

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

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 2 hours

Maximum Marks: 35

General Instructions

- (i) This question paper contains **12** questions. **All** questions are compulsory.
- (ii) This question paper is divided into **three** Sections – **Section A, B and C**.
- (iii) **Section - A** Q. Nos. **1 to 3** are very short answer type questions carrying **2** marks each.
- (iv) **Section - B** Q. Nos. **4 to 11** are short answer type questions carrying **3** marks each.
- (v) **Section - C** Q. No. **12** is case based question carrying **5** marks.
- (vi) Use of log tables and calculators is NOT allowed.

Section A (6 marks)

1. Define rate of reaction. Write two factors that affect the rate of reaction.

[2 marks]

Solution:

Concept:

- Reaction rate measures the change in concentration of a reactant or a product per unit time. Reactants disappear, whereas products form as the reaction proceeds.
- For a reaction with unit stoichiometric coefficients, the instantaneous rate is $r = -d[R]/dt = d[P]/dt$, where $[R]$ and $[P]$ are reactant and product concentrations and t is time.

Step 1: Define the rate of reaction The rate of a reaction is the decrease in concentration of a reactant or the increase in concentration of a product per unit time. For a finite time interval, the average rate for unit stoichiometric coefficients is

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}.$$

The negative sign for the reactant makes the rate positive because its concentration decreases. A usual unit is $\text{mol L}^{-1}\text{s}^{-1}$.

Step 2: Identify two factors affecting the rate **Concentration of reactants:** Increasing reactant concentration generally increases the frequency of collisions between reacting particles and hence increases the rate.

Temperature: Increasing temperature generally increases the fraction of particles with energy at least equal to the activation energy. More collisions are effective, so the reaction is faster.

Step 3: Conclusion Rate of reaction is the change in reactant or product concentration per unit time. Two factors affecting it are **reactant concentration** and **temperature**.

Quick Tip to Solve: Use a minus sign with decreasing reactant concentration and a plus sign with increasing product concentration; name concentration and temperature as two distinct rate factors.

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

(i) In decreasing order of basic strength in aqueous solution: $\text{C}_2\text{H}_5\text{NH}_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$

(ii) In increasing order of solubility in water: $(\text{C}_2\text{H}_5)_2\text{NH}$, $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NH}_2$

(iii) In decreasing order of their pK_b values: $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_2\text{H}_5\text{NH}_2$, NH_3

[2 marks]

Solution:

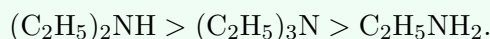
Concept:

- The basic strength of an amine in water depends on the electron-releasing effect of its alkyl groups, solvation of the conjugate acid and steric effects.
- Hydrogen bonding favours water solubility, whereas a larger hydrocarbon group reduces it. Also, $pK_b = -\log K_b$: a stronger base has a smaller pK_b .

Step 1: Compare basic strength in aqueous solution For the given ethylamines in water, the combined

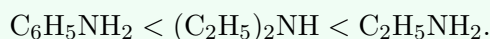
Quick Tip to Solve: For aqueous ethylamines use secondary, tertiary, primary in decreasing basic strength; reverse the basic-strength order whenever decreasing pK_b is asked.

effects of electron release and hydration give the decreasing order



Diethylamine has the most favourable balance. Triethylamine is less well hydrated than diethylamine, but its stronger electron-releasing effect makes it more basic than ethylamine in this series. The gas-phase order based only on electron release must not be used here.

Step 2: Compare solubility in water The increasing order of solubility is



All three can interact with water through hydrogen bonding. However, aniline has a large hydrophobic phenyl group, while diethylamine has a larger hydrocarbon portion than ethylamine. Ethylamine therefore has the most favourable balance for dissolution in water.

Step 3: Convert basic strength into the order of pK_b Ethylamine is more basic than ammonia because its ethyl group releases electron density towards nitrogen. Aniline is less basic than ammonia because the nitrogen lone pair is delocalised into the benzene ring. Thus the base-strength order is



Since pK_b decreases as K_b increases, reverse this order to obtain decreasing pK_b .

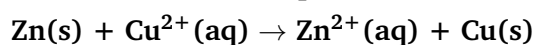
Step 4: Conclusion The required orders are:

- (i) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2$,
- (ii) $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$,
- (iii) $pK_b(\text{C}_6\text{H}_5\text{NH}_2) > pK_b(\text{NH}_3) > pK_b(\text{C}_2\text{H}_5\text{NH}_2)$.

Any two of these arrangements may be written as requested.

Quick Tip to Solve: For aqueous ethylamines use secondary, tertiary, primary in decreasing basic strength; reverse the basic-strength order whenever decreasing pK_b is asked.

3. Write the Nernst equation for the following cell reaction:



How will the E_{cell} be affected when concentration of

- (i) Cu^{2+} ions is increased and
- (ii) Zn^{2+} ions is increased?

[2 marks]

Solution:

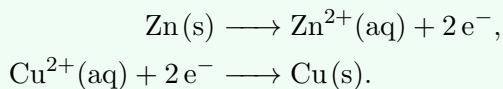
Concept:

- The Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (RT/nF) \ln Q$, where Q is the reaction quotient, n is the number of transferred electrons, R is the gas constant, T is temperature and F is the Faraday constant.

Quick Tip to Solve: Put the dissolved product ion over the dissolved reactant ion in Q ; the minus sign in the Nernst equation means a larger Q gives a smaller cell potential.

- Pure solids have unit activity and do not appear in Q . For dilute solutions, ionic activities are approximated by concentrations relative to the standard concentration.

Step 1: Form the reaction quotient and Nernst equation Zinc loses two electrons and copper(II) ions gain them:



Therefore $n = 2$. Omitting the pure solids gives $Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}]$. Hence,

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}.$$

At 298 K, this becomes

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591\text{ V}}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}.$$

Step 2: Increase the copper(II) ion concentration At fixed temperature and fixed $[\text{Zn}^{2+}]$, increasing $[\text{Cu}^{2+}]$ decreases Q . Its logarithm decreases, so the term subtracted from E_{cell}° becomes smaller. Thus E_{cell} increases.

Step 3: Increase the zinc ion concentration At fixed temperature and fixed $[\text{Cu}^{2+}]$, increasing $[\text{Zn}^{2+}]$ increases Q . Its logarithm increases, so a larger term is subtracted from E_{cell}° . Thus E_{cell} decreases.

Step 4: Conclusion The Nernst equation is

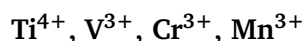
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}.$$

Increasing $[\text{Cu}^{2+}]$ increases the cell potential, whereas increasing $[\text{Zn}^{2+}]$ decreases it, keeping the other concentration and temperature fixed.

Quick Tip to Solve: Put the dissolved product ion over the dissolved reactant ion in Q ; the minus sign in the Nernst equation means a larger Q gives a smaller cell potential.

Section B (24 marks)

4. Following ions of 3d-transition series are given:



(Atomic number: Ti = 22, V = 23, Cr = 24, Mn = 25)

Identify the ion which is

- (i) most stable in aqueous solution.
- (ii) a strong oxidising agent.
- (iii) colourless in aqueous solution.

Give suitable reason in each.

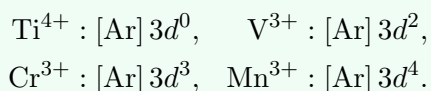
[3 marks]

Solution:

Concept:

- To obtain a transition-metal ion's configuration, remove the 4s electrons before the 3d electrons. The resulting d-electron count helps explain its stability and colour.
- An oxidising agent accepts electrons and is itself reduced. Formation of a stable half-filled $3d^5$ configuration can favour reduction.
- In an aqueous transition-metal ion, absorption of visible light can promote a d electron between split d levels. A d^0 ion cannot undergo this d-d transition.

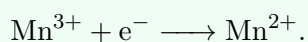
Step 1: Determine the ionic configurations Using the given atomic numbers and removing the outer 4s electrons first gives



These counts refer to the ions, rather than to the neutral atoms.

Step 2: Identify the most stable aqueous ion (i) Cr^{3+} is particularly stable in aqueous solution because its $3d^3$ configuration places one electron in each of the three lower-energy t_{2g} orbitals of the octahedral aqua complex. Its configuration is $t_{2g}^3 e_g^0$, with no electron pairing required. The crystal-field stabilisation is $-1.2\Delta_o$, where Δ_o is the octahedral splitting energy. This stabilised configuration favours the chromium(III) state.

Step 3: Identify the strong oxidising agent (ii) Mn^{3+} readily accepts one electron:



The $3d^4$ configuration changes to the especially stable half-filled $3d^5$ configuration of Mn^{2+} . Since Mn^{3+} gains an electron, it causes another species to lose an electron and therefore acts as a strong oxidising agent.

Step 4: Identify the colourless aqueous ion (iii) Ti^{4+} has the $3d^0$ configuration. There is no d electron available for excitation between the split d orbitals, so no visible-light d-d absorption occurs. It is therefore colourless in aqueous solution. The other listed ions have partly occupied d subshells.

Step 5: Conclusion (i) Most stable: Cr^{3+} , owing to its stabilised t_{2g}^3 configuration. (ii) Strong oxidising agent: Mn^{3+} , which is reduced to half-filled $3d^5$ Mn^{2+} . (iii) Colourless: Ti^{4+} , because it is

Quick Tip to Solve: First write the four ion counts as d^0, d^2, d^3, d^4 . Use d^0 for colourlessness, d^3 for chromium(III) stability, and the change $d^4 \rightarrow d^5$ for manganese(III)'s oxidising action.

$3d^0$.

Quick Tip to Solve: First write the four ion counts as d^0, d^2, d^3, d^4 . Use d^0 for colourlessness, d^3 for chromium(III) stability, and the change $d^4 \rightarrow d^5$ for manganese(III)'s oxidising action.

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

[3 marks]

Solution:

Concept:

- In an octahedral field, t_{2g} orbitals lie below e_g orbitals. If the splitting energy Δ_o is less than the pairing energy P , electrons occupy upper orbitals before pairing.
- In valence bond theory, the available metal orbitals determine hybridisation. A complex with all electrons paired is diamagnetic.
- A complex's charge is the metal oxidation state plus ligand charges. Ethane-1,2-diamine, en, is neutral and bidentate; chlorido carries charge -1 .

Step 1: Fill the octahedral orbitals for part (i) The first three electrons of a d^4 ion singly occupy the three t_{2g} orbitals. Since $\Delta_o < P$, the fourth electron occupies an e_g orbital rather than pairing in t_{2g} . The high-spin configuration is therefore



with four unpaired electrons.

Step 2: Apply valence bond theory for part (ii) In $[\text{Ni}(\text{CN})_4]^{2-}$, each cyanido ligand has charge -1 . The nickel oxidation state x satisfies

$$x + 4(-1) = -2 \Rightarrow x = +2.$$

Nickel has configuration $[\text{Ar}] 3d^8 4s^2$, so Ni^{2+} is $[\text{Ar}] 3d^8$. Strong-field CN^- ligands cause the eight $3d$ electrons to pair in four orbitals, leaving one $3d$ orbital vacant. This orbital, the $4s$ and two $4p$ orbitals form four dsp^2 hybrid orbitals that accept ligand electron pairs. The complex is square planar. All electrons are paired, so it is diamagnetic.

Step 3: Construct the formula for part (iii) Dichlorido specifies two Cl^- ligands; bis(ethane-1,2-diamine) specifies two neutral en ligands. Cobalt(III) has oxidation state $+3$, giving the complex charge

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

The formula is $[\text{CoCl}_2(\text{en})_2]^+$. Two bidentate en ligands and two chlorido ligands give coordination number six. The name specifies no counter-ion, so write the charged coordination entity.

Quick Tip to Solve: For $\Delta_o < P$, promote before pairing. For the cobalt formula, add two neutral en ligands and two Cl^- ligands to cobalt(III), giving overall charge $+1$.

Step 4: Conclusion (i) $t_{2g}^3 e_g^1$, high spin. (ii) dsp^2 hybridisation and diamagnetic character (square planar). (iii) $[\text{CoCl}_2(\text{en})_2]^+$.

Quick Tip to Solve: For $\Delta_o < P$, promote before pairing. For the cobalt formula, add two neutral en ligands and two Cl^- ligands to cobalt(III), giving overall charge +1.

OR

5(b). When a co-ordination compound $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is mixed with AgNO_3 , 2 moles of AgCl are precipitated per mole of the compound. Write

(i) Structural formula of the complex.

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

(iii) IUPAC name of the complex.

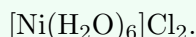
[3 marks]

Solution:

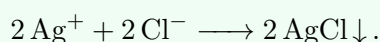
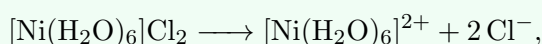
Concept:

- In Werner's theory, primary valency is the oxidation state of the metal, whereas secondary valency is its coordination number: the number of donor atoms directly bonded to it.
- Chloride ions outside the coordination sphere are ionisable and precipitate with silver ions as AgCl . Water is a neutral, monodentate ligand called aqua.

Step 1: Locate the chloride ions and write the structural formula One mole of the compound gives two moles of AgCl , so both chloride ions are outside the coordination sphere. They are counterions, rather than ligands bonded directly to nickel. The six water molecules occupy the coordination sphere around Ni^{2+} . Thus, for part (i), the structural formula is



Its ionisation and the precipitation test can be represented as



This accounts for exactly the observed amount of silver chloride.

Step 2: Count the donor atoms for the secondary valency For part (ii), each of the six water ligands donates one oxygen lone pair to nickel. The coordination number, and hence the secondary valency of nickel, is therefore 6. Do not confuse it with the primary valency, which is 2 here.

Step 3: Name the complex using IUPAC rules For part (iii), six aqua ligands give the prefix hexaaqua. Since water is neutral and the complex cation has charge +2, nickel is in oxidation state +2. Name the cation before the chloride counterion. The IUPAC name is **hexaaquanickel(II) chloride**.

Step 4: Conclusion (i) Structural formula: $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$; (ii) secondary valency: 6; (iii) IUPAC name: **hexaaquanickel(II) chloride**.

Quick Tip to Solve: First count the chloride ions precipitated by silver nitrate: put these outside the square brackets, then count the donor atoms inside to obtain the secondary valency.

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

[Given: $\log 2 = 0.3010$, $\log 10 = 1$]

[3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial amount, x is the amount reacted in time t , and k is the rate constant. The logarithm is to base ten.
- At half-completion, the amount remaining is $a/2$, so $t_{1/2} = 2.303 \log 2/k$. The half-life of a first-order reaction is independent of its initial amount.

Step 1: Use the half-completion time to find the rate constant The reaction is 50% complete in 40 min, so $t_{1/2} = 40$ min. At this time the initial-to-remaining amount ratio is $a/(a/2) = 2$. Substituting the given logarithm,

$$\begin{aligned}k &= \frac{2.303}{40} \log 2 \\&= \frac{2.303 \times 0.3010}{40} \\&= 0.017330075 \text{ min}^{-1}.\end{aligned}$$

Retain the given logarithms in the next calculation to avoid unnecessary rounding.

Step 2: Calculate the time for ninety percent completion When 90% has reacted, 10% remains. Hence $a - x = 0.10a$, and the ratio in the integrated rate law is $a/(0.10a) = 10$, not $100/90$. Therefore,

$$\begin{aligned}t_{90} &= \frac{2.303}{k} \log 10 \\&= 40 \frac{\log 10}{\log 2} \\&= \frac{40 \times 1}{0.3010} \\&\approx 132.89 \text{ min}.\end{aligned}$$

This is the total elapsed time from the start of the reaction. It exceeds three half-lives, as three half-lives give only 87.5% completion, which is consistent with the calculated value.

Step 3: Conclusion The time required for 90% completion is 132.9 min, approximately 133 min.

Quick Tip to Solve: Divide the first-order time formula by the half-life formula: $t_{90}/t_{1/2} = \log 10 / \log 2$. Always use the percentage remaining in the denominator.

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

(i) Gabriel phthalimide synthesis.

(ii) Carbylamine reaction.

(iii) Hoffmann bromamide degradation reaction.

[3 marks]

Solution:

Concept:

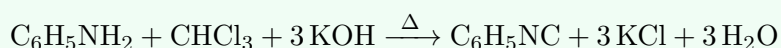
- Gabriel synthesis makes a primary aliphatic amine by alkylating potassium phthalimide, followed by hydrolysis. In the condensed formula below, $C_6H_4(CO)_2NH$ denotes cyclic phthalimide with adjacent carbonyl groups.
- The carbylamine reaction converts a primary amine into an isocyanide on heating with chloroform and alcoholic potassium hydroxide. Secondary and tertiary amines do not give this test.
- Hoffmann bromamide degradation converts a primary amide into a primary amine containing one carbon atom fewer, using bromine and aqueous alkali.

Step 1: Illustrate Gabriel phthalimide synthesis Treat phthalimide with alcoholic KOH to replace its acidic nitrogen-bound hydrogen with potassium. React the resulting salt with bromoethane and then hydrolyse the N-ethyl derivative:



The last equation represents the overall hydrolysis and isolation of ethylamine. The alkyl group becomes attached to nitrogen without further alkylation of the product.

Step 2: Illustrate the carbylamine reaction Heat aniline with chloroform and alcoholic KOH. The primary amino group becomes an isocyanide group, giving phenyl isocyanide with an offensive smell:



Both aliphatic and aromatic primary amines respond. The product has the connectivity $R-NC$, rather than the nitrile connectivity $R-CN$; this distinction is essential when writing the product.

Step 3: Illustrate Hoffmann bromamide degradation Warm ethanamide with bromine and aqueous sodium hydroxide:



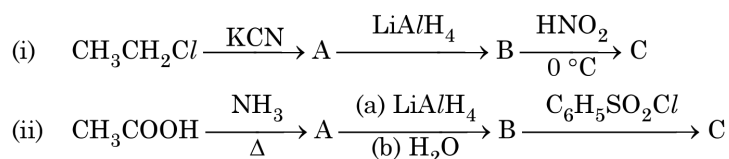
The carbonyl carbon is removed from the organic chain and appears in carbonate. Thus ethanamide, with two carbon atoms, gives methylamine, with one carbon atom. The alkyl group attached to the carbonyl carbon becomes attached directly to nitrogen.

Step 4: Conclusion The examples give ethylamine by Gabriel synthesis, phenyl isocyanide by the carbylamine reaction, and methylamine by Hoffmann degradation.

Quick Tip to Solve: Track the carbon skeleton: Gabriel retains the alkyl-halide chain, carbylamine adds an isocyanide carbon, and Hoffmann degradation removes the amide carbonyl carbon.

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

[3 marks]

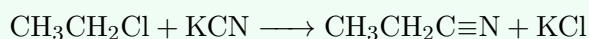


Solution:

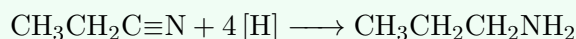
Concept:

- Cyanide ion replaces halide through its carbon atom to form a nitrile, increasing the carbon chain by one. LiAlH_4 reduces a nitrile group $-\text{CN}$ to $-\text{CH}_2\text{NH}_2$.
- Nitrous acid converts a primary aliphatic amine into the corresponding alcohol with liberation of nitrogen gas.
- Heating a carboxylic acid with ammonia gives an amide. Reduction gives an amine, which reacts with benzenesulphonyl chloride to form a sulphonamide.

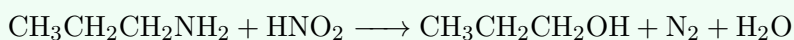
Step 1: Identify the products in sequence (i) Chloroethane undergoes nucleophilic substitution with KCN:



A is propanenitrile. The nitrile carbon increases the chain to three carbons. Reduction retains all three:



B is propan-1-amine. Nitrous acid at 0°C replaces its amino group by hydroxyl:

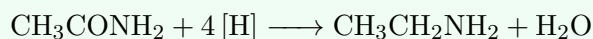


C is propan-1-ol; the intermediate aliphatic diazonium salt is unstable.

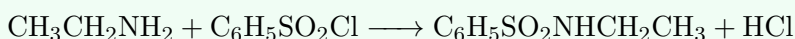
Step 2: Identify the products in sequence (ii) Ethanoic acid first forms ammonium ethanoate with ammonia. Heating eliminates water to form the amide:



A is ethanamide. Reduction with LiAlH_4 , followed by water, converts carbonyl to methylene:



B is ethanamine. Benzenesulphonyl chloride replaces one nitrogen-bound hydrogen:



C is N-ethylbenzenesulphonamide; its nitrogen retains one hydrogen.

Step 3: Conclusion (i) A: $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$, B: $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, C: $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$.

(ii) A: $\text{CH}_3\text{C}(=\text{O})\text{NH}_2$, B: $\text{CH}_3\text{CH}_2\text{NH}_2$, C: $\text{C}_6\text{H}_5-\text{S}(=\text{O})_2-\text{NH}-\text{CH}_2\text{CH}_3$.

Quick Tip to Solve: Count carbons after each arrow: KCN adds one carbon, whereas LiAlH_4 retains every carbon. In the last product of (ii), connect the ethyl group to nitrogen, not to sulphur.

8(a). Account for the following:

- (i) Transition elements have higher enthalpies of atomisation.
- (ii) Separation of a mixture of Lanthanoid elements is difficult.
- (iii) The $E_{M^{2+}/M}^\circ$ value for copper is positive.

[3 marks]

Solution:

Concept:

- Enthalpy of atomisation is the enthalpy required to form one mole of gaseous atoms from an element in its standard state; stronger metallic bonding requires more energy.
- The separation of elements depends on differences in their chemical properties, which are strongly affected by ionic charge and ionic radius.
- The standard reduction potential E° describes reduction relative to the standard hydrogen electrode. For copper it refers to $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$.

Step 1: (i) Relate atomisation to metallic bonding Transition elements have several unpaired electrons in their partly filled d subshells. Electrons from both the $(n - 1)d$ and ns subshells participate in metallic bonding. This produces strong interatomic attraction in their metallic lattices, so considerable energy is needed to separate the atoms into gaseous atoms. Hence their enthalpies of atomisation are generally high.

Step 2: (ii) Compare the lanthanoid ions Lanthanoids occur predominantly in the +3 oxidation state. Their tripositive ions have very similar ionic radii because the radius decreases only gradually across the series through lanthanoid contraction. Equal charge and very similar size give them almost identical chemical properties. Consequently, ordinary chemical methods do not readily distinguish one lanthanoid from another, making separation of their mixture difficult.

Step 3: (iii) Examine the energy balance for copper Formation of aqueous Cu^{2+} from copper metal involves atomisation, the first and second ionisation enthalpies, and hydration of the resulting gaseous ion. Copper has a large atomisation enthalpy and a large total ionisation enthalpy; in particular, the second electron must be removed from the stable $3d^{10}$ configuration of Cu^+ . The hydration enthalpy of Cu^{2+} does not compensate for these energy requirements. Thus copper resists oxidation to $\text{Cu}^{2+}(\text{aq})$ relative to hydrogen, and its standard reduction potential is positive.

Step 4: Conclusion Strong metallic bonding explains high atomisation enthalpies; similar +3 ions explain difficult lanthanoid separation; and insufficient hydration compensation for copper's atomisation and ionisation requirements explains its positive $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$.

Quick Tip to Solve: Link atomisation to metallic bond strength, lanthanoid separation to ionic similarity, and copper's potential to the full atomisation–ionisation–hydration balance.

8(b). Define transition elements. Which of the d-block elements may not be regarded as the transition elements? Why transition metals generally form coloured compounds? [3 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its common oxidation states.
- A d^{10} configuration has all five d orbitals completely filled. Being in the d -block alone does not ensure that an element satisfies the definition of a transition element.
- Ligands split the metal ion's d orbitals into groups of different energies. Absorption of light with energy $h\nu = \Delta$, where Δ is the energy gap, can cause a $d-d$ electronic transition.

Step 1: State the definition of transition elements Transition elements are elements whose atoms have partially filled d orbitals, or which form cations with partially filled d orbitals in a common oxidation state. The electronic configurations of both the atom and its ions must therefore be considered. A completely filled d subshell in the neutral atom alone does not exclude an element if one of its common cations has an incomplete d subshell.

Step 2: Identify the excluded d-block elements Zinc, cadmium and mercury are generally not regarded as transition elements. Their atomic outer configurations are respectively $3d^{10}4s^2$, $4d^{10}5s^2$ and $5d^{10}6s^2$. Their common +2 ions, Zn^{2+} , Cd^{2+} and Hg^{2+} , retain the completely filled d^{10} subshell. Thus they lack a partially filled d subshell in their atoms and usual ions.

Step 3: Explain the origin of colour In a transition-metal compound, the electric field of the surrounding ligands removes the equal-energy character of the five d orbitals. When the metal ion has a partially filled d subshell, an electron can absorb a suitable wavelength of visible light and move from a lower-energy d orbital to a higher-energy one. The remaining transmitted or reflected light gives the compound the colour complementary to the absorbed light. Different ions and ligands produce different energy gaps, so the colours vary. This explains the general trend; d^0 and d^{10} ions cannot undergo these $d-d$ transitions, although other mechanisms can sometimes give their compounds colour.

Step 4: Conclusion Transition elements possess an incomplete d subshell in the atom or a common ion. Zinc, cadmium and mercury are excluded because their d subshells remain full in their usual states. Transition-metal compounds are generally coloured because they absorb visible light during $d-d$ transitions.

Quick Tip to Solve: Check the atom and its common ions before classifying an element; for colour, connect a partly filled d subshell to ligand splitting and selective visible-light absorption.

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

(i) Structure of the compound 'X'.

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

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

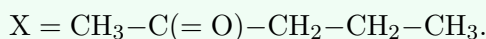
[3 marks]

Solution:

Concept:

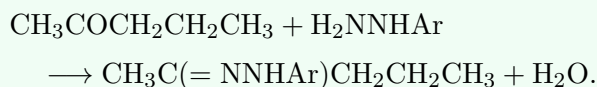
- Formation of a 2,4-dinitrophenylhydrazone identifies an aldehyde or ketone. A negative Tollens' test indicates that the given carbonyl compound is a ketone.
- A methyl ketone, $RCOCH_3$, gives the iodoform test. With iodine and aqueous sodium hydroxide it forms yellow CHI_3 and the sodium carboxylate $RCOONa$.

Step 1: (i) Identify the carbon skeleton The 2,4-DNP test and negative Tollens' test establish a ketone, while the positive iodoform test requires the group CH_3CO- . With molecular formula $C_5H_{10}O$, the remaining group contains three carbon atoms. Vigorous oxidation giving ethanoic acid and propanoic acid is consistent with the straight-chain methyl ketone:



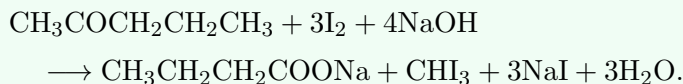
This is pentan-2-one. Pentan-3-one lacks the methyl ketone group, while the branched methyl ketone does not give the stated oxidation products.

Step 2: (ii) Form the 2,4-DNP derivative Condensation with 2,4-dinitrophenylhydrazine eliminates water. Put $Ar = C_6H_3(NO_2)_2$, where the nitro groups occupy positions 2 and 4 relative to the hydrazine substituent. Then



The organic product is pentan-2-one 2,4-dinitrophenylhydrazone.

Step 3: (iii) Obtain the iodoform-reaction products In CH_3CO-R , here $R = CH_2CH_2CH_3$. The methyl carbon becomes iodoform, while the carbonyl carbon remains in the carboxylate. The balanced reaction is



The organic products are sodium butanoate, $CH_3CH_2CH_2C(=O)O^-Na^+$, and yellow iodoform, $H-C(I)_3$. The alkaline medium gives the sodium carboxylate.

Step 4: Conclusion (i) $X = CH_3COCH_2CH_2CH_3$, pentan-2-one. (ii) Its 2,4-DNP derivative is $CH_3C(=NNHC_6H_3(NO_2)_2)CH_2CH_2CH_3$, with nitro groups at positions 2 and 4. (iii) The organic products are $CH_3CH_2CH_2COONa$ and CHI_3 .

Quick Tip to Solve: For an iodoform reaction, separate the methyl carbon from CH_3CO-R : it becomes CHI_3 , while $RCOONa$ retains the carbonyl carbon.

10(a). Write any three differences between physisorption and chemisorption.

[3 marks]

Solution:

Concept:

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

Step 1: First difference: nature of the attractive forces In physisorption, adsorbate particles are held on the surface by weak van der Waals forces, without formation of chemical bonds with the surface. In chemisorption, particles are held through chemical bond formation, so the interaction is much stronger. This distinction concerns the way a particle attaches to the surface, rather than simply the amount adsorbed.

Step 2: Second difference: enthalpy of adsorption Physisorption has a relatively low magnitude of enthalpy of adsorption, usually about $20\text{--}40\text{ kJ mol}^{-1}$. Chemisorption has a relatively high magnitude, usually about $80\text{--}240\text{ kJ mol}^{-1}$, because chemical bonds form. Adsorption is generally exothermic; these positive numerical ranges state the magnitudes of the heat released, while the enthalpy change itself is negative.

Step 3: Third difference: specificity Physisorption is not highly specific: van der Waals forces can act between many different adsorbates and surfaces. Chemisorption is highly specific: it occurs when the particular adsorbate and surface can form suitable chemical bonds. Consequently, a surface that chemisorbs one gas need not chemisorb every other gas under the same conditions.

Step 4: Conclusion The three differences are: physisorption involves weak van der Waals forces, low adsorption enthalpy magnitude and little specificity; chemisorption involves chemical bonds, high adsorption enthalpy magnitude and high specificity.

Quick Tip to Solve: Start with the force involved: weak van der Waals attraction predicts low heat release and little specificity, while chemical bonding predicts stronger heat release and high specificity.

OR

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

(i) Lyophilic sol

(ii) Macromolecular colloid

(iii) Coagulation

[3 marks]

Solution:

Concept:

- A colloid contains a dispersed phase distributed throughout a dispersion medium; the dispersed particles have dimensions in the colloidal range.
- Lyophilic describes affinity for the medium, while macromolecular describes the size and molecular

Quick Tip to Solve: Pair each definition with its defining feature: lyophilic means solvent affinity, macromolecular means one giant molecule per particle, and coagulation means aggregation followed by separation.

nature of the dispersed particles.

- Coagulation is the aggregation of colloidal particles to form larger particles that separate from the dispersion.

Step 1: Define a lyophilic sol A lyophilic sol is a colloidal dispersion in which the dispersed phase has a strong affinity for the dispersion medium. It is readily formed by directly mixing the substance with a suitable medium and is generally stable and reversible because the particles are strongly solvated. For example, starch dispersed in water forms a lyophilic sol; with water as the medium it is also called a hydrophilic sol.

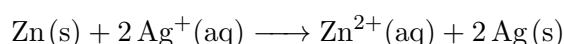
Step 2: Define a macromolecular colloid A macromolecular colloid is a dispersion of substances whose individual molecules are already large enough to have colloidal dimensions. On dissolution in a suitable solvent, each giant molecule acts as a colloidal particle; it need not arise by aggregation of many small molecules. For example, a protein solution in water is a macromolecular colloid. Starch and cellulose are other examples of macromolecular substances.

Step 3: Explain coagulation with an example Coagulation is the process in which colloidal particles aggregate into larger particles and separate out as a precipitate. In a charged sol, an added electrolyte can neutralise the particle charge, reducing electrostatic repulsion and allowing aggregation. For example, adding sufficient NaCl solution to a negatively charged arsenic sulphide sol, As_2S_3 , coagulates it; Na^+ acts as the oppositely charged coagulating ion.

Step 4: Conclusion Lyophilic sols have strong dispersed-phase-medium affinity (starch in water); macromolecular colloids contain individual giant molecules of colloidal size (protein in water); coagulation is aggregation and precipitation of colloidal particles (As_2S_3 sol on adding sufficient NaCl).

Quick Tip to Solve: Pair each definition with its defining feature: lyophilic means solvent affinity, macromolecular means one giant molecule per particle, and coagulation means aggregation followed by separation.

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



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

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

Solution:

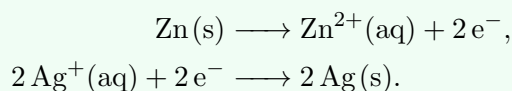
Concept:

- Standard Gibbs energy and cell potential satisfy $\Delta_r G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred and $F = 96500 \text{ C mol}^{-1}$ is the Faraday constant.
- Kohlrausch's law gives limiting molar conductivity as the sum of limiting ionic conductivities multiplied by the respective stoichiometric coefficients.

Step 1: Determine the electron transfer in part (a) Zinc loses two electrons, while each silver ion

Quick Tip to Solve: Use two electrons for zinc oxidation, convert kJ to J before finding volts, and count two chloride ions in the conductivity sum.

gains one:



The balanced cell reaction therefore transfers $n = 2$ electrons.

Step 2: Calculate the standard cell potential Convert -300 kJ mol^{-1} to $-300000\text{ J mol}^{-1}$, so that division by charge gives volts:

$$\begin{aligned}E_{\text{cell}}^{\circ} &= -\frac{\Delta_{\text{r}}G^{\circ}}{nF} \\ &= -\frac{-300000}{2 \times 96500}\text{ J C}^{-1} \\ &= 1.5544 \dots \text{ V}.\end{aligned}$$

The positive potential agrees with the negative standard Gibbs energy of the forward reaction.

Step 3: Add the ionic conductivities in part (b) One mole of MgCl_2 gives one mole of Mg^{2+} and two moles of Cl^{-} . Thus

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

The factor two counts chloride ions; ionic conductivities need no extra charge factor.

Step 4: Conclusion (a) $E_{\text{cell}}^{\circ} = +1.55\text{ V}$ approximately. (b) $\Lambda_{\text{m}}^{\circ}(\text{MgCl}_2) = 258.6\text{ S cm}^2\text{ mol}^{-1}$.

Quick Tip to Solve: Use two electrons for zinc oxidation, convert kJ to J before finding volts, and count two chloride ions in the conductivity sum.

Section C (5 marks)

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

Aldehydes, ketones and carboxylic acids are some of the important classes of organic compounds containing carbonyl group. These are highly polar molecules due to higher electro-negativity of oxygen relative to carbon in the carbonyl group. Aldehydes are prepared by dehydrogenation or controlled oxidation of primary alcohols and controlled reduction of acyl halides. Ketones are prepared by oxidation of secondary alcohols and hydration of alkynes.

Aldehydes and ketones undergo nucleophilic addition reactions onto the carbonyl group but carboxylic acid does not undergo nucleophilic addition reaction. The alpha (α) hydrogens of aldehydes and ketones are acidic. Therefore aldehydes and ketones having at least one α -hydrogen undergo Aldol condensation.

Aldehydes are easily oxidised by mild oxidising agents such as Tollens' reagent and Fehling's reagent. Carboxylic acids are prepared by the oxidation of primary alcohols, aldehydes and by hydrolysis of nitriles. Aromatic carboxylic acids are prepared by side-chain oxidation of alkyl benzenes. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

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

CH_3COCH_3 , CH_3CHO , HCHO , $\text{C}_6\text{H}_5\text{COCH}_3$

[1 mark]

Solution:

Concept:

- Nucleophiles attack the electron-deficient carbonyl carbon. Greater positive character and less steric hindrance favour nucleophilic addition.
- Alkyl groups donate electron density by the +I effect; conjugation of a carbonyl group with a phenyl ring also reduces its susceptibility to nucleophilic attack.

Step 1: Compare the aliphatic carbonyl compounds Formaldehyde, HCHO , has no alkyl group and the least steric hindrance. Ethanal, CH_3CHO , has one electron-donating methyl group, while acetone, CH_3COCH_3 , has two. Increasing alkyl substitution reduces the positive character of the carbonyl carbon and makes nucleophilic approach more difficult.

Step 2: Place acetophenone relative to acetone In acetophenone, $\text{C}_6\text{H}_5\text{COCH}_3$, the carbonyl group is conjugated with the phenyl ring. Resonance decreases the electrophilic character of the carbonyl carbon, and the bulky phenyl group increases steric hindrance. It is therefore less reactive towards nucleophilic addition than acetone.

Step 3: Conclusion The increasing order of reactivity is



Quick Tip to Solve: Put formaldehyde last in an increasing-reactivity order, then check whether an aromatic carbonyl is further deactivated by conjugation.

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

[1 mark]

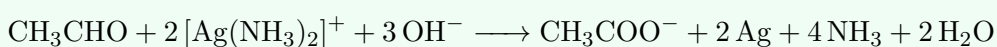
Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing the complex ion $[\text{Ag}(\text{NH}_3)_2]^+$. It oxidises an aldehyde while silver(I) is reduced to metallic silver.
- Ethanal, CH_3CHO , is an aldehyde; propanone, CH_3COCH_3 , is a ketone and does not undergo this mild oxidation.

Step 1: Apply Tollens' test Add freshly prepared Tollens' reagent separately to small samples of the two compounds in clean test tubes and warm gently in a water bath. Look for a deposit of metallic silver on the tube wall.

Step 2: Compare the observations Ethanal produces a silver mirror as it is oxidised to ethanoate in the alkaline reagent. Propanone gives no silver mirror under the same conditions.



Step 3: Conclusion Tollens' test distinguishes the compounds: ethanal gives a silver mirror, whereas propanone does not.

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

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

[1 mark]

Solution:

Concept:

- Nucleophilic addition is favoured when the carbonyl carbon is sufficiently electrophilic, as in aldehydes and ketones.
- In a carboxylic acid, RCOOH , a lone pair on the hydroxyl oxygen participates in resonance with the carbonyl group. Here R denotes a hydrogen atom or an organic group.

Step 1: Examine electron delocalisation The hydroxyl oxygen donates electron density towards the carbonyl carbon through resonance. This reduces the positive character of that carbon and makes it less susceptible to nucleophilic attack than the carbonyl carbon of an aldehyde or ketone.

Step 2: Relate the structure to the reaction Consequently, carboxylic acids do not show the usual nucleophilic addition reactions of aldehydes and ketones. When they react at the acyl group under suitable conditions, the addition intermediate can eliminate a group to restore the carbonyl, giving an acyl substitution product. Basic nucleophiles can also remove the acidic proton instead.

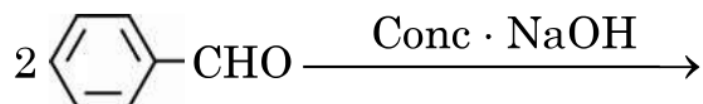
Step 3: Conclusion Resonance donation from the hydroxyl oxygen decreases the electrophilicity of the carbonyl carbon, so carboxylic acids do not undergo typical aldehyde- and ketone-like nucleophilic addition.

Quick Tip to Solve: Identify the oxygen directly bonded to the carbonyl carbon: its lone-pair donation explains the reduced tendency towards nucleophilic addition.

12(d). (i) Why α -hydrogen of aldehydes and ketones are acidic in nature?

(ii) Write the products in the following:

[2 marks]

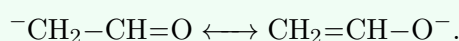


Solution:

Concept:

- An α -hydrogen is bonded to the carbon adjacent to the carbonyl carbon. Its removal as a proton produces an enolate ion stabilised by resonance.
- Aldehydes without an α -hydrogen undergo the Cannizzaro reaction in concentrated alkali: one molecule is oxidised and another is reduced.

Step 1: Explain the acidity in part (i) The electron-withdrawing carbonyl group increases the tendency of an adjacent carbon-hydrogen bond to lose a proton. The resulting enolate ion delocalises its negative charge over the α -carbon and the oxygen atom, making the conjugate base more stable. For example, the resonance forms obtained from ethanal are



This stabilisation explains why the α -hydrogens of aldehydes and ketones are acidic compared with ordinary alkane hydrogens.

Step 2: Identify the reaction in part (ii) Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no α -hydrogen and therefore undergoes disproportionation with concentrated NaOH . One aldehyde molecule is reduced to benzyl alcohol, while the other is oxidised to sodium benzoate:



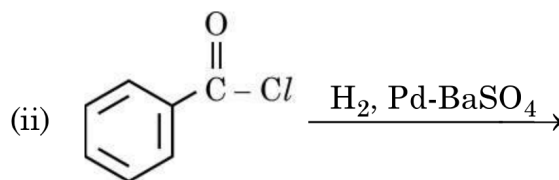
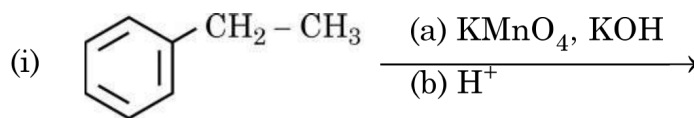
The product remains the carboxylate salt in this strongly alkaline medium; no acidification is specified.

Step 3: Conclusion (i) The α -hydrogens are acidic because proton loss forms a resonance-stabilised enolate ion. (ii) The products are benzyl alcohol, $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$, and sodium benzoate, $\text{C}_6\text{H}_5\text{COONa}$.

Quick Tip to Solve: Check for an α -hydrogen first: benzaldehyde lacks one, so concentrated alkali gives Cannizzaro products, including a carboxylate salt.

12(d). Write the major products of the following reactions:

[2 marks]



Solution:

Concept:

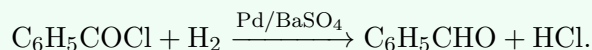
- Strong oxidation of an alkylbenzene having at least one benzylic hydrogen converts its side chain into a carboxyl group attached directly to the benzene ring.
- Rosenmund reduction converts an acyl chloride to an aldehyde using hydrogen over palladium supported on barium sulphate, Pd/BaSO₄.

Step 1: Oxidise the side chain in part (i) The starting compound is ethylbenzene, C₆H₅CH₂CH₃, which has benzylic hydrogens on the carbon next to the ring. Alkaline KMnO₄ oxidises the side chain to potassium benzoate. The subsequent acidification gives benzoic acid:



Only the carbon originally bonded directly to the ring becomes the carboxyl carbon; the ethyl side chain is not retained as a two-carbon carboxylic acid chain.

Step 2: Reduce the acyl chloride in part (ii) The starting compound is benzoyl chloride, C₆H₅COCl. Under Rosenmund conditions, hydrogen replaces the chlorine of the acyl chloride to give benzaldehyde. The controlled catalyst activity prevents further reduction to benzyl alcohol:



Step 3: Conclusion The major products are (i) benzoic acid, C₆H₅COOH, and (ii) benzaldehyde, C₆H₅CHO.

Quick Tip to Solve: For (i), shorten the benzylic side chain to -COOH after acidification; for (ii), recognise H₂/Pd-BaSO₄ as reduction of -COCl to -CHO.