atomic radii.

(ii) Transition metals show variable oxidation states.

(iii) Zinc has lowest enthalpy of atomisation. [3 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series because $4f$ electrons shield the increasing nuclear charge poorly.
- The $(n-1)d$ and ns orbitals of transition metals have comparable energies; electrons from both can participate in bonding.
- Enthalpy of atomisation measures the energy needed to form isolated gaseous atoms from the element. Stronger metallic bonding gives a larger atomisation enthalpy.

Step 1: (i) Relate the radii to lanthanoid contraction Hf follows the lanthanoid series, whereas Zr precedes it. Across the lanthanoids, added electrons enter the $4f$ subshell and shield the nuclear charge inefficiently. The resulting increase in effective nuclear charge contracts the electron cloud. This lanthanoid contraction offsets the normal increase in atomic size expected when moving from Zr to Hf down the group. Consequently, their atomic radii are almost equal.

Step 2: (ii) Explain the availability of different bonding electrons In a transition metal, the energy separation between the outer ns and inner $(n-1)d$ orbitals is small. Different numbers of electrons from these orbitals can therefore be lost or shared in different compounds, producing variable oxidation states. For example, Fe forms Fe^{2+} and Fe^{3+}: after removal of the two $4s$ electrons, an additional $3d$ electron can also be removed.

Step 3: (iii) Connect zinc's configuration with weak metallic bonding Zinc has the electronic configuration $[Ar]\,3d^{10}4s^2$. Its completely filled $3d$ subshell has no unpaired electrons, so the contribution of d electrons to strong metallic bonding is small compared with the other elements of the first d-block series. The metal–metal bonds are consequently relatively weak. Less energy is required to separate the solid into gaseous atoms, accounting for zinc's lowest enthalpy of atomisation in this series.

Step 4: Conclusion The similar radii of Zr and Hf arise from lanthanoid contraction; variable oxidation states arise from the similar energies of ns and $(n-1)d$ electrons; zinc's low atomisation enthalpy arises from its filled $3d^{10}$ subshell and weak metallic bonding.

Quick Tip to Solve: Link each observation to its electronic cause: Zr/Hf to poor $4f$ shielding, oxidation states to nearby s, d energies, and Zn to its filled $3d$ subshell.

OR

8(b). Why transition metals and their compounds act as good catalysts? How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples. [3 marks]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with a lower activation energy and is regenerated during the reaction.
- Transition metals have accessible d orbitals and variable oxidation states, enabling adsorption, intermediate formation and electron transfer.
- Transition-metal oxidation states often differ by one because both ns and $(n-1)d$ electrons can participate; non-transition-metal states commonly differ by two.

Step 1: Explain catalysis by transition metals and their compounds Transition metals can use different oxidation states to accept and donate electrons during a reaction. Their ability to form complexes allows unstable intermediate compounds to form with the reactants. These intermediates then give the products and regenerate the catalyst through a pathway of lower activation energy. Finely divided metals also provide a large surface on which reactants are adsorbed. Adsorption brings reactants together and weakens their bonds, making reaction easier. For example, finely divided Fe catalyses the Haber process, Ni catalyses hydrogenation, and $\mathrm{V_2O_5}$ catalyses oxidation of $\mathrm{SO_2}$ to $\mathrm{SO_3}$ in the Contact process.

Step 2: Compare the pattern of variable oxidation states In transition metals, the ns and $(n-1)d$ orbitals have similar energies, so successive participation of their electrons gives several oxidation states that commonly differ by one. For example, manganese exhibits $+2, +3, +4, +5, +6$ and $+7$, illustrated by $\mathrm{MnCl_2}$, $\mathrm{Mn_2O_3}$, $\mathrm{MnO_2}$, $\mathrm{K_3MnO_4}$, $\mathrm{K_2MnO_4}$ and $\mathrm{KMnO_4}$, respectively.

Non-transition metals commonly exhibit oxidation states differing by two. This is associated with the involvement or non-involvement of the pair of valence ns electrons, particularly through the inert-pair effect in heavier p-block metals. Thus tin shows $+2$ in $\mathrm{SnCl_2}$ and $+4$ in $\mathrm{SnCl_4}$, while lead shows $+2$ in PbO and $+4$ in $\mathrm{PbO_2}$. The comparison describes the usual pattern, rather than requiring every possible oxidation state to follow it.

Step 3: Conclusion Transition metals and their compounds catalyse reactions through adsorption and intermediate formation, assisted by accessible oxidation states. Their oxidation states commonly differ by one, as in manganese, whereas non-transition metals commonly show a difference of two, as in tin and lead.

Quick Tip to Solve: For the comparison, write manganese's consecutive states $+2$ to $+7$, then contrast tin's $+2, +4$; for catalysis, connect variable states with electron transfer and intermediate formation.

9. (a) The standard Gibbs energy $\Delta_r G^\circ$ for the following cell reaction is $-300\,\text{kJ mol}^{-1}$:

$$\text{Zn(s)} + 2\text{Ag}^+\text{(aq)} \longrightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{Ag(s)}$$

Calculate E°_{cell} for the reaction. (Given: $1\,\text{F} = 96500\,\text{mol}^{-1}$)

(b) Calculate Λ°_m for $MgCl_2$ if λ° values for Mg^{2+} ion and Cl^- ion are $106\,\text{S cm}^2\,\text{mol}^{-1}$ and $76.3\,\text{S cm}^2\,\text{mol}^{-1}$ respectively. [3 marks]

Solution:

Concept:

- Standard Gibbs energy and standard cell potential obey $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred per balanced cell reaction and $F = 96500\,\text{C mol}^{-1}$ is the Faraday constant.
- Kohlrausch's law of independent migration of ions gives $\Lambda^\circ_m = \sum_i \nu_i \lambda^\circ_i$, where ν_i is the number of ions of type i furnished by one formula unit and λ°_i is its limiting ionic molar conductivity.

Step 1: (a) Determine the electron transfer and convert the energy The oxidation and reduction half-reactions are

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

Hence two electrons are transferred for the reaction as written, so $n = 2$. Convert the energy into joules to match the coulomb-based Faraday constant:

$$\Delta_r G^\circ = -300 \times 1000 = -300000\,\text{J mol}^{-1}.$$

Step 2: (a) Substitute in the Gibbs energy relation Rearranging $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$ gives

$$E^\circ_{\text{cell}} = -\frac{\Delta_r G^\circ}{nF} = \frac{300000}{2 \times 96500}\,\text{J C}^{-1} = 1.5544\,\text{V}.$$

The potential is positive, consistent with the negative standard Gibbs energy for the spontaneous forward cell reaction under standard conditions.

Step 3: (b) Add the ionic contributions with their stoichiometric coefficients At infinite dilution, each formula unit of $MgCl_2$ supplies one Mg^{2+} ion and two Cl^- ions. Therefore,

$$\begin{aligned}\Lambda^\circ_m(\text{MgCl}_2) &= \lambda^\circ(\text{Mg}^{2+}) + 2\lambda^\circ(\text{Cl}^-)\\ &= 106 + 2(76.3)\\ &= 258.6\,\text{S cm}^2\,\text{mol}^{-1}.\end{aligned}$$

The factor two counts chloride ions; it is not an extra multiplication by the ionic charge.

Step 4: Conclusion (a) $\boxed{E^\circ_{\text{cell}} = 1.55\,\text{V}}$. (b) $\boxed{\Lambda^\circ_m(\text{MgCl}_2) = 258.6\,\text{S cm}^2\,\text{mol}^{-1}}$.

Quick Tip to Solve: Count electrons from the balanced half-reactions before using Gibbs energy, and count the two chloride ions before adding limiting ionic conductivities.

10. Following ions of 3d transition series are given:

Ti^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}

(Atomic number: Ti = 22, Fe = 26, Cu = 29, Zn = 30)

Identify the ion, which is

(i) a strong reducing agent in aqueous solution.

(ii) more stable than its +1 oxidation state.

(iii) colourless in aqueous solution.

Give a suitable reason in each. [3 marks]

Solution:

Concept:

- Electrons are removed from the $4s$ subshell before the $3d$ subshell when forming first-row transition-metal cations. The configurations here are Ti^{2+} : $[Ar]3d^2$, Fe^{2+} : $[Ar]3d^6$, Cu^{2+} : $[Ar]3d^9$, and Zn^{2+} : $[Ar]3d^{10}$.
- A reducing agent donates electrons and is itself oxidised. Stability in aqueous solution depends on the overall energy balance, including hydration; it cannot be judged from the isolated ion's electron configuration alone.
- In ordinary aqueous transition-metal ions, visible absorption commonly arises from transitions between split d orbitals. A completely filled d^{10} subshell cannot undergo such d-d transitions.

Step 1: (i) Identify the strong reducing agent Ti^{2+} is the strong reducing agent. It readily donates one electron and is oxidised to the more stable Ti^{3+} ion in aqueous solution:

$$Ti^{2+}(aq) \longrightarrow Ti^{3+}(aq) + e^-.$$

Its configuration changes from $3d^2$ to $3d^1$. The favourable oxidation of titanium(II) explains its reducing action; a reducing agent must lose, rather than gain, electrons.

Step 2: (ii) Compare copper's aqueous oxidation states Cu^{2+} is more stable than Cu^+ in aqueous solution. Although Cu^+ has the filled $3d^{10}$ configuration, the much more negative hydration enthalpy of Cu^{2+} compensates for the energy required to remove the second electron. The aqueous $+2$ state is consequently stabilised. Aqueous Cu^+ undergoes disproportionation:

$$2Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s).$$

This reaction demonstrates why a filled subshell alone does not make copper(I) the more stable aqueous state.

Step 3: (iii) Identify the colourless ion Zn^{2+} is colourless in aqueous solution. Zinc has configuration $[Ar]3d^{10}4s^2$; removal of its two $4s$ electrons leaves $[Ar]3d^{10}$. All five d orbitals are fully occupied, so there is no available d-d transition to absorb visible light. In contrast, the other listed ions have partially filled d subshells and their ordinary aqueous ions are coloured.

Step 4: Conclusion (i) $\boxed{Ti^{2+}}$: readily oxidised to Ti^{3+}. (ii) $\boxed{Cu^{2+}}$: greater hydration stabilisation than Cu^+. (iii) $\boxed{Zn^{2+}}$: filled $3d^{10}$ subshell prevents d-d transitions.

Quick Tip to Solve: Remove 4s electrons first; use titanium(II)'s ready oxidation, copper(II)'s hydration stabilisation, and zinc(II)'s filled d subshell for the three parts.

11. A first order reaction is 50% complete in 40 minutes. Calculate the time required for the completion of 90% of reaction.

[Given: log 2 = 0.3010, log 10 = 1] [3 marks]

Solution:

Concept:

- For a first-order reaction, the integrated rate law is $k = \dfrac{2.303}{t} \log \dfrac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations, t is elapsed time, and k is the rate constant.
- Percentage completion refers to the amount consumed. Thus, 50% completion leaves 50% of the initial reactant, while 90% completion leaves 10%. The concentration ratio can therefore be obtained directly from percentages.

Step 1: Determine the rate constant from 50% completion Take the initial amount as 100 units. At 50% completion, 50 units remain after $40\,\text{min}$. Substitute the ratio $100/50 = 2$ in the integrated rate law:

$$k = \frac{2.303}{40} \log 2 = \frac{2.303 \times 0.3010}{40} = 0.0173301\,\text{min}^{-1}.$$

The given time is also the half-life, since exactly half of the reactant has been consumed. The rate constant is fixed for the same reaction under the same conditions.

Step 2: Apply the rate law at 90% completion At 90% completion, only $100 - 90 = 10$ units remain, so the required concentration ratio is $100/10 = 10$. Therefore,

$$t_{90} = \frac{2.303}{k} \log 10.$$

Eliminating k using the first observation avoids unnecessary rounding:

$$t_{90} = 40 \frac{\log 10}{\log 2} = 40 \frac{1}{0.3010} = 132.89\,\text{min}.$$

This is the total elapsed time from the start of the reaction, as requested, rather than the additional time after the first 40 minutes. It is about 3.32 half-lives, consistent with leaving one-tenth of the initial amount.

Step 3: Conclusion The time required for 90% completion is $\boxed{132.9\,\text{min}}$, approximately $133\,\text{min}$.

Quick Tip to Solve: For first-order percentage problems, use the percentage remaining in the denominator: $t_{90}/t_{50} = \log(100/10)/\log(100/50)$.

Section C (5 marks)

12(a). Read the passage given below and answer the questions that follow :

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules due to higher electro-negativity of oxygen relative to carbon in the carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes. Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group but carboxylic acid does not undergo nucleophilic addition reaction. The α-hydrogens of aldehydes and ketones are acidic. Therefore aldehydes and ketones having at least one α-hydrogen undergo Aldol condensation. Aldehydes are easily oxidised by mild oxidising agents such as Tollens' reagent and Fehling's reagent. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and by hydrolysis of nitriles. Aromatic carboxylic acids are prepared by side-chain oxidation of alkyl benzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction:

CH_3COCH_3, CH_3CHO, HCHO, $C_6H_5COCH_3$ [1 mark]

Solution:

Concept:

- Nucleophilic addition is favoured by a more electrophilic carbonyl carbon and less steric hindrance around it.
- Alkyl groups donate electron density by the inductive effect. Conjugation with a phenyl ring also reduces the electrophilic character of the carbonyl carbon.

Step 1: Compare the aldehydes Formaldehyde, $HCHO$, has no alkyl group and the least steric hindrance. Ethanal, CH_3CHO, has one electron-donating methyl group, so its carbonyl carbon is less electrophilic than that of formaldehyde.

Step 2: Compare the ketones Propanone, CH_3COCH_3, has two methyl groups and is less reactive than ethanal. In acetophenone, $C_6H_5COCH_3$, conjugation of the carbonyl group with the phenyl ring lowers its reactivity further; the bulky phenyl group also hinders nucleophilic approach.

Step 3: Conclusion The increasing order is

$$\boxed{C_6H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO}.$$

Quick Tip to Solve: Put formaldehyde last in increasing reactivity, then compare alkyl donation and phenyl conjugation to order the remaining carbonyl compounds.

12(b). Give a simple chemical test to distinguish between Ethanal and Propanone. [1 mark]

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing $[Ag(NH_3)_2]^+$. Aldehydes reduce it to metallic silver while being oxidised to carboxylate ions.
- Ordinary ketones such as propanone do not reduce Tollens' reagent under these conditions.

Step 1: Perform Tollens' test Add freshly prepared Tollens' reagent to separate samples of ethanal and propanone and warm gently in a water bath. Use clean test tubes so that deposited silver forms a visible mirror.

Step 2: Compare the observations Ethanal, CH_3CHO, gives a silver mirror on the inner wall of the test tube because it is oxidised while silver(I) is reduced. Propanone, CH_3COCH_3, gives no silver mirror because it is a ketone and resists oxidation by this mild reagent.

Step 3: Conclusion Tollens' test distinguishes them: ethanal gives a silver mirror; propanone does not.

Quick Tip to Solve: Choose Tollens' test here; the iodoform test cannot distinguish these two compounds because both ethanal and propanone give a positive result.

12(c). Why carboxylic acid does not give nucleophilic addition reactions like aldehydes and ketones? [1 mark]

Solution:

Concept:

- Nucleophilic addition to a carbonyl group requires an electrophilic carbonyl carbon.
- In a carboxylic acid, the lone pair on the hydroxyl oxygen participates in resonance with the carbonyl group, reducing the positive character of the carbonyl carbon.

Step 1: Identify the effect of the hydroxyl group In RCOOH, electron donation from the hydroxyl oxygen is delocalised over the carboxyl group. This resonance stabilises the group and makes its carbonyl carbon less electrophilic than that of an aldehyde or ketone.

Step 2: Relate resonance to the reaction type A nucleophile therefore cannot attack this carbon as readily as it attacks an aldehyde or ketone. Carboxylic acids do not give the characteristic simple nucleophilic addition reactions of those carbonyl compounds; when suitable acyl reactions occur, they involve substitution rather than a stable simple addition product.

Step 3: Conclusion Resonance donation by the $-OH$ oxygen lowers the electrophilicity of the carboxyl carbon, so carboxylic acids do not undergo nucleophilic addition like aldehydes and ketones.

Quick Tip to Solve: In explaining this difference, point to resonance donation from the hydroxyl oxygen and its reduction of the carbonyl carbon's positive character.

12(d). (i) Why α-hydrogen of aldehydes and ketones are acidic in nature?
(ii) Write the products in the following: [2 marks]



Solution:

Concept:

- An α-hydrogen is attached to the carbon adjacent to the carbonyl group. Loss of this hydrogen as a proton produces a resonance-stabilised enolate ion.
- An aldehyde without an α-hydrogen undergoes the Cannizzaro reaction with concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Explain the acidity of the alpha-hydrogen (i) The electron-withdrawing carbonyl group facilitates removal of an α-hydrogen as H^+. The resulting conjugate base is an enolate ion, whose negative charge is delocalised between the α-carbon and oxygen. For ethanal, its resonance forms may be represented as

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

This resonance stabilisation favours proton loss and makes the α-hydrogens acidic relative to hydrogens of ordinary alkanes.

Step 2: Apply the Cannizzaro reaction to benzaldehyde (ii) In benzaldehyde, C_6H_5CHO, the carbon adjacent to the aldehyde group is a carbon of the benzene ring and bears no hydrogen. Thus benzaldehyde has no α-hydrogen and undergoes disproportionation in concentrated $NaOH$. One aldehyde molecule gives the carboxylate salt while the other gives the alcohol:

$$2\,C_6H_5CHO + NaOH \longrightarrow C_6H_5COONa + C_6H_5CH_2OH.$$

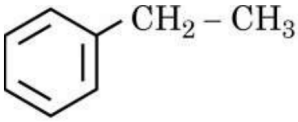
The carboxylic product remains as its sodium salt in this alkaline reaction mixture; no acidification is specified.

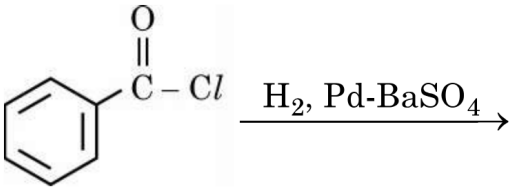
Step 3: Conclusion (i) The α-hydrogens are acidic because their removal forms a resonance-stabilised enolate ion. (ii) The products are sodium benzoate, C_6H_5COONa, and benzyl alcohol, $C_6H_5CH_2OH$.

Quick Tip to Solve: Check for an alpha-hydrogen before choosing aldol or Cannizzaro: benzaldehyde has none, so concentrated alkali yields an alcohol and a carboxylate salt.

OR

12(d). Write the major products of the following reactions: [2 marks]

(i) 

(ii) 

Solution:

Concept:

- Alkaline $KMnO_4$ oxidises an alkylbenzene with a benzylic hydrogen to a benzoate salt. Acidification then gives benzoic acid.
- Rosenmund reduction converts an acyl chloride into an aldehyde using H_2 over palladium supported on $BaSO_4$.

Step 1: Oxidise the ethyl side chain (i) The starting compound is ethylbenzene, $C_6H_5CH_2CH_3$. Its carbon directly attached to the benzene ring carries hydrogens, so the side chain undergoes oxidation by alkaline $KMnO_4$. The carbon bonded to the ring becomes the carboxyl carbon; the benzene ring is retained. The organic product in the alkaline medium is potassium benzoate, C_6H_5COOK. The subsequent H^+ treatment protonates the carboxylate:

$$C_6H_5COO^- + H^+ \longrightarrow C_6H_5COOH.$$

Therefore the isolated major organic product is benzoic acid, rather than an alcohol or an aldehyde.

Step 2: Reduce the benzoyl chloride selectively (ii) The second reactant is benzoyl chloride, C_6H_5COCl. The combination H_2, $Pd{-}BaSO_4$ identifies Rosenmund reduction. The moderated catalyst allows reduction of the acyl chloride to the aldehyde without continuing to the primary alcohol:

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

The major organic product is consequently benzaldehyde, with the benzene ring and the carbonyl carbon retained.

Step 3: Conclusion The major products are (i) benzoic acid, C_6H_5COOH, and (ii) benzaldehyde, C_6H_5CHO.

Quick Tip to Solve: Include the acid work-up when naming the permanganate product; recognise hydrogen with palladium on barium sulphate as selective acyl-chloride-to-aldehyde reduction.