CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-5-3

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 comprises of **three** sections– **Section A, B** and **C**.

(iii) **Section A** – Q. No. 1 to 3 are very short-answer type questions carrying 2 marks each.

(iv) **Section B** – Q. No. 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. Explain the following reactions:

(a) Wolff Kishner reduction

(b) Cannizzaro reaction [2 marks]

Solution:

Concept:

- Wolff–Kishner reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using hydrazine and a strong base on heating.
- Cannizzaro reaction is the disproportionation of an aldehyde having no alpha-hydrogen in concentrated alkali: one molecule is reduced and another is oxidised.

Step 1: (a) Wolff–Kishner reduction An aldehyde or ketone reacts with hydrazine, NH_2NH_2, to form a hydrazone. Heating this hydrazone with KOH in a high-boiling solvent such as ethylene glycol replaces the carbonyl oxygen by two hydrogen atoms, with liberation of nitrogen:

$$R_2C{=}O \xrightarrow{NH_2NH_2} R_2C{=}NNH_2 \xrightarrow[\text{ethylene glycol, heat}]{KOH} R_2CH_2 + N_2.$$

Water is also formed in the hydrazone-formation step. For example, acetone gives propane; the carbon skeleton remains unchanged.

Step 2: (b) Cannizzaro reaction Aldehydes lacking an alpha-hydrogen, such as benzaldehyde, undergo self-oxidation and reduction in concentrated aqueous NaOH or KOH. Two aldehyde molecules produce one alcohol molecule and one carboxylate ion:

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

Thus benzaldehyde gives benzyl alcohol and sodium benzoate. The acid is obtained only after acidification of the salt; the direct product in alkali is the carboxylate.

Step 3: Conclusion Wolff–Kishner reduction removes the carbonyl oxygen to give an alkane. Cannizzaro reaction converts a non-enolisable aldehyde into an alcohol and a carboxylate salt by disproportionation.

Quick Tip to Solve: Recall hydrazine plus hot alkali for Wolff–Kishner; first check absence of alpha-hydrogen before applying Cannizzaro.

2. Arrange the following in the increasing order of the property mentioned:

(a) CH_3COOH, $ClCH_2COOH$, FCH_2COOH (Acid strength)

(b) CH_3CHO, CH_3CH_2OH, $CH_3CH_2CH_3$ (Boiling Points) [2 marks]

Solution:

Concept:

- Electron-withdrawing substituents increase carboxylic acid strength by stabilising the conjugate carboxylate ion through the negative inductive effect.
- Boiling requires separation of molecules. For these small molecules, hydrogen bonding is stronger than ordinary dipole–dipole attraction, which is stronger than London dispersion forces alone.

Step 1: (a) Compare acid strengths Acid strength depends on how readily $RCOOH$ releases H^+ and how stable the resulting $RCOO^-$ is. The methyl group in acetic acid has a positive inductive effect and does not stabilise the carboxylate charge as a halogen substituent does. Both chlorine and fluorine withdraw electron density through sigma bonds and stabilise the conjugate base. Fluorine is more electronegative than chlorine, so its negative inductive effect is stronger at the same position. Therefore the increasing order is

$$CH_3COOH < ClCH_2COOH < FCH_2COOH.$$

Step 2: (b) Compare boiling points Propane, $CH_3CH_2CH_3$, is non-polar and its molecules attract one another primarily through weak dispersion forces. Ethanal, CH_3CHO, has a polar carbonyl group, giving additional dipole–dipole attraction. Ethanol, CH_3CH_2OH, has an $O-H$ bond and forms intermolecular hydrogen bonds, so more energy is required to separate its molecules. Their molecular masses are similar, making these differences in attraction decisive. Hence

$$CH_3CH_2CH_3 < CH_3CHO < CH_3CH_2OH.$$

Ethanal can accept hydrogen bonds from water, but it cannot form the ethanol-type hydrogen-bonded network in the pure liquid because it has no hydrogen attached to oxygen.

Step 3: Conclusion (a) Acid strength: $CH_3COOH < ClCH_2COOH < FCH_2COOH$.

(b) Boiling point: $CH_3CH_2CH_3 < CH_3CHO < CH_3CH_2OH$.

Quick Tip to Solve: For acid strength rank the halogen's inductive withdrawal; for boiling point check the strongest intermolecular attraction first.

3. Answer the following questions (Do any two):

(a) Identify the order of reaction from the following unit for its rate constant: L mol^{-1} s^{-1}

(b) The conversion of molecules A to B follow second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

(c) Write the expression of integrated rate equation for zero order reaction. [2 marks]

Solution:

Concept:

- For a rate law $r = k[A]^n$, the reaction order is n. Since rate has units $\mathrm{mol\,L^{-1}\,s^{-1}}$, the units of k are $(\mathrm{mol\,L^{-1}})^{1-n}\mathrm{s^{-1}}$.
- A second-order reaction in A has $r = k[A]^2$. A zero-order reaction has a constant rate $r = k$, independent of concentration while that rate law applies.

Step 1: (a) Identify the order from the units For $r = k[A]^n$, dividing rate by concentration raised to n gives

$$[k] = \mathrm{L^{n-1}\,mol^{1-n}\,s^{-1}}.$$

Comparing with the given $\mathrm{L\,mol^{-1}\,s^{-1}}$, we have $n - 1 = 1$, so $n = 2$. The rate constant therefore belongs to a second-order reaction.

Step 2: (b) Find the effect of tripling concentration The rate of formation of B follows the second-order law $r = k[A]^2$. At the same temperature, k remains unchanged. When the concentration changes from $[A]$ to $3[A]$,

$$\frac{r'}{r} = \frac{k(3[A])^2}{k[A]^2} = 3^2 = 9.$$

Thus the rate of formation becomes nine times its original value, rather than three times.

Step 3: (c) Write the integrated zero-order equation The differential law for disappearance of A is $-d[A]/dt = k$. Integrating from concentration $[A]_0$ at $t = 0$ to $[A]_t$ at time t yields

$$[A]_t = [A]_0 - kt, \qquad k = \frac{[A]_0 - [A]_t}{t}.$$

Here $[A]_0$ is the initial concentration and $[A]_t$ is the concentration remaining after time t. The concentration falls linearly while zero-order kinetics applies.

Step 4: Conclusion (a) Second order. (b) The rate becomes nine times the initial rate. (c) $[A]_t = [A]_0 - kt$. Any two of these parts may be attempted as instructed.

Quick Tip to Solve: Match the concentration exponent in the units of k, then use the same exponent on any concentration multiplier.

Section B (24 marks)

4(a). Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Aniline does not undergo Friedel-Crafts reaction.

(iii) Primary amines have higher boiling points than tertiary amines. [3 marks]

Solution:

Concept:

- Amines act as bases by donating the nitrogen lone pair to a proton. For the base-dissociation constant K_b, $pK_b = -\log K_b$; a weaker base therefore has a higher pK_b.
- Resonance can reduce the availability of a lone pair, while the electron-releasing inductive effect of an alkyl group increases electron density on nitrogen.
- Intermolecular hydrogen bonding requires a hydrogen attached to an electronegative atom such as nitrogen; stronger intermolecular attraction increases the boiling point.

Step 1: (i) Compare lone-pair availability In aniline, $C_6H_5NH_2$, the nitrogen lone pair is delocalised into the benzene ring through resonance. It is therefore less readily available to accept H^+. In methylamine, CH_3NH_2, the lone pair is localised on nitrogen and the methyl group's $+I$ effect further increases its availability. Thus aniline is the weaker base: its K_b is smaller, so its pK_b is larger than that of methylamine.

Step 2: (ii) Examine the catalyst interaction Friedel-Crafts alkylation or acylation uses a Lewis-acid catalyst such as anhydrous $AlCl_3$. The lone pair of aniline's amino group strongly coordinates to the catalyst, producing a Lewis acid-base complex. This ties up the catalyst and makes the nitrogen substituent electron withdrawing, strongly deactivating the aromatic ring towards the required electrophilic substitution. Consequently aniline does not undergo the usual Friedel-Crafts reaction.

Step 3: (iii) Compare intermolecular attractions A primary amine, RNH_2, has two $N-H$ bonds and can form intermolecular hydrogen bonds with the lone pairs of neighbouring amine molecules. A tertiary amine, R_3N, has no $N-H$ bond, so its pure liquid cannot form these hydrogen bonds between its own molecules. For amines of comparable molecular mass, primary amines therefore have stronger intermolecular attraction and require more energy to vaporise, giving higher boiling points than tertiary amines.

Step 4: Conclusion Aniline has a higher pK_b because resonance reduces its basicity; it fails to undergo Friedel-Crafts reaction because it complexes with and is deactivated by the Lewis-acid catalyst. Primary amines have higher boiling points because they form intermolecular hydrogen bonds.

Quick Tip to Solve: For these comparisons, first locate the nitrogen lone pair, then check whether nitrogen carries an N-H bond: the former controls basicity and catalyst binding, the latter controls self hydrogen bonding.

OR

4(b). (i) Arrange the following compounds in the increasing order of their basic strength in aqueous solution: CH_3NH_2, $(CH_3)_3N$, $(CH_3)_2NH$

(ii) What is Hinsberg's reagent?

(iii) What is the role of pyridine in the acylation reaction of amines? [3 marks]

Solution:

Concept:

- Basicity in aqueous solution depends on both the availability of the nitrogen lone pair and the stability of the protonated amine through hydration. Alkyl groups supply electron density by their $+I$ effect.
- Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$, used to distinguish primary, secondary and tertiary amines through their reactions and the solubility of the products in alkali.
- Acylation of an amine with an acid chloride forms an amide and liberates HCl. A base removes this acid and keeps the reacting amine available as a nucleophile.

Step 1: (i) Balance electron donation and hydration Methyl groups increase electron density on nitrogen, favouring proton acceptance. However, the conjugate acid of trimethylamine is bulky and is hydrated less effectively than those of methylamine and dimethylamine. In water, this reduced hydration outweighs the extra electron donation of the third methyl group. Dimethylamine has a favourable combination of two electron-releasing groups and adequate hydration of its conjugate acid. The increasing order of basic strength is therefore

$$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH.$$

This order is specifically for aqueous solution; using the inductive effect alone would give an incorrect order here.

Step 2: (ii) Identify Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. Its sulphonyl chloride group reacts with primary and secondary amines to form sulphonamides. The primary-amine product retains an acidic nitrogen-bound hydrogen and dissolves in alkali, whereas the secondary-amine product lacks that hydrogen and does not dissolve. Tertiary amines do not form a sulphonamide under this test.

Step 3: (iii) Explain pyridine's role During acylation with an acid chloride, an amine attacks the acyl carbon and forms an amide, releasing hydrogen chloride. Pyridine acts as a base and absorbs the released acid as pyridinium chloride:

$$C_5H_5N + HCl \longrightarrow C_5H_5NH^+\,Cl^-.$$

Removal of HCl prevents the reacting amine from being converted into its less reactive ammonium salt and favours continuation of the acylation reaction.

Step 4: Conclusion The increasing aqueous basicity order is $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$. Hinsberg's reagent is $C_6H_5SO_2Cl$. Pyridine removes the HCl produced during acylation by forming pyridinium chloride.

Quick Tip to Solve: For methylamines in water, remember secondary > primary > tertiary. In acylation, identify the HCl by-product to explain why a base such as pyridine is added.

5. (a) Write the IUPAC name of the following complex: $K_3[Cr(C_2O_4)_3]$

(b) On the basis of crystal field theory, write the electronic configuration of d^5 ion if $\Delta_o < P$.

(c) What are ambidentate ligands? [3 marks]

Solution:

Concept:

- In naming a coordination salt, name the cation first. An anionic chromium complex uses the metal name chromate, followed by the oxidation state in Roman numerals.
- For an octahedral complex, the three lower-energy t_{2g} orbitals and two higher-energy e_g orbitals fill according to the relative magnitudes of crystal-field splitting Δ_o and pairing energy P.
- An ambidentate ligand has two different possible donor atoms, but coordinates to a particular metal centre through only one of them at a time.

Step 1: (a) Determine the oxidation state and name the salt Each potassium ion is K^+, so the three potassium ions require a complex ion of charge -3. Each oxalato ligand, $C_2O_4{}^{2-}$, has charge -2. If the oxidation state of chromium is x, charge balance gives

$$x + 3(-2) = -3 \quad \Rightarrow \quad x = +3.$$

There are three oxalato ligands. The prefix tris is used with this ligand name, and the anionic metal name is chromate. The full IUPAC name is potassium tris(oxalato)chromate(III).

Step 2: (b) Fill the orbitals for the weak-field case Since $\Delta_o < P$, promoting an electron to an e_g orbital costs less energy than pairing it in a t_{2g} orbital. The five electrons therefore occupy all five d orbitals singly, in accordance with Hund's rule. The electronic configuration is

$$t_{2g}^3 e_g^2.$$

This is the high-spin configuration, with five unpaired electrons. The alternative $t_{2g}^5 e_g^0$ would require a strong field with $\Delta_o > P$, so it does not apply here.

Step 3: (c) Define ambidentate ligands with an example Ambidentate ligands can attach through either of two different donor atoms. For example, the nitrite ion $NO_2{}^-$ can coordinate through nitrogen or through oxygen. Another example is SCN^-, which can coordinate through sulfur or nitrogen. In either case, only one donor atom binds to the same metal centre at a time; this differs from a bidentate ligand that binds through two donor atoms simultaneously.

Step 4: Conclusion (a) Potassium tris(oxalato)chromate(III). (b) The high-spin configuration is $t_{2g}^3 e_g^2$, with five unpaired electrons. (c) Ambidentate ligands coordinate through either of two different donor atoms, one at a time, for example $NO_2{}^-$.

Quick Tip to Solve: Find the complex charge from potassium before calculating chromium's oxidation state; for d^5 with $\Delta_o < P$, place one electron in each d orbital before pairing.

6. (a) Write any two consequences of Lanthanoid Contraction.

(b) Name the element of 3d series which exhibits the largest number of oxidation states. Give reason. [3 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series with increasing atomic number. The added $4f$ electrons shield the increasing nuclear charge poorly.
- Similar ionic radii give lanthanoids similar chemical properties; contraction also affects the sizes of the transition elements that follow the lanthanoids.
- In the $3d$ series, the $3d$ and $4s$ electrons have comparable energies and can participate in bonding, producing variable oxidation states.

Step 1: (a) Explain the difficulty of separating lanthanoids As nuclear charge increases across the lanthanoid series, the added $4f$ electrons provide ineffective shielding. Consequently, the effective nuclear attraction increases and the ionic radii decrease gradually. The successive Ln^{3+} ions therefore have very similar sizes and closely similar chemical properties. One consequence is that individual lanthanoids are difficult to separate from one another by ordinary chemical methods.

Step 2: (a) Compare corresponding second and third transition series elements The contraction intervenes before the $5d$ transition series. It offsets much of the increase in size expected on moving down from a $4d$ element to the corresponding $5d$ element. Thus zirconium and hafnium have almost equal atomic and ionic radii and show very similar chemical properties. This near equality of the sizes of corresponding $4d$ and $5d$ elements is a second consequence of lanthanoid contraction.

Step 3: (b) Identify the element with the widest range of oxidation states Manganese exhibits the largest number of oxidation states in the $3d$ series. Its ground-state electronic configuration is

$$Mn : [Ar]\, 3d^5 4s^2.$$

It has five $3d$ electrons and two $4s$ electrons available for participation in bonding. Because the energies of these subshells are close, different numbers of these seven valence electrons can be involved, giving oxidation states from $+2$ to $+7$. The highest state $+7$, for example in MnO_4^-, involves all seven valence electrons in formal oxidation-state accounting.

Step 4: Conclusion (a) Two consequences are the difficulty of separating lanthanoids and the almost equal sizes and similar properties of corresponding $4d$ and $5d$ elements, such as zirconium and hafnium. (b) Manganese shows the largest number of oxidation states because its $3d^5 4s^2$ configuration allows different numbers of seven valence electrons to participate in bonding.

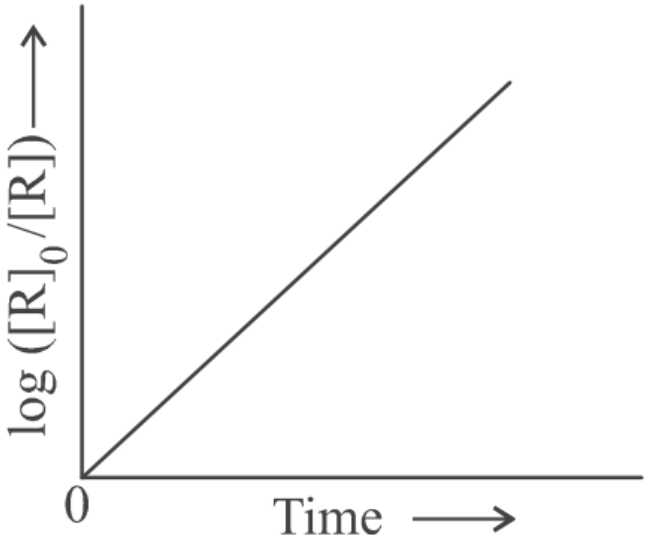
Quick Tip to Solve: Recall one consequence within the lanthanoid series and one after it: difficult separation and the similar sizes of zirconium and hafnium. For manganese, count $5 + 2 = 7$ valence electrons.

7. Observe the graph shown in figure and answer the following questions:

(a) What is the order of the reaction?

(b) What is the slope of the curve?

(c) Write the relationship between k and $t_{1/2}$ (half life period). [3 marks]



Solution:

Concept:

- For a first-order reaction, the rate is proportional to the reactant concentration: $-d[\mathrm{R}]/dt = k[\mathrm{R}]$. Here k is the rate constant and $[\mathrm{R}]$ is the concentration at time t.
- Its integrated rate equation is $\log([\mathrm{R}]_0/[\mathrm{R}]) = kt/2.303$, where $[\mathrm{R}]_0$ is the initial concentration and $\log$ denotes the common logarithm.
- The half-life $t_{1/2}$ is the time required for the reactant concentration to become half its initial value.

Step 1: (a) Identify the reaction order from the axes The ordinate in the printed graph is $\log([\mathrm{R}]_0/[\mathrm{R}])$, and the abscissa is time. The straight line passes through the origin, so this logarithmic concentration ratio is directly proportional to time. Comparing this with the integrated first-order equation,

$$\log \frac{[\mathrm{R}]_0}{[\mathrm{R}]} = \frac{k}{2.303}t,$$

identifies a first-order reaction. A straight line alone does not identify the order: the quantity plotted on the vertical axis is essential.

Step 2: (b) Obtain the slope by comparison with a straight-line equation Write the equation in the form $y = mt + c$, with $y = \log([\mathrm{R}]_0/[\mathrm{R}])$. The intercept is zero and the coefficient of time is $k/2.303$. Thus,

$$m = \frac{\Delta \log([\mathrm{R}]_0/[\mathrm{R}])}{\Delta t} = \frac{k}{2.303}.$$

The slope is positive, consistent with the increasing logarithmic ratio as reactant is consumed. It is not $-k$, which belongs to a plot of $\ln[\mathrm{R}]$ against time.

Quick Tip to Solve: Read whether the axis uses log or ln before finding the slope: common log introduces the factor 2.303.

Step 3: (c) Relate the half-life to the rate constant At $t = t_{1/2}$, substitute $[\mathrm{R}] = [\mathrm{R}]_0/2$ in the integrated equation:

$$\log 2 = \frac{kt_{1/2}}{2.303},$$
$$kt_{1/2} = 2.303 \log 2 = \ln 2 \simeq 0.693.$$

Consequently, the first-order half-life is inversely proportional to k and is independent of the initial concentration. If time is in seconds, k and the graph's slope have units s^{-1}.

Step 4: Conclusion (a) The reaction is first order. (b) The slope is $k/2.303$. (c) $t_{1/2} = 0.693/k$, or equivalently $k = 0.693/t_{1/2}$.

Quick Tip to Solve: Read whether the axis uses log or ln before finding the slope: common log introduces the factor 2.303.

8. Give reasons for the following statements:

(a) Transition elements and their compounds act as good catalysts.

(b) E° (Mn^{2+}/Mn) value is highly negative as compared to other elements.

(c) Cr^{2+} is a strong reducing agent. [3 marks]

Solution:

Concept:

- A catalyst provides an alternative reaction pathway with lower activation energy and is regenerated during the reaction. Transition metals commonly exhibit variable oxidation states.
- Standard electrode potential reflects the overall energetics of forming the aqueous ion from the metal, including atomisation, ionisation and hydration. A particularly stable aqueous ion can make its reduction to the metal less favourable.
- A reducing agent donates electrons and is itself oxidised. Stability gained in the higher oxidation state favours such electron donation.

Step 1: (a) Explain the catalytic activity Transition elements have accessible, variable oxidation states and suitable d orbitals. They can form intermediate compounds with reactants, changing oxidation state during the reaction and returning to the original state at the end. This supplies a pathway of lower activation energy. For example, an ion can first accept an electron from one reactant and subsequently donate it to another, mediating the net redox reaction. In heterogeneous catalysis, transition-metal surfaces also adsorb reactant molecules, bring them together and weaken their bonds, facilitating reaction. These features explain why both transition metals and many of their compounds are effective catalysts.

Step 2: (b) Explain the highly negative manganese electrode potential Manganese has configuration $[\mathrm{Ar}]\,3d^5 4s^2$, while aqueous Mn^{2+} has the particularly stable half-filled $3d^5$ configuration. Formation of this stable ion from manganese is favoured; conversely, the reduction

$$\mathrm{Mn}^{2+}(\mathrm{aq}) + 2e^- \longrightarrow \mathrm{Mn}(\mathrm{s})$$

Quick Tip to Solve: For reducing behaviour, write the oxidation half-equation first and compare the d configurations of the initial and final ions.

is relatively unfavourable. Consequently, $E^\circ(\mathrm{Mn}^{2+}/\mathrm{Mn})$ is highly negative. The special stability of the half-filled ion explains the manganese trend within the series; the electrode potential is an overall energy balance, not a consequence of electron configuration alone.

Step 3: (c) Explain why chromium(II) is strongly reducing Chromium(II) has configuration $[\mathrm{Ar}]\,3d^4$ and readily loses an electron:

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

Chromium(III) has the $3d^3$ configuration. In the octahedral environment of its aqueous complex, the three electrons occupy the lower-energy t_{2g} orbitals, giving the stable t_{2g}^3 arrangement. This favours oxidation of Cr^{2+} to Cr^{3+}. Because chromium(II) supplies an electron to another species while itself being oxidised, it acts as a strong reducing agent.

Step 4: Conclusion (a) Variable oxidation states, intermediate formation and surface adsorption enable catalytic activity. (b) Stable half-filled $3d^5$ manganese(II) makes reduction to Mn unfavourable. (c) Chromium(II) readily oxidises to the stable $3d^3$ chromium(III) ion.

Quick Tip to Solve: For reducing behaviour, write the oxidation half-equation first and compare the d configurations of the initial and final ions.

9(a). (i) Define coagulation.

(ii) State Hardy-Schulze rule.

(iii) What is Electrophoresis? [3 marks]

Solution:

Concept:

- Colloidal particles carry like charges, so electrostatic repulsion helps prevent them from aggregating into larger particles.
- Coagulation occurs when this stabilising charge is neutralised; an electrolyte supplies ions of opposite charge to the colloidal particles.
- An electric field acts on the charge of a colloidal particle and causes its movement towards the oppositely charged electrode.

Step 1: (i) Define coagulation Coagulation is the process of precipitation of colloidal particles by their aggregation into larger particles. When the charge on the particles is neutralised, the repulsion between them decreases, allowing them to come together and separate from the dispersion medium as a precipitate.

Step 2: (ii) State the Hardy-Schulze rule The greater the valency of the ion carrying a charge opposite to that of the colloidal particles, the greater is its coagulating power. Thus, the ion responsible for coagulation is the counter-ion, not the ion with the same sign of charge as the sol. For a negatively charged sol, the coagulating power follows $\mathrm{Al}^{3+} > \mathrm{Ba}^{2+} > \mathrm{Na}^{+}$; for a positively charged sol, anions cause coagulation.

Step 3: (iii) Define electrophoresis Electrophoresis is the movement of colloidal particles towards an oppositely charged electrode under the influence of an applied electric field. Positively charged

Quick Tip to Solve: First identify the sign of the sol: choose the opposite ion for coagulation and the opposite electrode for electrophoresis.

particles move towards the cathode, whereas negatively charged particles move towards the anode. It provides evidence that colloidal particles carry electric charge.

Step 4: Conclusion Coagulation is aggregation and precipitation of colloidal particles; the Hardy-Schulze rule relates coagulating power to the valency of the counter-ion; electrophoresis is the movement of charged colloidal particles in an electric field.

Quick Tip to Solve: First identify the sign of the sol: choose the opposite ion for coagulation and the opposite electrode for electrophoresis.

OR

9(b). Write three differences between Physisorption and Chemisorption. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance, the adsorbate, on the surface of another substance, the adsorbent.
- Physisorption arises from weak van der Waals forces, whereas chemisorption involves the formation of chemical bonds between the adsorbate and the surface.
- The nature and strength of the attractive forces determine the enthalpy of adsorption and whether the process is specific to a particular adsorbate-adsorbent pair.

Step 1: Difference 1: Nature of the attractive forces In physisorption, the adsorbate is held on the surface by weak van der Waals forces. In chemisorption, the adsorbate is held by strong chemical bonds formed with the surface atoms. Thus, no chemical bond formation is required for physisorption, while bond formation is the defining feature of chemisorption.

Step 2: Difference 2: Enthalpy of adsorption Physisorption has a low enthalpy of adsorption, usually with a magnitude of about 20–$40\,\text{kJ}\,\text{mol}^{-1}$. Chemisorption has a much higher enthalpy of adsorption, usually about 80–$240\,\text{kJ}\,\text{mol}^{-1}$ in magnitude, because chemical bonds are stronger than van der Waals interactions. Both processes are generally exothermic, so these ranges describe the magnitude of the heat released.

Step 3: Difference 3: Specificity Physisorption is not highly specific: van der Waals forces can operate between many adsorbates and adsorbents. Chemisorption is highly specific: it occurs only when the adsorbate and the adsorbent can form suitable chemical bonds. Hence, a surface may chemisorb one gas while showing little or no chemisorption of another gas.

Step 4: Conclusion The three differences are: weak van der Waals forces versus chemical bonds, low versus high enthalpy of adsorption, and low specificity versus high specificity for physisorption and chemisorption, respectively.

Quick Tip to Solve: Start with the force holding the adsorbate: weak forces imply low adsorption enthalpy; chemical bonds imply high enthalpy and specificity.

10(a). **An aromatic compound 'A' ($C_7H_6O_2$) on reaction with aqueous ammonia and heating forms compound 'B'. 'B' on heating with Br_2 and alcoholic potash forms a compound 'C' of molecular formula C_6H_7N. Write the reactions involved and identify 'A', 'B', 'C'.** [3 marks]

Solution:

Concept:

- A carboxylic acid reacts with ammonia to form an ammonium carboxylate; heating this salt eliminates water and gives the corresponding primary amide.
- In the Hofmann bromamide reaction, a primary amide $RCONH_2$ reacts with bromine and potassium hydroxide to give RNH_2. The amine has one carbon atom fewer than the amide because the carbonyl carbon is removed.
- Aniline, $C_6H_5NH_2$, has molecular formula C_6H_7N; its phenyl group is retained in this reaction sequence.

Step 1: Use the product to identify the precursor The aromatic amine of formula C_6H_7N is aniline. Working backwards through the Hofmann reaction, its precursor must contain the group C_6H_5CO- attached to NH_2. Thus the required amide is benzamide, $C_6H_5CONH_2$. The acid that forms benzamide with ammonia is benzoic acid, C_6H_5COOH, whose molecular formula is the given $C_7H_6O_2$.

Step 2: Form the amide through the ammonium salt Aqueous ammonia first neutralises benzoic acid to form ammonium benzoate. On heating, the salt loses water to give benzamide:

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4,$$
$$C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

The acid and amide each have seven carbon atoms; amide formation does not shorten the carbon skeleton.

Step 3: Carry out Hofmann bromamide degradation Heating benzamide with the stated bromine and alcoholic potash gives aniline. The balanced overall reaction is

$$C_6H_5CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta} C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

The carbonyl carbon enters potassium carbonate, leaving the six-carbon phenyl group bonded to the amino group. This explains the change from a seven-carbon amide to a six-carbon amine.

Step 4: Conclusion A is benzoic acid, C_6H_5COOH; B is benzamide, $C_6H_5CONH_2$; and C is aniline, $C_6H_5NH_2$. The sequence is acid to ammonium salt to amide, followed by Hofmann bromamide degradation to aniline.

Quick Tip to Solve: Work backwards from aniline: add a carbonyl group before its NH_2 to obtain benzamide, then replace NH_2 by OH to identify benzoic acid.

OR

10(b). A compound 'A' on reduction with iron scrap and hydrochloric acid gives compound 'B' with molecular formula C_6H_7N. Compound 'B' on reaction with $CHCl_3$ and alcoholic KOH produces an obnoxious smell of carbylamine due to the formation of 'C'. Identify 'A', 'B' and 'C' and write the chemical reactions involved. [3 marks]

Solution:

Concept:

- Iron and hydrochloric acid reduce the nitro group, $-NO_2$, to the primary amino group, $-NH_2$, while retaining the aromatic carbon skeleton.
- A primary amine reacts with chloroform, $CHCl_3$, and alcoholic potassium hydroxide to form an isocyanide, $R-N\equiv C$, with an offensive smell. This is the carbylamine reaction.
- The formula C_6H_7N corresponds here to aniline, $C_6H_5NH_2$. Aromatic primary amines also give the carbylamine test.

Step 1: Identify the reduction substrate and product The six-carbon aromatic primary amine with the specified molecular formula is aniline. Since reduction with iron scrap and hydrochloric acid converts an aromatic nitro group into an amino group, the precursor is nitrobenzene, $C_6H_5NO_2$. The benzene ring stays intact during this reduction; only the nitrogen-containing functional group changes.

Step 2: Write the reduction reaction The transformation and its balanced overall equation can be written as

$$C_6H_5NO_2 + 6[H] \xrightarrow{Fe/HCl} C_6H_5NH_2 + 2H_2O,$$

$$C_6H_5NO_2 + 3Fe + 6HCl \longrightarrow C_6H_5NH_2 + 3FeCl_2 + 2H_2O.$$

Here $[H]$ denotes reducing hydrogen equivalents. In the acidic reaction mixture the amine can be present as its anilinium salt; alkaline work-up liberates free aniline for the next reaction.

Step 3: Identify the carbylamine and write its formation Aniline has the primary amino group required for the carbylamine test. With chloroform and alcoholic potassium hydroxide on heating, it forms phenyl isocyanide:

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

In this product the phenyl group is bonded to nitrogen, giving $C_6H_5-N\equiv C$. Its offensive smell accounts for the observation in the question. It is an isocyanide, with nitrogen attached to the ring, rather than the nitrile C_6H_5CN.

Step 4: Conclusion A is nitrobenzene, $C_6H_5NO_2$; B is aniline, $C_6H_5NH_2$; and C is phenyl isocyanide (phenyl carbylamine), C_6H_5NC. Reduction gives aniline, and its carbylamine reaction produces the offensive-smelling isocyanide.

Quick Tip to Solve: Track the atom bonded to the phenyl ring: carbylamine formation gives C_6H_5-NC, so write phenyl isocyanide rather than benzonitrile.

11(a). Complete the following:

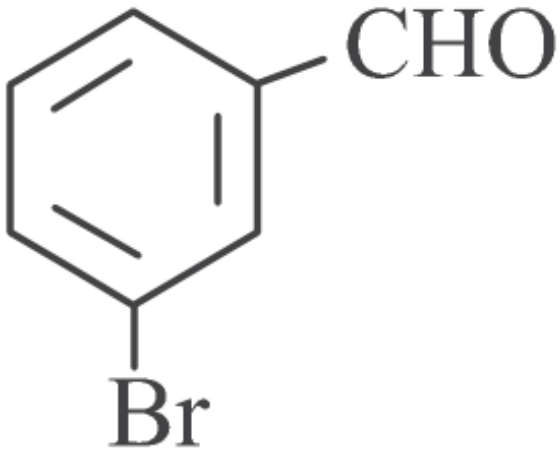
(i) Identify A and B in the reaction sequence:

(ii) Write IUPAC name of the following compound:

(iii) Write chemical test to distinguish between the following compounds: Phenol and Benzoic acid.

[3 marks]

$$CH_3CN \xrightarrow[2.\ H_2O]{1.\ AlH(i\text{-}Bu)_2} \text{'A'} \xrightarrow[H^+]{H_2N\text{-}OH} \text{'B'}$$



Solution:

Concept:

- Diisobutylaluminium hydride (DIBAL-H) partially reduces a nitrile; hydrolysis of the resulting intermediate gives an aldehyde with the same carbon skeleton.
- Hydroxylamine, NH_2OH, condenses with the carbonyl group to form an oxime, eliminating water.
- In a substituted benzaldehyde, the ring carbon bonded to CHO is numbered 1. Carboxylic acids react with sodium hydrogen carbonate to release CO_2; phenol does not.

Step 1: (i) Identify the products A and B The starting nitrile is ethanenitrile, CH_3CN. Reduction with DIBAL-H followed by water converts the nitrile group into an aldehyde group without removing either carbon:

$$CH_3CN \xrightarrow[2.\ H_2O]{1.\ \text{DIBAL-H}} CH_3CHO\ (A).$$

Ethanal then reacts with hydroxylamine in acid-catalysed condensation. Its carbonyl oxygen is replaced by $N - OH$, with elimination of water:

$$CH_3CHO + NH_2OH \xrightarrow{H^+} CH_3CH = NOH + H_2O.$$

Thus A is ethanal and B is ethanal oxime (acetaldoxime). DIBAL-H under these conditions does not give the primary amine obtained by complete nitrile reduction.

Quick Tip to Solve: Retain both carbons during DIBAL-H reduction, number the CHO-bearing ring carbon as 1, and use bicarbonate effervescence to identify the carboxylic acid.

Step 2: (ii) Name the substituted benzaldehyde Choose benzaldehyde as the parent because the formyl group, $-\mathrm{CHO}$, is the principal functional group. Number its attached ring carbon as 1, and proceed around the ring in the direction that gives bromine the lower locant. The printed bromine substituent is at carbon 3, in the meta position relative to CHO. The IUPAC name is therefore 3-bromobenzaldehyde.

Step 3: (iii) Distinguish phenol from benzoic acid Add aqueous sodium hydrogen carbonate, $\mathrm{NaHCO_3}$, separately to the two samples. Benzoic acid produces brisk effervescence of carbon dioxide:

$$\mathrm{C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 \uparrow + H_2O.}$$

Phenol gives no effervescence because it is too weak an acid to liberate carbon dioxide from hydrogen carbonate. The evolved gas from benzoic acid can be confirmed by turning limewater milky.

Step 4: Conclusion (i) $A = \mathrm{CH_3CHO}$ and $B = \mathrm{CH_3CH{=}NOH}$; (ii) 3-bromobenzaldehyde; (iii) benzoic acid evolves $\mathrm{CO_2}$ with $\mathrm{NaHCO_3}$, whereas phenol does not.

Quick Tip to Solve: Retain both carbons during DIBAL-H reduction, number the CHO-bearing ring carbon as 1, and use bicarbonate effervescence to identify the carboxylic acid.

OR

11(b). Convert the following:

(i) Benzoic acid to Benzaldehyde

(ii) Propan-1-ol to 2-Bromopropanoic acid

(iii) Acetaldehyde to But-2-enal [3 marks]

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride to an aldehyde using hydrogen over poisoned palladium supported on barium sulphate.
- A primary alcohol is oxidised to a carboxylic acid. The Hell-Volhard-Zelinsky (HVZ) reaction brominates its alpha carbon using bromine and red phosphorus, followed by hydrolysis.
- Aldehydes having alpha hydrogens undergo aldol addition in dilute alkali. Heating the aldol gives an alpha,beta-unsaturated aldehyde by loss of water.

Step 1: (i) Benzoic acid to benzaldehyde First convert benzoic acid to benzoyl chloride with thionyl chloride. Then carry out Rosenmund reduction:

$$\mathrm{C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl,}$$

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

The poisoned catalyst limits reduction to the aldehyde. This route retains the carboxyl carbon as the aldehyde carbon; strong hydride reduction would instead give benzyl alcohol.

Step 2: (ii) Propan-1-ol to 2-bromopropanoic acid Oxidise propan-1-ol completely using acidified

Quick Tip to Solve: For these conversions, match the target change: acyl chloride to CHO uses Rosenmund, alpha bromination uses HVZ, and a doubled carbon chain suggests aldol condensation.

potassium dichromate under reflux to obtain propanoic acid:

$$CH_3CH_2CH_2OH + 2[O] \xrightarrow{K_2Cr_2O_7/H^+} CH_3CH_2COOH + H_2O.$$

Propanoic acid has alpha hydrogens at carbon 2. Treat it with bromine in the presence of red phosphorus, then hydrolyse the acyl bromide intermediate:

$$CH_3CH_2COOH \xrightarrow[2.\ H_2O]{1.\ Br_2/\text{red P}} CH_3CHBrCOOH.$$

This HVZ sequence substitutes bromine on the carbon adjacent to the carboxyl group and produces the required 2-bromopropanoic acid.

Step 3: (iii) Acetaldehyde to but-2-enal Acetaldehyde has alpha hydrogens. Two molecules react with cold dilute aqueous sodium hydroxide to form the aldol, 3-hydroxybutanal. On heating, it loses water:

$$2CH_3CHO \xrightarrow{\text{dilute NaOH}} CH_3CH(OH)CH_2CHO,$$

$$CH_3CH(OH)CH_2CHO \xrightarrow{\Delta} CH_3CH = CHCHO + H_2O.$$

Numbering from the aldehyde carbon gives the double bond between carbons 2 and 3, so this condensation product is but-2-enal. The four-carbon chain arises by combining two two-carbon molecules.

Step 4: Conclusion (i) Use $SOCl_2$, then $H_2/Pd - BaSO_4$; (ii) oxidise to propanoic acid, then use $Br_2/\text{red P}$ and hydrolysis; (iii) use dilute $NaOH$ for aldol addition, then heat to obtain $CH_3CH = CHCHO$.

Quick Tip to Solve: For these conversions, match the target change: acyl chloride to CHO uses Rosenmund, alpha bromination uses HVZ, and a doubled carbon chain suggests aldol condensation.

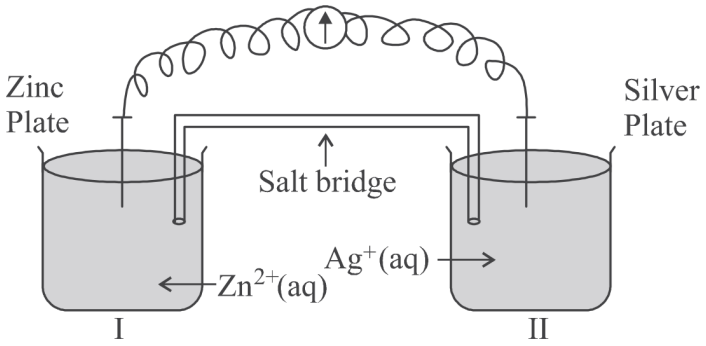
Section C (5 marks)

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

Oxidation-reduction reactions are commonly known as redox reactions. They involve transfer of electrons from one species to another. In a spontaneous reaction, energy is released which can be used to do useful work. The reaction is split into two half reactions. Two different containers are used and a wire is used to drive the electrons from one side to the other and a Voltaic/Galvanic cell is created. It is an electrochemical cell that uses spontaneous redox reactions to generate electricity. A salt bridge also connects to the half cells. The reading of the voltmeter gives the cell voltage or cell potential or electromotive force. If E°_{cell} is positive the reaction is spontaneous and if it is negative the reaction is non-spontaneous and is referred to as electrolytic cell. Electrolysis refers to the decomposition of a substance by an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

The conductance of material is the property of materials due to which a material allows the flow of ions through itself and thus conducts electricity. Conductivity is represented by k and it depends upon nature and concentration of electrolyte, temperature etc. A more common term molar conductivity of a solution at a given concentration is conductance of the volume of solution containing one mole of electrolyte kept between two electrodes with the unit area of cross-section and distance of unit length. Limiting molar conductivity of weak electrolytes cannot be obtained graphically.

Is silver plate the anode or cathode? [1 mark]



Solution:

Concept:

- In a galvanic cell, oxidation occurs at the anode and reduction at the cathode. Electrons travel through the external circuit from anode to cathode.
- In the zinc-silver cell, zinc supplies electrons by oxidation and silver ions accept them by reduction to silver metal.

Step 1: Identify the electron-supplying electrode Zinc is oxidised at the zinc plate:

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

Thus zinc is the anode and sends electrons through the wire towards the silver plate.

Step 2: Identify the reaction at the silver plate Silver ions in the second half-cell gain these electrons

Quick Tip to Solve: Write the half-reaction first: the electrode where ions gain electrons is always the cathode.

and deposit as silver on the plate:

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s).$$

Since electron gain is reduction, the silver plate is the cathode. It is the positive electrode of this operating galvanic cell; the metal's name alone does not define its role.

Step 3: Conclusion The silver plate is the cathode, where Ag^{+} ions are reduced to silver metal.

Quick Tip to Solve: Write the half-reaction first: the electrode where ions gain electrons is always the cathode.

12(b). What will happen if the salt bridge is removed? [1 mark]

Solution:

Concept:

- A salt bridge completes the internal ionic circuit between the two half-cells.
- Migration of its ions maintains electrical neutrality as oxidation and reduction proceed.

Step 1: Identify the charge buildup At the zinc anode, $Zn \rightarrow Zn^{2+} + 2e^{-}$ adds positive ions to the solution. At the silver cathode, $Ag^{+} + e^{-} \rightarrow Ag$ removes positive ions. Salt-bridge ions normally compensate these changes.

Step 2: Examine removal of the bridge Without the salt bridge, the internal ionic path is interrupted and uncompensated charge builds up in the half-cells. This opposes further electron transfer, so a sustained current cannot flow through the external wire.

Step 3: Conclusion Removing the salt bridge stops the cell from supplying a sustained electric current because the ionic circuit is broken and electrical neutrality is lost.

Quick Tip to Solve: Link the salt bridge to both circuit completion and charge balance; the external wire alone cannot sustain current.

12(c). When does electrochemical cell behaves like an electrolytic cell? [1 mark]

Solution:

Concept:

- A galvanic cell drives a spontaneous redox reaction and generates electrical energy.
- An electrolytic cell consumes externally supplied electrical energy to drive a non-spontaneous reaction.

Step 1: Apply an opposing potential Connect an external source with a polarity that opposes the cell's own emf. If the opposing potential equals the cell emf, electron flow stops; equality alone does not reverse the reaction.

Step 2: Exceed the cell emf When the applied opposing potential exceeds the cell emf, the external source forces electrons to flow in the reverse direction. The redox reaction is then driven backwards

Quick Tip to Solve: Distinguish equality from excess: opposing emf equal to the cell emf stops current, while a greater emf reverses it.

and the cell consumes electrical energy, behaving as an electrolytic cell.

Step 3: Conclusion An electrochemical cell behaves as an electrolytic cell when an external opposing potential greater than its cell emf is applied, reversing the spontaneous reaction.

Quick Tip to Solve: Distinguish equality from excess: opposing emf equal to the cell emf stops current, while a greater emf reverses it.

12(d). (i) What will happen to the concentration of Zn^{2+} and Ag^{+} when $E_{cell} = 0$?
(ii) Why does conductivity of a solution decreases with dilution? [2 marks]

Solution:

Concept:

- For a cell reaction, $\Delta G = -nFE_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant. At equilibrium, $E_{\text{cell}} = 0$.
- Conductivity κ measures conduction by ions in a given volume of solution; it depends on the number of charge carriers per unit volume.

Step 1: (i) Identify the equilibrium state The zinc-silver cell reaction is

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

During spontaneous operation, $[Zn^{2+}]$ increases and $[Ag^{+}]$ decreases. When $E_{\text{cell}} = 0$, $\Delta G = 0$: the cell is at equilibrium and there is no net progress of this reaction. Both ion concentrations therefore remain constant at their equilibrium values; they do not have to become equal or zero.

Step 2: (ii) Explain the effect of dilution Dilution increases the volume of solution and reduces the number of ions per unit volume. Hence a unit volume contains fewer mobile charge carriers, so the conductivity decreases. Even if dilution increases the fraction of a weak electrolyte that ionises, the decrease in ionic concentration per unit volume governs this decrease. This should be distinguished from molar conductivity, which increases with dilution.

Step 3: Conclusion (i) At $E_{\text{cell}} = 0$, the concentrations of Zn^{2+} and Ag^{+} remain constant at equilibrium. (ii) Conductivity decreases on dilution because there are fewer ions per unit volume.

Quick Tip to Solve: Read zero cell emf as equilibrium, and distinguish conductivity per unit volume from molar conductivity per mole.

OR

12(d). The molar conductivity of a 1.5 M solution of an electrolyte is found to be 138.9 S cm^2 mol^{-1}. Calculate the conductivity of this solution. [2 marks]

Solution:

Concept:

- Molar conductivity Λ_m is related to conductivity κ and concentration C by $\Lambda_m = 1000\kappa/C$ when C is in $\mathrm{mol\,L^{-1}}$, κ in $\mathrm{S\,cm^{-1}}$, and Λ_m in $\mathrm{S\,cm^2\,mol^{-1}}$.
- The factor 1000 converts litres to cubic centimetres: $1\,\mathrm{L} = 1000\,\mathrm{cm^3}$.

Step 1: Express concentration in compatible units The supplied concentration is $C = 1.5\,\mathrm{mol\,L^{-1}}$. Since the molar conductivity uses centimetres, the concentration per cubic centimetre is

$$c = \frac{1.5}{1000} = 1.5 \times 10^{-3}\,\mathrm{mol\,cm^{-3}}.$$

In these units, $\kappa = \Lambda_m c$; equivalently, $\kappa = \Lambda_m C/1000$ when concentration is expressed as molarity.

Step 2: Substitute the molar conductivity Using $\Lambda_m = 138.9\,\mathrm{S\,cm^2\,mol^{-1}}$,

$$\begin{aligned}\kappa &= 138.9 \times 1.5 \times 10^{-3} \\ &= 0.20835\,\mathrm{S\,cm^{-1}}.\end{aligned}$$

The units combine as $\mathrm{S\,cm^2\,mol^{-1}} \times \mathrm{mol\,cm^{-3}} = \mathrm{S\,cm^{-1}}$, confirming that the result is conductivity rather than molar conductivity.

Step 3: Conclusion The conductivity of the solution is $\boxed{\kappa = 0.20835\,\mathrm{S\,cm^{-1}}}$ (approximately $0.21\,\mathrm{S\,cm^{-1}}$ to two significant figures).

Quick Tip to Solve: With molarity in mol per litre and conductivity in S per cm, multiply molar conductivity by molarity and divide by 1000.