CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-5-2

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. Arrange the following in the increasing order of their property indicated:

(a) Ethanal, Propanone, Propanal, Butanone (reactivity towards nucleophilic addition)

(b) 4-Nitrobenzoic acid, benzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (Acid strength)

[2 marks]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electrophilic carbonyl carbon. Alkyl groups decrease its positive character by their electron-releasing inductive effect and hinder the approaching nucleophile.
- Acid strength increases when an electron-withdrawing substituent stabilises the carboxylate conjugate base; an electron-donating substituent has the opposite effect.

Step 1: (a) Compare carbonyl reactivity Aldehydes have only one alkyl group attached to the carbonyl carbon, whereas ketones have two. Thus, the aldehydes are less hindered and more electrophilic than the ketones. Within each pair, replacing a methyl group by an ethyl group increases steric hindrance and electron donation: propanone reacts more readily than butanone, and ethanal more readily than propanal.

Step 2: (b) Compare stabilisation of the conjugate bases The para-methoxy group donates electrons by resonance and decreases acidity relative to benzoic acid. A nitro group withdraws electrons and stabilises the benzoate ion, increasing acidity. Two nitro groups produce a stronger overall electron-withdrawing effect than one, so 3,4-dinitrobenzoic acid is the strongest acid listed.

Step 3: Conclusion The increasing orders are:

(a) Butanone $<$ propanone $<$ propanal $<$ ethanal.

(b) 4-Methoxybenzoic acid $<$ benzoic acid $<$ 4-nitrobenzoic acid $<$ 3,4-dinitrobenzoic acid.

Quick Tip to Solve: For (a), rank ketones below aldehydes first; for (b), place the electron-donating methoxy group lowest and the two nitro groups highest in acidity.

2. Explain the following reactions:

(a) Clemmensen reduction

(b) Stephen reaction

[2 marks]

Solution:

Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- In the Stephen reaction, a nitrile is partially reduced to an imine salt with tin(II) chloride and hydrochloric acid; hydrolysis then gives an aldehyde with the same number of carbon atoms.

Quick Tip to Solve: Pair Clemmensen with carbonyl-to-methylene and Stephen with nitrile-to-aldehyde; always include the hydrolysis step in Stephen's reaction.

Step 1: (a) Clemmensen reduction Heating an aldehyde or ketone with $\mathrm{Zn(Hg)}$ and concentrated HCl replaces its carbonyl oxygen by two hydrogen atoms. For a ketone, the general change is

$$\mathrm{RCOR' + 4[H] \xrightarrow{Zn(Hg),\ conc.\ HCl} RCH_2R' + H_2O.}$$

Thus, propanone gives propane. Similarly, an aldehyde RCHO gives $\mathrm{RCH_3}$. The carbon skeleton is retained, and the reaction occurs in strongly acidic medium.

Step 2: (b) Stephen reaction A nitrile is reduced using $\mathrm{SnCl_2/HCl}$ to its imine hydrochloride. On hydrolysis this intermediate produces an aldehyde:

$$\mathrm{RCN + 2[H] + HCl \xrightarrow{SnCl_2} RCH{=}NH \cdot HCl,}$$
$$\mathrm{RCH{=}NH \cdot HCl + H_2O \longrightarrow RCHO + NH_4Cl.}$$

For example, ethanenitrile, $\mathrm{CH_3CN}$, gives ethanal, $\mathrm{CH_3CHO}$. Hydrolysis of the intermediate is essential to obtain the aldehyde.

Step 3: Conclusion Clemmensen reduction gives a hydrocarbon from an aldehyde or ketone using $\mathrm{Zn(Hg)/HCl}$; the Stephen reaction gives an aldehyde from a nitrile using $\mathrm{SnCl_2/HCl}$, followed by hydrolysis.

Quick Tip to Solve: Pair Clemmensen with carbonyl-to-methylene and Stephen with nitrile-to-aldehyde; always include the hydrolysis step in Stephen's reaction.

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 the rate law $r = k[A]^n$, n is the order, k the rate constant and $[A]$ the reactant concentration. 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 zero-order reaction has a concentration-independent rate: $-d[A]/dt = k$. Integrating relates the concentration at time t to its initial value.

Step 1: (a) Determine order from the units The supplied units are $\mathrm{L\,mol^{-1}\,s^{-1}} = (\mathrm{mol\,L^{-1}})^{-1}\mathrm{s^{-1}}$. Comparing the concentration exponent with the general expression gives

$$1 - n = -1 \quad \Longrightarrow \quad n = 2.$$

Thus, these are the units of the rate constant for a second-order reaction.

Step 2: (b) Compare the two rates For second-order conversion of A into B, $r = k[A]^2$. At the same

Quick Tip to Solve: For a concentration multiplied by three, raise three to the reaction order; for zero order, remember that concentration falls linearly with time.

temperature, k is unchanged. If the original concentration is $[A]$ and the new concentration is $3[A]$,

$$\frac{r_{\text{new}}}{r_{\text{old}}} = \frac{k(3[A])^2}{k[A]^2} = 9.$$

Therefore, the rate of formation of B becomes nine times the original rate.

Step 3: (c) Write the zero-order integrated equation Integrating $-d[A]/dt = k$ from $[A]_0$ at time zero to $[A]_t$ at time t gives

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

Here $[A]_0$ denotes the initial concentration and $[A]_t$ the concentration remaining at time t. The relation applies while the reaction follows zero-order kinetics and reactant remains.

Step 4: Conclusion (a) Second order. (b) The rate becomes 9 times its original value. (c) $[A]_t = [A]_0 - kt$. All three parts are provided; any two may be attempted as directed.

Quick Tip to Solve: For a concentration multiplied by three, raise three to the reaction order; for zero order, remember that concentration falls linearly with time.

Section B (24 marks)

4(a). (i) Define coagulation.

(ii) State Hardy-Schulze rule.

(iii) What is Electrophoresis? [3 marks]

Solution:

Concept:

- Colloidal particles usually carry the same type of electrical charge. Their mutual repulsion helps to keep the sol stable and prevents particles from joining together.
- An electrolyte supplies ions of both signs. The ion whose charge is opposite to that on the colloidal particles is the effective coagulating ion.

Step 1: (i) Define coagulation Coagulation is the process of precipitation of colloidal particles: the particles aggregate into larger particles and settle down. For example, adding a suitable electrolyte neutralises the charge on the particles, reduces their mutual repulsion and allows aggregation. Coagulation is also called flocculation.

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, for a negatively charged sol, the effectiveness of cations increases in the order

$$\text{Na}^+ < \text{Ca}^{2+} < \text{Al}^{3+}.$$

For a positively charged sol, the anions are the effective coagulating ions. The rule concerns the oppositely charged ion, not the ion with the same charge as the sol.

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

Step 3: (iii) Define electrophoresis Electrophoresis is the movement of colloidal particles towards the oppositely charged electrode under the influence of an applied electric field. Positively charged particles move towards the cathode, whereas negatively charged particles move towards the anode. This motion provides evidence that colloidal particles possess an electrical charge.

Step 4: Conclusion Coagulation is the precipitation of aggregated colloidal particles; the Hardy–Schulze rule relates greater counter-ion valency to greater coagulating power; electrophoresis is the motion of charged colloidal particles in an electric field towards the opposite electrode.

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

OR

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

Solution:

Concept:

- Adsorption is the accumulation of a substance at the surface of another substance. The substance accumulated is the adsorbate, and the surface providing material is the adsorbent.
- Physisorption results from weak van der Waals forces, whereas chemisorption results from the formation of chemical bonds between the adsorbate and the adsorbent.

Step 1: Difference 1: Nature of the attractive forces In physisorption, the adsorbate is held on the surface by relatively weak van der Waals forces. No chemical bond is formed with the surface. In chemisorption, the adsorbate is held by strong chemical bonds with the adsorbent. This difference in the type of interaction is the basis for distinguishing physical adsorption from chemical adsorption.

Step 2: Difference 2: Specificity Physisorption is not specific in nature because van der Waals forces can act between many different substances. A given surface can therefore physically adsorb different gases. Chemisorption is highly specific: it occurs only when the adsorbate and the adsorbent can form suitable chemical bonds with one another.

Step 3: Difference 3: Number of layers Physisorption may form multimolecular layers. After the first layer forms, further molecules can be held to the adsorbed molecules by van der Waals forces. Chemisorption forms a unimolecular layer, since it requires direct chemical bonding to available sites on the adsorbent surface. Once these sites are occupied, another chemically bonded layer cannot form in the same way.

Step 4: Conclusion The three differences are: weak van der Waals forces versus strong chemical bonds; non-specific versus highly specific adsorption; and possible multimolecular layers versus a unimolecular layer, for physisorption and chemisorption respectively.

Quick Tip to Solve: Compare the same property on both sides: forces, specificity and layers give three clear paired differences.

5(a). (i) Write the IUPAC name of the following complex: $[Pt(NH_3)_6]Cl_4$.
(ii) On the basis of crystal field theory, write the electronic configuration of d^4 ion, if $\Delta_o < P$.
(iii) What are Heteroleptic complexes? [3 marks]

Solution:

Concept:

- Name ligands before the central metal, and give the metal oxidation state in Roman numerals. Neutral NH_3 is named ammine; chloride outside the coordination sphere is the counter-ion.
- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. The comparison of splitting energy Δ_o with pairing energy P determines whether electrons pair or occupy the higher set.
- Ligand types, rather than the total number of ligands, distinguish homoleptic and heteroleptic complexes.

Step 1: (i) Determine the platinum oxidation state and name the salt The four external chloride ions each carry charge -1, so the coordination entity has charge $+4$. Since all six ammonia ligands are neutral, if the platinum oxidation state is x, charge balance gives

$$x + 6(0) + 4(-1) = 0, \qquad x = +4.$$

Six ammine ligands give the prefix hexaammine. The complex ion is positive, so the metal retains the name platinum; its oxidation state is written (IV). Name the chloride counter-ion after the complex cation.

Step 2: (ii) Fill the orbitals for the given field strength There are four d electrons. First place one electron in each of the three lower t_{2g} orbitals. Because $\Delta_o < P$, promoting the fourth electron to an e_g orbital costs less energy than pairing it in t_{2g}. Hence the fourth electron occupies the higher set singly. This is the high-spin arrangement, with four unpaired electrons; the low-spin alternative $t_{2g}^4 e_g^0$ would require pairing and is not favoured here.

Step 3: (iii) Identify a heteroleptic complex A heteroleptic complex has its central metal atom or ion bonded to more than one kind of ligand. For example, $[Co(NH_3)_4Cl_2]^+$ contains both ammine and chlorido ligands. By contrast, the platinum coordination entity in part (i) contains only ammine ligands; the chloride ions outside its brackets do not count as coordinated ligands.

Step 4: Conclusion (i) Hexaammineplatinum(IV) chloride.
(ii) $\boxed{t_{2g}^3 e_g^1}$, the high-spin d^4 configuration.
(iii) Heteroleptic complexes contain more than one type of ligand bonded to the central metal.

Quick Tip to Solve: Count only ligands inside the square brackets, and for $\Delta_o < P$, fill a higher vacant orbital before pairing an electron in the lower set.

OR

5(b). (i) Using IUPAC norms write the formulas for the following:

(i.i) Pentaamminenitrito-N-Cobalt (III)

(i.ii) Tetrahydroxidozincate (II)

(ii) What is crystal field splitting energy? [3 marks]

Solution:

Concept:

- A complex ion's charge equals the metal oxidation state plus the charges on its ligands. Ammonia is neutral, whereas nitrito and hydroxido ligands each have charge -1.
- The donor-atom designation nitrito-N specifies bonding through nitrogen. The suffix -ate in a metal name indicates an anionic coordination entity.
- Ligand approach removes the degeneracy of the five metal d orbitals. Crystal field splitting energy is the energy separation between the resulting sets of orbitals.

Step 1: (i.i) Translate the cobalt complex name into its formula Pentaammine means five neutral NH_3 ligands. Nitrito-N means one NO_2^- ligand attached through its nitrogen atom, written as NO_2 in the coordination formula. Cobalt(III) supplies metal charge $+3$. The total charge is therefore

$$+3 + 5(0) + (-1) = +2.$$

Place the metal and all six ligands inside square brackets and show this net charge outside. No counter-ion is named in the question, so the formula represents the complex cation itself.

Step 2: (i.ii) Translate the zinc complex name into its formula Tetrahydroxido specifies four OH^- ligands around zinc. The Roman numeral (II) gives the zinc oxidation state as $+2$, so the charge calculation is

$$+2 + 4(-1) = -2.$$

The negative result agrees with the suffix zincate. Parenthesise the hydroxido ligand before applying the subscript four, and attach the $2-$ charge to the entire coordination entity.

Step 3: (ii) Explain the energy separation caused by ligands The five d orbitals of an isolated metal ion have the same energy. When ligands surround the ion, their interactions with orbitals of different orientations differ, producing sets at different energies. The energy difference between these sets is called crystal field splitting energy. For an octahedral complex, the lower set is t_{2g} and the upper set is e_g, so

$$\Delta_o = E(e_g) - E(t_{2g}).$$

The symbol Δ_t is used for tetrahedral splitting. Splitting energy describes the orbital energy gap; it is distinct from the energy needed to pair electrons in one orbital.

Step 4: Conclusion (i.i) $\boxed{[Co(NH_3)_5(NO_2)]^{2+}}$, with N-bonded nitrito.

(i.ii) $\boxed{[Zn(OH)_4]^{2-}}$.

(ii) Crystal field splitting energy is the energy difference between the sets of metal d orbitals formed by splitting in the ligand field.

Quick Tip to Solve: Add ligand charges to the Roman-numeral metal oxidation state: neutral ammine contributes zero, while each nitrito or hydroxido ligand contributes -1.

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 as atomic number increases. The poor shielding by $4f$ electrons makes the effective nuclear attraction increase.
- The $3d$ and $4s$ orbitals have comparable energies, so electrons from both can participate in bonding. Their availability accounts for the variable oxidation states of transition elements.

Step 1: (a) Relate contraction to the sizes of transition elements One consequence is the close similarity in the radii of corresponding second and third transition-series elements. The decrease in size caused by filling the $4f$ subshell offsets the normal increase in size on going to the next period. Thus zirconium and hafnium have nearly equal radii and very similar chemical properties, making their separation difficult.

Step 2: (a) Explain the trend in basic character A second consequence is that the basic character of lanthanoid hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. As the radius of the tripositive metal ion decreases, its charge density and polarising power increase. The metal–oxygen bond acquires greater covalent character, so the hydroxides become less ionic and less basic.

Step 3: (b) Examine the valence configuration of manganese Manganese, Mn, exhibits the largest number of oxidation states in the $3d$ series. Its ground-state electronic configuration is

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

It has five $3d$ electrons and two $4s$ electrons available for bonding. Because these subshells are close in energy, different numbers of these seven electrons can participate, giving oxidation states from $+2$ to $+7$.

Step 4: Conclusion (a) Two consequences are nearly equal radii and similar chemistry of pairs such as zirconium and hafnium, and decreasing basicity of lanthanoid hydroxides from $La(OH)_3$ to $Lu(OH)_3$. (b) Manganese shows the most oxidation states because both its five $3d$ and two $4s$ electrons can participate in bonding.

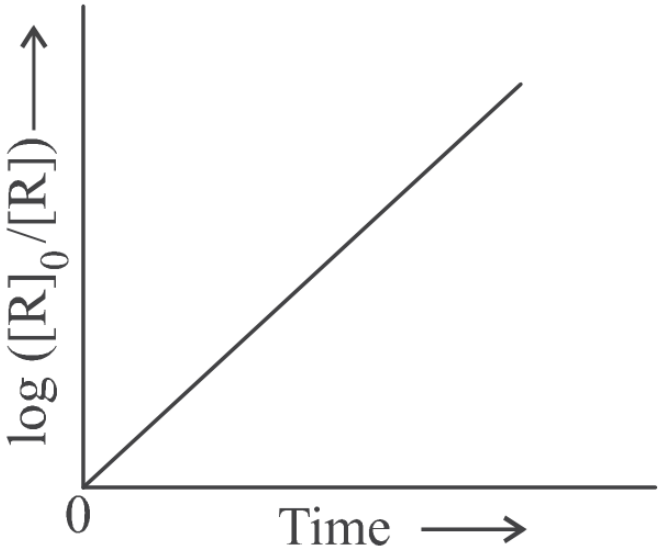
Quick Tip to Solve: Link each consequence to decreasing ionic radius; for oxidation-state variety, count both the $3d$ and $4s$ valence electrons of manganese.

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 integrated rate equation is $\ln([R]_0/[R]) = kt$, or $\log([R]_0/[R]) = kt/2.303$. Here $[R]_0$ is initial reactant concentration, $[R]$ is its concentration at time t, and k is the rate constant; $\log$ denotes logarithm to base ten.
- In a straight-line equation $y = mt + c$, m is the slope. The half-life $t_{1/2}$ is the time at which the reactant concentration becomes half of its initial value.

Step 1: (a) Identify the plotted quantities The vertical axis is $\log([R]_0/[R])$ and the horizontal axis is time. The graph is a straight line through the origin, showing that the logarithm of this concentration ratio is proportional to time. This agrees with the integrated equation

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

so the reaction follows first-order kinetics. At $t = 0$, $[R] = [R]_0$, and the logarithm is zero, consistent with the plotted intercept.

Step 2: (b) Compare with the straight-line equation Compare the integrated equation with $y = mt + c$. The coefficient of time is the slope:

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

The slope is positive because reactant concentration decreases with time, so $[R]_0/[R]$ increases. The denominator 2.303 appears because the graph uses common logarithms rather than natural logarithms.

Quick Tip to Solve: Read the logarithm and ratio on the vertical axis carefully: $\log([R]_0/[R])$ gives positive slope $k/2.303$, while a natural-log plot gives slope k.

Step 3: (c) Substitute the half-life condition At half-life, $[R] = [R]_0/2$. Substitution into the first-order equation gives

$$kt_{1/2} = 2.303 \log \frac{[R]_0}{[R]_0/2}$$
$$= 2.303 \log 2 = 0.693.$$

Thus the first-order half-life is inversely proportional to the rate constant and independent of initial concentration.

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

Quick Tip to Solve: Read the logarithm and ratio on the vertical axis carefully: $\log([R]_0/[R])$ gives positive slope $k/2.303$, while a natural-log plot gives slope k.

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8. Give reasons for the following statements:

(a) Scandium (Z = 21) is a transition element but Zn (Z = 30) is not.

(b) $[Ti(H_2O)]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.

(c) Physical and chemical properties of the 4d and 5d series of the transition elements are quite similar than expected. [3 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in one of its commonly formed ions.
- In a transition-metal complex, ligands split the metal d-orbital energies. Absorption of visible light for a d-d transition can produce colour when suitable d electrons are present.
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoids, caused by poor shielding by $4f$ electrons.

Step 1: (a) Compare the electronic configurations Scandium has atomic configuration $[\mathrm{Ar}]\,3d^1 4s^2$. Its atom therefore contains an incompletely filled $3d$ subshell and satisfies the definition of a transition element, even though Sc^{3+} is $3d^0$. Zinc has configuration $[\mathrm{Ar}]\,3d^{10}4s^2$, and its usual ion Zn^{2+} has configuration $[\mathrm{Ar}]\,3d^{10}$. The d subshell is completely filled in both, so zinc does not satisfy the definition.

Step 2: (b) Count the metal-ion d electrons Water is a neutral ligand, so the metal oxidation state in both printed complexes is $+3$. Titanium has atomic configuration $[\mathrm{Ar}]\,3d^2 4s^2$; removing the two $4s$ electrons and one $3d$ electron gives Ti^{3+}, with configuration $3d^1$. Its electron can absorb visible light and move between the ligand-split d levels, giving the complex its colour. In contrast, Sc^{3+} has configuration $3d^0$, so no d-d transition is possible and its aqua complex is colourless.

Step 3: (c) Apply lanthanoid contraction The $4f$ subshell fills before the later $5d$ transition elements. The $4f$ electrons shield the increasing nuclear charge poorly, causing a contraction in size. This largely offsets the increase in radius expected from adding a shell, so corresponding $4d$ and $5d$ elements,

Quick Tip to Solve: For transition-metal ions, remove the $4s$ electrons before the $3d$ electrons; for $4d$-$5d$ size similarity, identify lanthanoid contraction.

such as zirconium and hafnium, have nearly equal atomic and ionic radii. Together with their similar valence-shell configurations, this accounts for their unusually similar physical and chemical properties.

Step 4: Conclusion (a) Scandium has a partially filled $3d$ subshell, whereas zinc and its usual ion have $3d^{10}$. (b) Ti^{3+} is d^1 and permits colour-producing d-d transitions; Sc^{3+} is d^0. (c) Lanthanoid contraction makes corresponding $4d$ and $5d$ elements similar in size and properties.

Quick Tip to Solve: For transition-metal ions, remove the $4s$ electrons before the $3d$ electrons; for $4d$-$5d$ size similarity, identify lanthanoid contraction.

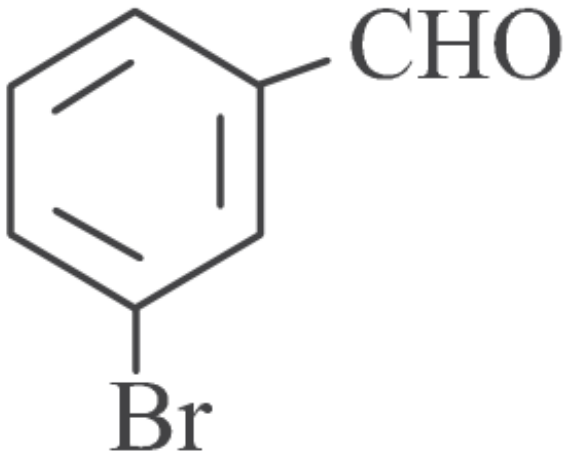
9(a). Complete the following:

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

(ii) Write IUPAC name of the following compound:

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

[3 marks]



Solution:

Concept:

- DIBAL-H partially reduces a nitrile; hydrolysis gives an aldehyde without changing the carbon skeleton. Hydroxylamine converts an aldehyde into an oxime.
- A carboxylic acid releases CO_2 from aqueous $NaHCO_3$; phenol is too weak an acid to do so.

Step 1: (i) Identify A and B Controlled reduction followed by hydrolysis changes the nitrile group into $-CHO$. Thus A is ethanal:

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

Quick Tip to Solve: Retain both carbon atoms during nitrile reduction; use $NaHCO_3$ effervescence to identify benzoic acid.

Condensation with hydroxylamine eliminates water and gives B, ethanal oxime (acetaldoxime):

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

Step 2: (ii) Number the benzaldehyde ring The aldehyde group determines the parent name, benzaldehyde. Assign position 1 to the ring carbon attached to $-CHO$ and number towards bromine for the lower locant. Bromine occupies position 3 (meta), so the IUPAC name is 3-bromobenzaldehyde.

Step 3: (iii) Apply the sodium hydrogencarbonate test Add aqueous $NaHCO_3$ to each sample. Benzoic acid gives brisk effervescence of carbon dioxide:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2\uparrow + H_2O.$$

The gas turns limewater milky. Phenol gives no effervescence because it cannot liberate CO_2 from hydrogencarbonate. The contrasting observations distinguish the two compounds.

Step 4: Conclusion (i) A: CH_3CHO; B: $CH_3CH{=}NOH$. (ii) 3-Bromobenzaldehyde. (iii) Benzoic acid releases CO_2 with aqueous $NaHCO_3$; phenol does not.

Quick Tip to Solve: Retain both carbon atoms during nitrile reduction; use $NaHCO_3$ effervescence to identify benzoic acid.

OR

9(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 acid chloride into an aldehyde using hydrogen over poisoned palladium supported on barium sulphate.
- A primary alcohol is oxidised to a carboxylic acid. The Hell-Volhard-Zelinsky reaction then replaces an alpha hydrogen of the acid by bromine.
- Aldehydes with alpha hydrogen undergo aldol addition; heating removes water to give an alpha,beta-unsaturated aldehyde.

Step 1: (i) Convert benzoic acid through its acid chloride Treat benzoic acid with thionyl chloride to form benzoyl chloride. Then carry out Rosenmund reduction; the poisoned catalyst limits reduction at the aldehyde stage.

$$C_6H_5COOH + SOCl_2 \longrightarrow C_6H_5COCl + SO_2 + HCl$$

Quick Tip to Solve: For these conversions, first identify the key change: acid to aldehyde needs controlled reduction, alpha bromination needs the acid first, and a two-carbon aldehyde becomes a four-carbon enal by aldol condensation.

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

Step 2: (ii) Oxidise the alcohol and brominate the alpha carbon Oxidise propan-1-ol with acidified potassium dichromate under reflux to obtain propanoic acid.

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

Treat the acid with bromine and red phosphorus, followed by hydrolysis. Bromination occurs at the alpha carbon, which is carbon 2 when the carboxyl carbon is carbon 1.

$$CH_3CH_2COOH + Br_2 \xrightarrow[\text{then } H_2O]{\text{red P}} CH_3CHBrCOOH + HBr$$

Step 3: (iii) Carry out aldol condensation of acetaldehyde In cold dilute sodium hydroxide, two molecules of acetaldehyde combine to form 3-hydroxybutanal, the aldol. Heating this product eliminates water from adjacent carbons and forms the conjugated double bond.

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

$$CH_3CH(OH)CH_2CHO \xrightarrow{\text{heat}} CH_3CH{=}CHCHO + H_2O$$

Step 4: Conclusion The products are (i) benzaldehyde, C_6H_5CHO, by Rosenmund reduction; (ii) 2-bromopropanoic acid, $CH_3CHBrCOOH$, by oxidation and alpha bromination; and (iii) but-2-enal, $CH_3CH{=}CHCHO$, by aldol condensation.

Quick Tip to Solve: For these conversions, first identify the key change: acid to aldehyde needs controlled reduction, alpha bromination needs the acid first, and a two-carbon aldehyde becomes a four-carbon enal by aldol condensation.

10. A primary amine 'A' C_2H_7N reacts with alkyl halide (C_2H_5I) to give secondary amine 'B'. 'B' reacts with $C_6H_5SO_2Cl$ to give a solid 'C' which is insoluble in alkali. Identify 'A', 'B', 'C' and write all the chemical reactions involved. [3 marks]

Solution:

Concept:

- A primary amine has one alkyl group attached to nitrogen, RNH_2. Alkylation replaces an N-H hydrogen with an alkyl group to form a secondary amine.
- Hinsberg's reagent, benzenesulphonyl chloride, $C_6H_5SO_2Cl$, reacts with a secondary amine to form an N,N-disubstituted sulphonamide.
- A sulphonamide dissolves in alkali only if it can form a salt by losing an acidic N-H proton. A product with no N-H bond cannot undergo this reaction.

Step 1: Identify the primary amine A The given molecular formula is C_2H_7N. Since A is a primary amine, both carbon atoms must belong to one ethyl group attached to NH_2. Thus A is ethanamine (ethylamine), $CH_3CH_2NH_2$. Dimethylamine has the same molecular formula but is secondary, so it

Quick Tip to Solve: Count the alkyl groups on nitrogen after each reaction. Two ethyl groups in B leave one N-H bond, and sulphonylation consumes that bond, making C insoluble in alkali.

cannot be A.

Step 2: Alkylate A to identify B Iodoethane introduces a second ethyl group on nitrogen. Initial nucleophilic substitution produces a dialkylammonium salt; treatment with base liberates the secondary amine B, diethylamine, $(C_2H_5)_2NH$.

$$C_2H_5NH_2 + C_2H_5I \longrightarrow [(C_2H_5)_2NH_2]I$$

$$[(C_2H_5)_2NH_2]I + NaOH \longrightarrow (C_2H_5)_2NH + NaI + H_2O$$

The secondary amine specified in the question is therefore the product of one ethylation of A.

Step 3: Apply the Hinsberg test to identify C Diethylamine reacts with benzenesulphonyl chloride in alkaline medium to give N,N-diethylbenzenesulphonamide. Alkali neutralises the hydrogen chloride formed during sulphonamide formation; the overall equation is

$$(C_2H_5)_2NH + C_6H_5SO_2Cl + NaOH \longrightarrow C_6H_5SO_2N(C_2H_5)_2 + NaCl + H_2O.$$

In C, nitrogen is bonded to the sulphonyl group and two ethyl groups, so it has no hydrogen. C therefore cannot form a soluble salt with alkali and remains insoluble, agreeing with the observation.

Step 4: Conclusion A is ethylamine, $C_2H_5NH_2$; B is diethylamine, $(C_2H_5)_2NH$; and C is N,N-diethylbenzenesulphonamide, $C_6H_5SO_2N(C_2H_5)_2$. The absence of an N-H bond in C explains its insolubility in alkali.

Quick Tip to Solve: Count the alkyl groups on nitrogen after each reaction. Two ethyl groups in B leave one N-H bond, and sulphonylation consumes that bond, making C insoluble in alkali.

11(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:

- Basicity depends on the availability of the nitrogen lone pair for accepting a proton. Since $pK_b = -\log K_b$, a weaker base has a larger pK_b.
- Lewis acids accept an electron pair; intermolecular hydrogen bonding increases the energy needed to separate molecules during boiling.

Step 1: Compare the lone-pair availability in part (i) In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance, so it is less available to bind a proton. In methylamine, the methyl group exerts a positive inductive effect and increases electron density on nitrogen; its lone pair is not delocalised into an aromatic ring. Thus aniline has a smaller base dissociation constant than methylamine and consequently a larger pK_b.

Quick Tip to Solve: Check lone-pair delocalisation for basicity, lone-pair binding to the catalyst for Friedel–Crafts reactions, and the presence of an N–H bond for self hydrogen bonding.

Step 2: Explain catalyst interaction in part (ii) A Friedel–Crafts reaction uses a Lewis-acid catalyst such as anhydrous $AlCl_3$. Aniline is a Lewis base and its nitrogen lone pair coordinates with $AlCl_3$, forming a salt-like complex. This makes nitrogen electron deficient and strongly deactivates the benzene ring towards electrophilic substitution. Therefore aniline does not undergo the normal Friedel–Crafts alkylation or acylation reaction.

Step 3: Compare intermolecular forces in part (iii) A primary amine, RNH_2, contains nitrogen–hydrogen bonds and forms intermolecular hydrogen bonds with other primary-amine molecules. A tertiary amine, R_3N, has no nitrogen–hydrogen bond and cannot form such hydrogen bonds with itself. For amines of comparable molar mass, the stronger intermolecular association in primary amines requires more energy to overcome, giving them higher boiling points.

Step 4: Conclusion (i) Resonance makes aniline less basic and gives it a larger pK_b. (ii) Complex formation with $AlCl_3$ deactivates its ring. (iii) Primary amines exhibit intermolecular hydrogen bonding, whereas pure tertiary amines do not.

Quick Tip to Solve: Check lone-pair delocalisation for basicity, lone-pair binding to the catalyst for Friedel–Crafts reactions, and the presence of an N–H bond for self hydrogen bonding.

OR

11(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:

- The basic strength of an amine in water depends on the electron-releasing effect of alkyl groups and the hydration and steric accessibility of its conjugate acid.
- Hinsberg's reagent is an aromatic sulphonyl chloride. During acylation, a base removes the acid formed and preserves the amine's nucleophilicity.

Step 1: Compare the methylamines in aqueous solution Methyl groups increase electron density on nitrogen through their positive inductive effect. However, protonated amines are also stabilised by hydration in water, and increasing alkyl substitution hinders this solvation. For these methylamines, the balance favours dimethylamine most strongly; trimethylamine is less basic than methylamine in water because its conjugate acid is less effectively hydrated. The increasing order is

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

An order based only on the inductive effect would neglect the explicitly stated aqueous medium.

Step 2: Identify Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It is used to distinguish primary, secondary and tertiary amines from the sulphonamide formation and alkali-solubility behaviour of their products. The reagent contains the sulphonyl chloride group,

Quick Tip to Solve: For methylamines in water, remember secondary greater than primary greater than tertiary; for pyridine in acylation, identify the acid by-product it traps.

$-SO_2Cl$, attached to a benzene ring.

Step 3: State the role of pyridine in acylation Acylation of an amine with an acid chloride produces hydrogen chloride. Pyridine acts as a base and absorbs this acid, forming pyridinium chloride:

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

Removing HCl prevents the reacting amine from being converted into its less nucleophilic ammonium salt and helps the acylation proceed.

Step 4: Conclusion (i) $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ in water. (ii) Hinsberg's reagent is $C_6H_5SO_2Cl$. (iii) Pyridine neutralises the acid formed during acylation.

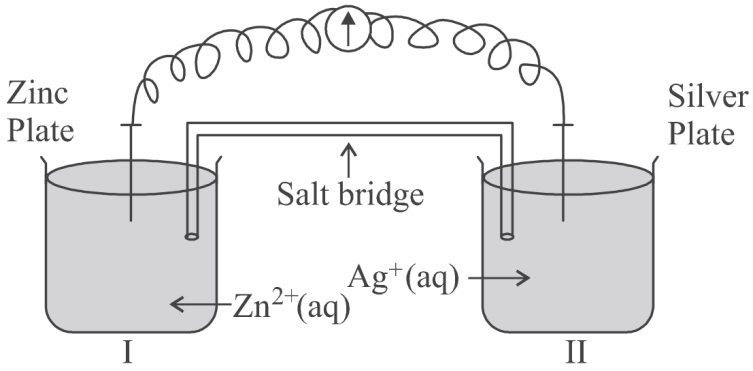
Quick Tip to Solve: For methylamines in water, remember secondary greater than primary greater than tertiary; for pyridine in acylation, identify the acid by-product it traps.

Section C (5 marks)

12. 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. [5 marks]



12(a). Is silver plate the anode or cathode? [1 mark]

Solution:

Concept:

- Oxidation takes place at the anode and reduction takes place at the cathode of an electrochemical cell.
- In the zinc-silver galvanic cell, zinc releases electrons and silver ions accept them at the silver electrode.

Step 1: Identify the electron source Zinc is oxidised according to $\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$. Electrons therefore pass through the external wire from the zinc plate to the silver plate.

Step 2: Identify the reaction at silver At the silver electrode, silver ions gain the arriving electrons and are deposited as silver metal: $\mathrm{Ag^+(aq)} + \mathrm{e^-} \longrightarrow \mathrm{Ag(s)}$. Gain of electrons is reduction, and the

Quick Tip to Solve: Identify the electrode by its half-reaction: silver ions gain electrons, so the silver plate is the cathode.

electrode at which reduction occurs is called the cathode.

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

Quick Tip to Solve: Identify the electrode by its half-reaction: silver ions gain electrons, so the silver plate is the cathode.

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

Solution:

Concept:

- A salt bridge completes the internal circuit by allowing ions to migrate between the half-cells.
- Electrical neutrality of each half-cell must be maintained for a galvanic cell to supply a sustained current.

Step 1: Identify the role of ion migration At the zinc anode, oxidation produces Zn^{2+} ions; at the silver cathode, reduction consumes Ag^+ ions. The salt bridge supplies compensating ions to prevent charge accumulation in the two solutions.

Step 2: Examine removal of the bridge Without the bridge, the ionic path is broken. Positive charge builds up in the zinc half-cell and excess negative charge develops in the silver half-cell. This charge separation opposes further electron transfer through the external wire.

Step 3: Conclusion On removing the salt bridge, the cell stops supplying a sustained current because the internal circuit is broken and electrical neutrality cannot be maintained.

Quick Tip to Solve: Link removal of the salt bridge to blocked ion flow and charge buildup, which stop the external electron current.

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

Solution:

Concept:

- A galvanic cell generates electrical energy through a spontaneous redox reaction.
- An electrolytic cell uses an external source of electrical energy to drive a non-spontaneous reaction.

Step 1: Apply an opposing external potential Connect a direct-current source so that its applied potential E_{ext} opposes the galvanic cell's emf E_{cell}. If the opposing potential equals the cell emf, there is no net current; equality alone does not drive electrolysis.

Step 2: Exceed the cell emf When $E_{ext} > E_{cell}$, the external source forces the current and the electrode reactions to reverse from their spontaneous directions. Electrical energy is then consumed to carry out the reverse, non-spontaneous chemical reaction.

Step 3: Conclusion The electrochemical cell behaves as an electrolytic cell when an external potential greater than its emf is applied in the opposing direction.

Quick Tip to Solve: Remember both conditions: the applied potential must oppose the cell emf and be greater than it, not merely equal to 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:

- The relation $\Delta G = -nFE_{\text{cell}}$ connects the reaction Gibbs energy ΔG to cell potential, with n electrons transferred and Faraday constant F.
- Conductivity κ depends on the number of charge-carrying ions per unit volume as well as their mobilities.

Step 1: (i) Examine the cell at zero potential The spontaneous cell reaction is

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

During operation, zinc-ion concentration rises and silver-ion concentration falls. When $E_{\text{cell}} = 0$, $\Delta G = 0$, so the cell reaction has reached equilibrium. There is no further net oxidation of zinc or reduction of silver ions. The concentrations therefore no longer change with time; they need not become equal or zero.

Step 2: (ii) Explain the effect of dilution Adding solvent increases the volume occupied by the electrolyte. The number of ions available to carry charge per unit volume decreases, so the conductivity decreases. This is distinct from molar conductivity, which refers to all the ions supplied by one mole of electrolyte and generally increases on dilution.

Step 3: Conclusion (i) The concentrations of Zn^{2+} and Ag^{+} remain constant at their equilibrium values when $E_{\text{cell}} = 0$. (ii) Conductivity decreases on dilution because the number of charge carriers per unit volume decreases.

Quick Tip to Solve: At zero cell emf, write equilibrium and constant concentrations; for dilution, distinguish conductivity from molar conductivity.

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 by $\Lambda_{\mathrm{m}} = 1000\kappa/C$ 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 because $1\,\mathrm{L} = 1000\,\mathrm{cm^3}$.

Step 1: Identify the given quantities and rearrange The concentration is $C = 1.5\,\mathrm{mol\,L^{-1}}$ and the molar conductivity is $\Lambda_{\mathrm{m}} = 138.9\,\mathrm{S\,cm^2\,mol^{-1}}$. Solving the molar-conductivity relation for conductivity

Quick Tip to Solve: With molarity in mol per litre and molar conductivity in centimetre units, divide the product by 1000 to obtain conductivity.

gives

$$\kappa = \frac{\Lambda_m C}{1000}.$$

Step 2: Substitute and check the units Substitution gives

$$\kappa = \frac{138.9 \times 1.5}{1000} = \frac{208.35}{1000} = 0.20835\,\mathrm{S\,cm^{-1}}.$$

Equivalently, the concentration is $0.0015\,\mathrm{mol\,cm^{-3}}$. Multiplying this by the given molar conductivity cancels mol and leaves $\mathrm{S\,cm^{-1}}$, confirming the required conductivity unit.

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 molar conductivity in centimetre units, divide the product by 1000 to obtain conductivity.