

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-6-2 - Compartment



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 – **A**, **B** and **C**.
- (iii) **Section A** – Questions no. **1** to **3** are very short answer type questions, carrying **2 marks** each.
- (iv) **Section B** – Questions no. **4** to **11** are short answer type questions, carrying **3 marks** each.
- (v) **Section C** – Question no. **12** is case based question, carrying **5 marks**.
- (vi) Use of log tables and calculators is **not** allowed.

Section A (6 marks)

1. (a) For a reaction $R \rightarrow P$, half life ($t_{1/2}$) is independent of the initial concentration of reactants. What is the order of the reaction?

(b) Write one difference between order and molecularity of a reaction.

[2 marks]

Solution:

Concept:

- For a first-order reaction, the half-life is $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant; it does not contain the initial reactant concentration.
- The order is the sum of the powers of concentrations in the experimentally determined rate law. Molecularity counts reacting species in an elementary step.

Step 1: (a) Identify the reaction order The stated half-life is independent of the initial concentration $[R]_0$. This is the characteristic half-life relation of a first-order reaction:

$$t_{1/2} = \frac{0.693}{k}.$$

Thus changing $[R]_0$ does not change the time needed for half of the reactant to disappear, provided the temperature and hence k remain fixed.

Step 2: (b) Distinguish order from molecularity Order is determined experimentally from the rate law and may be zero, fractional or an integer. Molecularity is the number of reacting species taking part in a single elementary step and is always a positive integer. For example, a fractional reaction order is possible, whereas a fractional molecularity is not.

Step 3: Conclusion (a) The reaction is first order. (b) Order can be zero, fractional or an integer, whereas molecularity is always a positive integer.

Quick Tip to Solve: Check whether the half-life formula contains the initial concentration: its absence identifies first-order kinetics.

2. Answer the following questions (Any two):

(a) Define Molar Conductivity (Λ_m).

(b) Write the unit of Λ_m .

(c) How does Λ_m vary with concentration?

[2 marks]

Solution:

Concept:

- Molar conductivity Λ_m is the conductance of the volume of solution containing one mole of electrolyte, placed between electrodes of unit separation and sufficient area.
- The relation is $\Lambda_m = \kappa/c$ in consistent SI units, where κ is conductivity and c is the molar concentration in mol m^{-3} .

Step 1: (a) Define molar conductivity Molar conductivity is the conductance associated with the

volume of solution that contains one mole of dissolved electrolyte when the electrodes have unit separation and enough cross-sectional area to contain that volume. Equivalently, it is the conductivity divided by the molar concentration:

$$\Lambda_m = \frac{\kappa}{c}$$

Step 2: (b) State its unit Using κ in S m^{-1} and c in mol m^{-3} , the SI unit of Λ_m is $\text{S m}^2 \text{mol}^{-1}$. The commonly used laboratory unit is $\text{S cm}^2 \text{mol}^{-1}$.

Step 3: (c) Explain the concentration dependence Molar conductivity increases as concentration decreases, that is, on dilution. For strong electrolytes, reduced interionic interactions improve ionic mobility. For weak electrolytes, dilution additionally increases ionisation, so the rise is much more pronounced. Thus Λ_m decreases as concentration increases. Any two of the three requested parts may be selected.

Step 4: Conclusion $\Lambda_m = \kappa/c$; its SI unit is $\text{S m}^2 \text{mol}^{-1}$, and it increases on dilution.

Quick Tip to Solve: Distinguish molar conductivity from conductivity: dilution raises conductance per mole even though conductivity usually falls.

3. (a) Arrange the following compounds in the increasing order of their acidic character:

FCH_2COOH , $\text{NO}_2\text{CH}_2\text{COOH}$, $\text{C}_6\text{H}_5\text{COOH}$

(b) Write the IUPAC name of the given compound:

$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CHO}$

[2 marks]

Solution:

Concept:

- An electron-withdrawing substituent stabilises the carboxylate conjugate base and increases the acidity of a carboxylic acid.
- For an aldehyde, select the longest chain containing the --CHO carbon, number that carbon as 1, and use the suffix -al.

Step 1: (a) Compare the acidic strengths Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, is weaker than the two substituted acetic acids listed. Fluorine withdraws electron density by the negative inductive effect and stabilises FCH_2COO^- . The strongly electron-withdrawing nitro group stabilises $\text{NO}_2\text{CH}_2\text{COO}^-$ still more effectively, making nitroacetic acid the strongest of these three. Hence the increasing order is



Step 2: (b) Name the aldehyde The displayed structure is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$. Its longest chain contains four carbon atoms, including the carbonyl carbon of the aldehyde group. The parent saturated hydrocarbon is butane; replacing the terminal -e with -al gives butanal. The aldehyde carbon is automatically carbon 1, so no position number is needed.

Step 3: Conclusion (a) $\text{C}_6\text{H}_5\text{COOH} < \text{FCH}_2\text{COOH} < \text{NO}_2\text{CH}_2\text{COOH}$. (b) The IUPAC name is butanal.

Quick Tip to Solve: Count the aldehyde carbon in the parent chain: three carbons before CHO give a four-carbon aldehyde, butanal.

Section B (24 marks)

4. The conductivity of 0.001 mol L^{-1} solution of acetic acid is $3.905 \times 10^{-5} \text{ S cm}^{-1}$. Calculate its molar conductivity. If Λ_m^0 for acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$, then calculate its degree of dissociation (α). [3 marks]

Solution:

Concept:

- Molar conductivity is the conductance of the volume of solution containing one mole of electrolyte. For conductivity κ in S cm^{-1} and concentration C in mol L^{-1} , $\Lambda_m = 1000\kappa/C$.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^0$, where Λ_m^0 is its limiting molar conductivity at infinite dilution, when dissociation is complete.

Step 1: Calculate the molar conductivity Here $C = 0.001 \text{ mol L}^{-1}$ and $\kappa = 3.905 \times 10^{-5} \text{ S cm}^{-1}$. The factor 1000 converts the concentration from moles per litre to moles per cubic centimetre. Thus,

$$\Lambda_m = \frac{1000(3.905 \times 10^{-5})}{0.001} = 39.05 \text{ S cm}^2 \text{ mol}^{-1}.$$

Step 2: Calculate the fraction of acid dissociated Acetic acid is a weak electrolyte. Its molar conductivity at this concentration is compared with its value at complete dissociation:

$$\alpha = \frac{39.05}{390.5} = 0.100.$$

The ratio is dimensionless because both conductivities have the same units. Hence the percentage dissociation is $100\alpha = 10.0\%$, consistent with only partial ionisation of the acid.

Step 3: Conclusion The molar conductivity is $39.05 \text{ S cm}^2 \text{ mol}^{-1}$, and the degree of dissociation is $\alpha = 0.100$, or 10.0% .

Quick Tip to Solve: When conductivity is in S per centimetre and concentration in mol per litre, include the factor 1000 before taking the ratio with limiting molar conductivity.

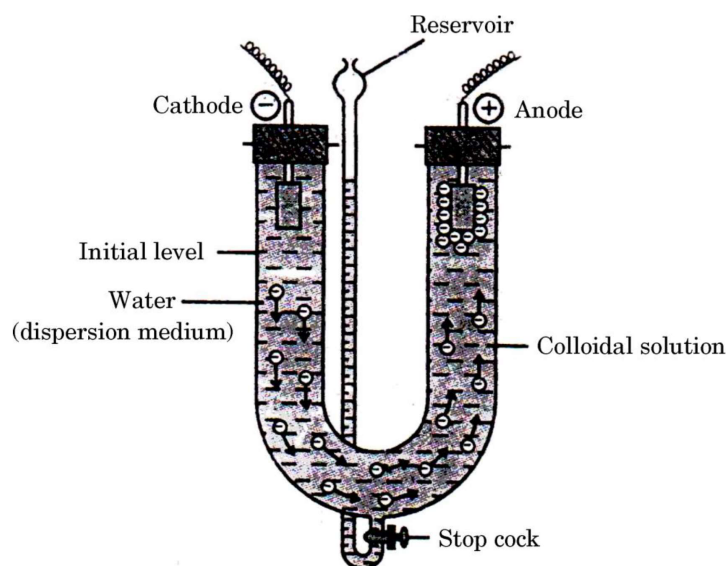
5(a). Answer the following questions on the basis of the given figure:

(a) Define the process depicted in the above figure.

(b) Can this process be used in the coagulation of the lyophobic sols?

(c) What is coagulation?

[3 marks]



Solution:

Concept:

- Colloidal particles carry an electric charge. Under an applied electric field, they migrate towards the electrode carrying the opposite charge; this migration is called electrophoresis.
- The similar charges on particles stabilise a lyophobic sol by mutual repulsion. Loss or neutralisation of this charge permits aggregation and precipitation, called coagulation.

Step 1: (a) Identify and define the process The figure depicts electrophoresis: the movement of charged colloidal particles towards the oppositely charged electrode under the influence of an applied electric potential. The particles shown carry negative charge and move towards the positive electrode, the anode. This directed movement demonstrates that the dispersed particles are electrically charged.

Step 2: (b) Explain its use in coagulation Yes, electrophoresis can be used to coagulate a lyophobic sol. When its charged colloidal particles reach the oppositely charged electrode, they lose their charge. Without their stabilising electrical repulsion, the discharged particles aggregate and are deposited or precipitated. In the illustrated sol, the negatively charged particles discharge at the anode.

Step 3: (c) Define coagulation Coagulation is the process of aggregation and precipitation of colloidal particles, brought about by the loss or neutralisation of their charge. The small dispersed particles combine into larger aggregates that can separate from the dispersion medium. It is also called flocculation; the resulting loss of stability is especially characteristic of lyophobic sols.

Step 4: Conclusion (a) The process is electrophoresis. (b) Yes: discharge of the particles at the oppositely charged electrode causes coagulation. (c) Coagulation is aggregation and precipitation of colloidal particles following loss or neutralisation of their charge.

Quick Tip to Solve: Use the sign on the particles to identify the destination electrode: negative colloidal particles migrate towards the positive anode.

5(b). Define the following terms:

(a) Adsorption

(b) Lyophobic sol

(c) Multimolecular colloid

[3 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon: the concentration of an adsorbate is greater at an interface than in the bulk.
- A sol is a colloidal dispersion of a solid in a liquid; classification depends on affinity for the medium and on the nature of the dispersed particles.

Step 1: (a) Adsorption Adsorption is the accumulation of molecules of a gas or liquid on the surface of a solid or liquid, so that their concentration at the surface becomes greater than that in the bulk. The substance accumulated is the adsorbate, and the surface on which it collects is the adsorbent. For example, charcoal adsorbs gases on its surface. This accumulation occurs at the interface; absorption instead involves entry throughout the bulk of a material.

Step 2: (b) Lyophobic sol A lyophobic sol is a colloidal sol in which the dispersed phase has little or no affinity for the dispersion medium. Such sols cannot normally be prepared simply by mixing the dispersed substance with the medium; special dispersion or condensation methods are needed. They are relatively unstable, are readily coagulated by small amounts of suitable electrolytes, and are generally irreversible. A gold sol in water is an example.

Step 3: (c) Multimolecular colloid A multimolecular colloid is one in which a large number of small atoms or molecules aggregate together to form each particle of colloidal dimensions. The constituent atoms or molecules are held together mainly by van der Waals forces. For example, a gold-sol particle consists of many gold atoms, while a sulphur-sol particle contains many sulphur molecules. The individual constituent species are small; it is their aggregate that has colloidal size.

Step 4: Conclusion Adsorption is surface accumulation; a lyophobic sol has little affinity between its dispersed phase and medium; a multimolecular colloid contains aggregates of many small atoms or molecules.

Quick Tip to Solve: For each definition, identify its distinguishing feature: surface accumulation, low affinity, or aggregation of small species.

6(a). (i) Which is the most common oxidation state in Lanthanoids?

(ii) Why is there a gradual decrease in the atomic sizes of transition metals in a series with increasing atomic numbers?

(iii) Calculate the number of unpaired electrons in the following gaseous ions: V^{3+} , Ti^{3+} [3 marks]

Solution:

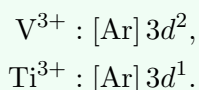
Concept:

- Lanthanoids most commonly lose two 6s electrons and one further electron to form trivalent ions.
- Across a transition series, increasing nuclear charge is only partly screened by the additional (n-1)d electrons.
- In forming cations of first-row transition metals, 4s electrons are removed before 3d electrons. Hund's rule places electrons singly in degenerate orbitals before pairing.

Step 1: (i) Most common oxidation state The most common oxidation state of the lanthanoids is +3. Formation of the trivalent ion involves removal of the two outer 6s electrons and one electron from the 5d or 4f subshell, depending on the element. Some lanthanoids also show other oxidation states, especially when these give particularly stable configurations, but +3 is the general characteristic oxidation state.

Step 2: (ii) Gradual decrease in atomic size As atomic number increases across a transition series, the nuclear charge increases by one at each successive element. The added electron enters the inner (n-1)d subshell. These added d electrons provide some shielding, but their shielding does not fully compensate for the increase in nuclear charge. Hence the effective nuclear attraction on the electron cloud increases, pulling it closer to the nucleus and causing a gradual decrease in atomic size. The partial shielding by added d electrons makes this decrease relatively small.

Step 3: (iii) Unpaired electrons in the gaseous ions The neutral configurations are V : $[Ar] 3d^3 4s^2$ and Ti : $[Ar] 3d^2 4s^2$. To form each 3+ ion, remove both 4s electrons and then one 3d electron:



By Hund's rule, the two d electrons of gaseous V^{3+} occupy separate d orbitals, giving two unpaired electrons. The single d electron of gaseous Ti^{3+} is unpaired, giving one unpaired electron.

Step 4: Conclusion (i) +3. (ii) Increasing effective nuclear charge contracts the atoms. (iii) V^{3+} : 2 unpaired electrons; Ti^{3+} : 1 unpaired electron.

Quick Tip to Solve: Write the neutral configuration first, remove the two 4s electrons before 3d electrons, then apply Hund's rule.

6(b). (i) The electronic configuration of Ce is: ${}_{58}\text{Ce} = [\text{Xe}]^{54} 4f^1 5d^1 6s^2$. Calculate the spin only magnetic moment of Ce^{3+} ion.

(ii) Why is copper regarded as a transition element although copper atom has completely filled d-orbitals in its ground state?

(iii) Why is Sc^{3+} colourless in aqueous solution whereas Ti^{3+} is coloured?

[3 marks]

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton.
- A transition element has an incompletely filled d-subshell in its atom or in at least one of its oxidation states. Colour in these aqueous ions is explained by absorption associated with d-d transitions.

Step 1: (i) Find the configuration and magnetic moment of cerium(III) Starting from Ce : $[\text{Xe}]4f^1 5d^1 6s^2$, remove the two 6s electrons and the 5d electron to obtain $\text{Ce}^{3+} : [\text{Xe}]4f^1$. Thus there is one unpaired electron, so $n = 1$. Substitution in the spin-only expression gives

$$\mu = \sqrt{1(1+2)} \mu_B = \sqrt{3} \mu_B \approx 1.73 \mu_B.$$

This is the requested spin-only value, calculated from the unpaired-electron count.

Step 2: (ii) Apply the definition of a transition element to copper Copper has the ground-state configuration $[\text{Ar}]3d^{10} 4s^1$; its atomic d-subshell is completely filled. However, its common ion Cu^{2+} has configuration $[\text{Ar}]3d^9$, with an incompletely filled d-subshell. Therefore copper satisfies the definition through its ionic oxidation state.

Step 3: (iii) Compare the d-electron configurations of the aqueous ions Sc^{3+} is $[\text{Ar}]3d^0$, so it has no d electron available for a d-d transition and is colourless in aqueous solution. Ti^{3+} is $[\text{Ar}]3d^1$. The water ligands split its d-orbitals into different energy levels; its d electron can absorb visible light and undergo a d-d transition. The transmitted light therefore appears coloured.

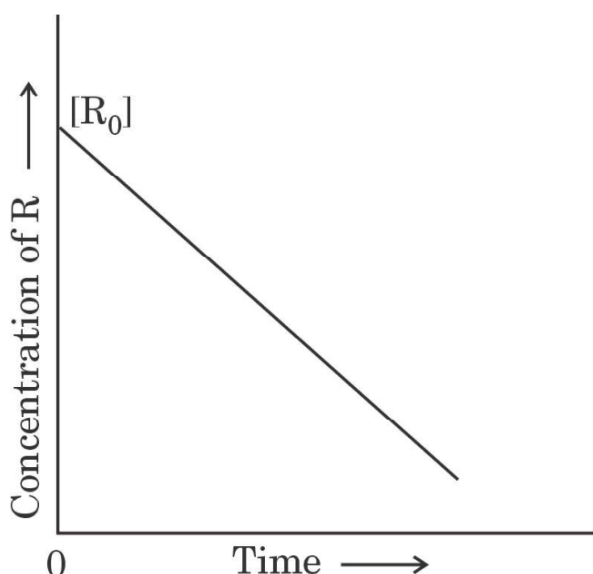
Step 4: Conclusion (i) $\mu_{\text{spin-only}}(\text{Ce}^{3+}) = 1.73 \mu_B$. (ii) Copper forms Cu^{2+} with an incomplete $3d^9$ subshell. (iii) Sc^{3+} is d^0 , whereas Ti^{3+} is d^1 and permits visible-light d-d absorption.

Quick Tip to Solve: Write each ion's configuration before counting unpaired electrons or explaining colour; remove the outer s electrons first.

7(a). The variation in the concentration (R) vs. time (t) plot is given below. Answer the following questions on the basis of the given figure:

- (i) Predict the order of the reaction.
- (ii) What is the slope of the curve?
- (iii) What are the units of the rate constant k ?

[3 marks]

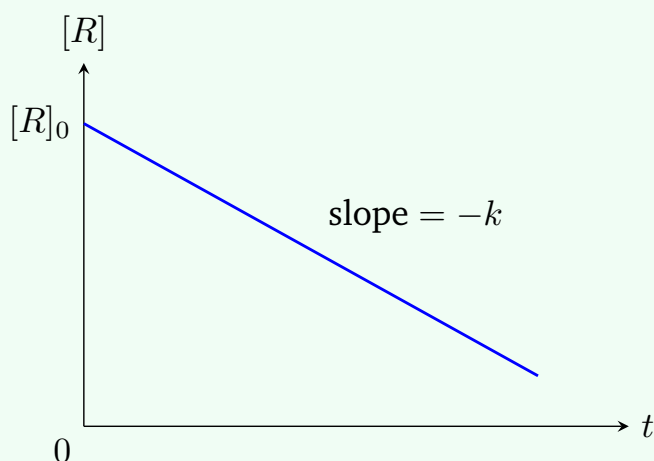


Solution:

Concept:

- For a zero-order reaction, the rate is independent of the reactant concentration: $-d[R]/dt = k$, where $[R]$ is the concentration of reactant R and k is the rate constant.
- Integration gives $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration and t is time. This has the straight-line form $y = c + mx$.

Step 1: (i) Identify the reaction order from the plotted variables The graph plots reactant concentration itself against time, and shows a straight line sloping downwards. Compare this with $[R] = [R]_0 - kt$: the vertical intercept is $[R]_0$, and concentration decreases by the same amount in equal time intervals. This is the characteristic concentration-time plot of a zero-order reaction. A first-order reaction would give a straight line for $\ln[R]$ against time, rather than for $[R]$ against time.



Zero-order concentration-time plot; the straight line has slope $-k$.

Step 2: (ii) Determine the slope On comparing $[R] = [R]_0 - kt$ with $y = c + mx$, the coefficient of time is the slope:

$$m = \frac{\Delta[R]}{\Delta t} = -k.$$

Its sign is negative because reactant concentration decreases as time increases. The rate constant itself is positive; the negative sign describes the direction of the plotted change.

Step 3: (iii) Obtain the units of the rate constant Rearranging the integrated rate equation gives $k = ([R]_0 - [R])/t$. Thus k has units of concentration divided by time. When concentration is in mol L^{-1} and time is in seconds,

$$[k] = \text{mol L}^{-1} \text{s}^{-1}.$$

Equivalently, its units are M s^{-1} . If another time unit is used on the graph, the corresponding inverse time unit is used for k .

Step 4: Conclusion (i) The reaction is zero order. (ii) The slope is $-k$. (iii) The rate constant has units $\text{mol L}^{-1} \text{s}^{-1}$ when time is measured in seconds.

Quick Tip to Solve: Check the vertical-axis quantity before identifying order: a straight concentration-time line has slope minus the zero-order rate constant.

7(b). A first order reaction takes 24 minutes for 50% decomposition. Calculate the time required for 25% decomposition.

(Given: $\log 4 = 0.6021$, $\log 3 = 0.4771$)

[3 marks]

Solution:

Concept:

- For a first order reaction, the integrated rate law is $kt = 2.303 \log([R]_0/[R]_t)$, where $[R]_0$ and $[R]_t$ are initial and remaining reactant concentrations and k is the rate constant.
- The half-life is $t_{1/2} = 0.693/k$, independent of initial concentration. A stated percentage decomposition must first be converted into the percentage of reactant remaining.

Step 1: Determine the rate constant from the half-life At 50% decomposition, half the original reactant remains. Thus the given time is the half-life, $t_{1/2} = 24$ min. Therefore,

$$k = \frac{0.693}{24} = 0.028875 \text{ min}^{-1}.$$

The unit is inverse minutes because the supplied half-life is in minutes.

Step 2: Substitute the fraction remaining at 25% decomposition Let the initial concentration be a . If 25% decomposes, the remaining concentration is $0.75a$, so the initial-to-remaining ratio is $4/3$, not 4. The integrated law gives

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{4}{3} \\ &= \frac{2.303}{0.028875} (0.6021 - 0.4771) \\ &= \frac{2.303 \times 0.1250}{0.028875} \simeq 9.97 \text{ min.} \end{aligned}$$

This is less than the half-life, as expected, because only one quarter of the reactant has decomposed. It is not 12 minutes: in a first order reaction, the rate decreases as the concentration falls, so equal fractions of the initial amount do not decompose in equal times.

Step 3: Conclusion The time required for 25% decomposition is 9.97 min, approximately 10 min.

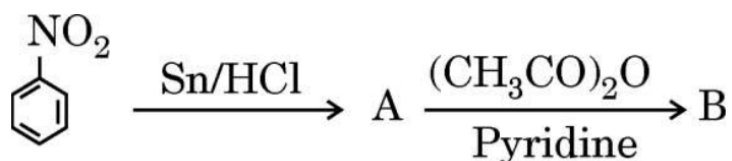
Quick Tip to Solve: For 25% decomposition use 75% remaining: the logarithm is $\log(4/3) = 0.1250$. Never put the decomposed fraction in the denominator of the integrated law.

8. (a) Which of the following is a secondary amine?

$\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$, $\text{CH}_3\text{-N(CH}_3\text{)-C}_2\text{H}_5$

(b) Complete the following:

[3 marks]



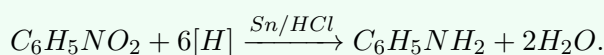
Solution:

Concept:

- An amine is primary, secondary or tertiary according as its nitrogen is bonded directly to one, two or three carbon groups. A secondary amine has the general formula R_2NH .
- Tin and hydrochloric acid reduce an aromatic nitro group to an amino group. Acetic anhydride acetylates the amino group to form an amide; pyridine acts as a base in this reaction.

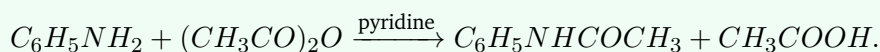
Step 1: (a) Count the carbon groups bonded directly to nitrogen In $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, nitrogen is attached to one propyl group and two hydrogen atoms, so it is a primary amine. In $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$, nitrogen is attached to two ethyl groups and one hydrogen atom, so this is the secondary amine, diethylamine. The third compound, $\text{CH}_3\text{N(CH}_3\text{)C}_2\text{H}_5$, has two methyl groups and one ethyl group bonded to nitrogen and no N-H bond; it is tertiary. Classification therefore depends on substitution at nitrogen, not on the length of the carbon chains.

Step 2: (b) Reduce nitrobenzene to identify A The starting benzene ring bears a nitro group. Reduction with Sn/HCl converts $-\text{NO}_2$ into $-\text{NH}_2$, giving aniline, $\text{A} = \text{C}_6\text{H}_5\text{NH}_2$, on liberation of the free amine. The overall reduction can be represented as



In the acidic reaction mixture the amine is protonated; the compound identified as A in the reaction sequence is aniline.

Step 3: Acetylate aniline to identify B Aniline reacts with acetic anhydride in pyridine. One hydrogen of the amino group is replaced by an acetyl group, forming acetanilide:

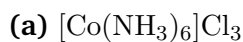


Hence B is the amide acetanilide, also called N-phenylethanamide. The benzene ring remains intact in both transformations.

Step 4: Conclusion (a) The secondary amine is $\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3$ (diethylamine). (b) $\text{A} = \text{C}_6\text{H}_5\text{NH}_2$ (aniline) and $\text{B} = \text{C}_6\text{H}_5\text{NHCOCH}_3$ (acetanilide).

Quick Tip to Solve: Count nitrogen's carbon neighbours to classify the amine. In the sequence, remember $-\text{NO}_2 \rightarrow -\text{NH}_2 \rightarrow -\text{NHCOCH}_3$: reduction first, then acetylation.

9. Using IUPAC norms write the systematic names of the following :



[3 marks]

Solution:

Concept:

- Name the cation before the anion. Inside a coordination entity, name ligands before the central metal and state the metal oxidation number in Roman numerals.
- Ammonia is the neutral ligand ammine; chloride and cyanide ligands are named chlorido and cyanido. An anionic complex has a metal name ending in -ate.

Step 1: (a) Name the cobalt compound In $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the three external chloride ions give the complex cation a charge of +3. Since ammonia is neutral, the cobalt oxidation number x satisfies $x + 6(0) = +3$, hence $x = +3$. Six ammonia ligands give hexaammine. The complex is cationic, so the metal name remains cobalt; the counter-ion is named chloride. Thus the name is hexaamminecobalt(III) chloride.

Step 2: (b) Name the nickel complex ion For $[\text{NiCl}_4]^{2-}$, each chlorido ligand has charge -1 . Therefore $x + 4(-1) = -2$, giving $x = +2$. Four chlorido ligands give tetrachlorido. Because the coordination entity is an anion, nickel becomes nickelate. Its name is tetrachloridonickelate(II) ion.

Step 3: (c) Name the potassium compound The three potassium ions in $\text{K}_3[\text{Fe}(\text{CN})_6]$ require a complex-anion charge of -3 . Each cyanido ligand has charge -1 , so $x + 6(-1) = -3$, giving $x = +3$. Six cyanido ligands give hexacyanido; iron in an anionic complex is named ferrate. Name the potassium cation first, giving potassium hexacyanidoferrate(III).

Step 4: Conclusion (a) Hexaamminecobalt(III) chloride.

(b) Tetrachloridonickelate(II) ion.

(c) Potassium hexacyanidoferrate(III).

Quick Tip to Solve: First calculate the charge on the bracketed entity; use the -ate metal ending only when that entity is an anion.

10(a). Account for the following :

(a) Transition elements show variable oxidation states.

(b) $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ value for copper is highly positive.

(c) Cr^{2+} is a strong reducing agent.

[3 marks]

Solution:

Concept:

- The energies of the $(n-1)d$ and ns orbitals of transition elements are close, so electrons from both can participate in bonding.
- Formation of an aqueous metal ion involves atomisation, ionisation and hydration. Their combined

energy balance determines the standard electrode potential.

- A reducing agent loses electrons and is oxidised. A particularly stable product configuration can favour this electron loss.

Step 1: (a) Explain variable oxidation states Transition elements have incompletely filled $(n - 1)d$ orbitals in their atoms or common ions. Because the ns and $(n - 1)d$ orbitals have comparable energies, varying numbers of their electrons can be used in bond formation or removed during ion formation. Consequently, several oxidation states are accessible. For example, iron shows +2 and +3, while manganese exhibits a wider range. The small energy difference between these orbitals is the essential reason.

Step 2: (b) Explain the positive copper electrode potential For oxidation of copper metal to aqueous Cu^{2+} , energy is needed to atomise the metal and remove two electrons. Copper has high atomisation and ionisation enthalpies; in particular, removing the second electron disrupts the stable $3d^{10}$ configuration of Cu^+ . The hydration enthalpy released on forming aqueous Cu^{2+} does not compensate sufficiently for these energy requirements. Thus oxidation of copper to Cu^{2+} is energetically unfavourable relative to hydrogen, and the reverse reduction $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ has a highly positive standard reduction potential.

Step 3: (c) Explain the reducing character of chromium(II) Cr^{2+} has configuration $3d^4$ and readily loses one electron:



The resulting Cr^{3+} has configuration $3d^3$, with the stable t_{2g}^3 arrangement in an octahedral aqueous environment. The tendency to form this more stable ion makes Cr^{2+} readily undergo oxidation and supply electrons to another species. Hence it acts as a strong reducing agent.

Step 4: Conclusion (a) Similar ns and $(n - 1)d$ energies allow variable electron participation. (b) Copper's atomisation and ionisation costs are insufficiently compensated by hydration, favouring its reduction. (c) Cr^{2+} reduces other species while forming stable Cr^{3+} , with a $3d^3$ configuration.

Quick Tip to Solve: For a reducing metal ion, write its oxidation product first and check whether that product has an especially stable electronic configuration.

OR

10(b). What is Lanthanoid contraction? Write its two consequences.

[3 marks]

Solution:

Concept:

- Across the lanthanoid series, electrons enter the inner $4f$ subshell while nuclear charge increases. The $4f$ electrons shield one another poorly.
- Increasing effective nuclear attraction decreases atomic and ionic radii. Similar ionic sizes lead to similar chemistry; smaller cations also polarise the hydroxide ion more strongly.

Step 1: Define lanthanoid contraction and explain its origin Lanthanoid contraction is the gradual decrease in atomic and ionic radii, especially the radii of Ln^{3+} ions, with increasing atomic number

from lanthanum to lutetium. The added $4f$ electron does not effectively screen the extra nuclear charge. Consequently, the effective nuclear attraction experienced by the electron cloud increases and the size decreases progressively.

Step 2: First consequence: similarity of corresponding transition elements The contraction largely compensates for the size increase expected on moving from the $4d$ to the $5d$ transition series. Thus corresponding elements such as zirconium and hafnium have almost equal radii and closely similar chemical properties. Their compounds are therefore difficult to separate from each other.

Step 3: Second consequence: decreasing basicity of hydroxides As the size of Ln^{3+} decreases, its charge density and polarising power increase. The metal–oxygen bond in the hydroxide acquires greater covalent character, so the basic strength of the hydroxides decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. Thus $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$.

Step 4: Conclusion Lanthanoid contraction is the progressive decrease in lanthanoid atomic and ionic radii across the series. Two consequences are the close similarity of zirconium and hafnium and the decreasing basicity of lanthanoid hydroxides from lanthanum to lutetium.

Quick Tip to Solve: Link poor shielding by $4f$ electrons to smaller ions, then recall the Zr–Hf similarity and decreasing hydroxide basicity.

11. (a) Aromatic primary amines cannot be prepared by Gabriel Phthalimide synthesis. Why?

(b) Aniline is a weaker base than alkyl amines. Why?

(c) Arrange the following in the increasing order of basic strength in aqueous solution:

$(\text{CH}_3\text{CH}_2)_2\text{NH}$, $(\text{C}_2\text{H}_5)_3\text{N}$, $\text{C}_2\text{H}_5\text{NH}_2$

[3 marks]

Solution:

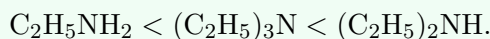
Concept:

- Gabriel phthalimide synthesis requires nucleophilic substitution of a halide by the phthalimide anion. Ordinary aryl halides resist this substitution.
- Basic strength depends on the availability of the nitrogen lone pair and, in water, on the stability and solvation of the conjugate acid. Alkyl groups exert an electron-releasing inductive effect.

Step 1: (a) Explain the limitation of Gabriel synthesis In Gabriel synthesis, potassium phthalimide reacts with an alkyl halide to form an N-alkylphthalimide, which on hydrolysis yields a primary amine. To obtain an aromatic primary amine in this way, an aryl halide would have to undergo the corresponding substitution. Aryl halides do not readily undergo nucleophilic substitution by the phthalimide anion: their carbon–halogen bond has partial double-bond character through resonance and is attached to an sp^2 -hybridised carbon. Hence this method cannot prepare aromatic primary amines such as aniline.

Step 2: (b) Compare aniline and alkylamines In aniline, the nitrogen lone pair is delocalised into the benzene ring by resonance and is less available to accept a proton. In alkylamines the lone pair is localised, and the electron-releasing $+I$ effect of alkyl groups increases electron density at nitrogen. Aniline therefore has a smaller tendency to accept a proton and is a weaker base than alkylamines.

Step 3: (c) Order the ethylamines in water In aqueous solution, both the electron-releasing effect of ethyl groups and hydration of the protonated amine must be considered. Diethylamine has a favourable balance of these effects and is the strongest base of the three. Although the triethylammonium ion is less effectively solvated because of steric crowding, the stronger inductive effect of three ethyl groups makes triethylamine more basic than ethylamine. Therefore the increasing order is



Step 4: Conclusion (a) Aryl halides resist nucleophilic substitution by the phthalimide anion. (b) Resonance makes aniline's lone pair less available for protonation. (c) In water: $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$.

Quick Tip to Solve: For ethylamines in water remember secondary > tertiary > primary; do not apply the methylamine order without checking the alkyl group.

Section C (5 marks)

12. Read the following passage and answer the questions that follow :

A class of organic molecules which contain a carbon atom connected to an oxygen atom by a double bond is called Aldehydes and Ketones. It is called as carbonyl group. Aldehydes are prepared by the oxidation of alcohols. Formaldehyde is sold in an aqueous solution called formalin. Propanone, a simplest ketone, is commercially prepared by fermenting corn or by oxidation of propan-2-ol. Carboxylic acids also have carbonyl carbon. They can be prepared by the oxidation of alcohols and aldehydes.

Formic acid was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings. Aldehydes undergo many nucleophilic addition reactions. They can be reduced to primary alcohols. The aldehydes with α -hydrogen undergo aldol condensation and the aldehydes without α -hydrogen undergo Cannizzaro reaction.

Ketones are highly reactive, although less so than aldehydes. Ketones are obtained by oxidation of secondary alcohols. Ketones possessing α -hydrogens also undergo aldol condensation. Carboxylic acids occur widely in nature and are used in the production of plastics, esters, etc. Aspirin is prepared from acetic acid. Similar to aldehydes and ketones, carboxylic acids can be halogenated at the α -carbon by reacting with a halogen in presence of phosphorus. [5 marks]

12(a). Which of the following compounds would undergo aldol condensation?

Methanal, Benzaldehyde, Ethanal

[1 mark]

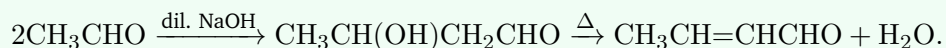
Solution:

Concept:

- Aldol condensation requires a carbonyl compound with at least one α -hydrogen, meaning a hydrogen on a carbon adjacent to the carbonyl carbon.

Step 1: Check the available alpha-hydrogens Ethanal, CH_3CHO , has three α -hydrogens on its methyl carbon and therefore undergoes aldol condensation. Methanal, HCHO , has no adjacent carbon, while benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, has no hydrogen on the ring carbon directly bonded to the carbonyl carbon.

Neither undergoes self-aldol condensation. For ethanal:



Step 2: Form the aldol and dehydrate it In dilute alkali, the enolate of ethanal adds to another ethanal molecule to produce 3-hydroxybutanal. On heating, this aldol loses water to give but-2-enal, an alpha,beta-unsaturated aldehyde. The presence of the methyl group next to the carbonyl is therefore decisive.

Step 3: Conclusion Ethanal, CH_3CHO , undergoes aldol condensation.

Quick Tip to Solve: Locate the carbon next to CHO and check whether that carbon carries a hydrogen.

12(b). Write the chemical test to distinguish between propanal and propanone.

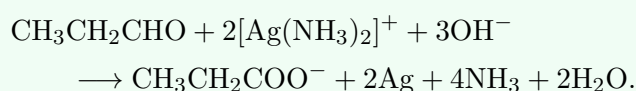
[1 mark]

Solution:

Concept:

- Tollens' reagent oxidises an aldehyde to a carboxylate ion and deposits metallic silver; an ordinary ketone does not give this test.
- Propanal is an aldehyde, whereas propanone is a ketone; a selective oxidation test distinguishes their functional groups.

Step 1: Apply Tollens' test Add freshly prepared Tollens' reagent to each sample and warm gently in a water bath. Propanal gives a silver mirror on the inner wall of the test tube, whereas propanone gives no silver mirror. The positive reaction is



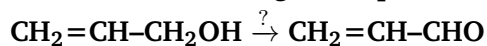
This test distinguishes the aldehyde group of propanal from the ketone group of propanone.

Step 2: Compare the observations Propanal is oxidised to the propanoate ion, reducing the silver(I) complex to metallic silver. Propanone is not oxidised by this mild reagent under the test conditions, so it does not deposit silver. The contrast is a silver mirror versus no reaction.

Step 3: Conclusion Tollens' test: propanal gives a silver mirror; propanone gives no silver mirror.

Quick Tip to Solve: Use the silver mirror as the positive observation; merely naming Tollens' reagent is insufficient.

12(c). Write the reagent required in the following reaction:



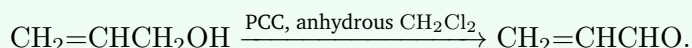
[1 mark]

Solution:

Concept:

- A primary alcohol can be oxidised to an aldehyde using pyridinium chlorochromate (PCC).
- A selective oxidant must retain the carbon-carbon double bond in this allylic alcohol.

Step 1: Oxidise the primary alcohol selectively Use pyridinium chlorochromate (PCC) in anhydrous dichloromethane. It oxidises the primary alcohol group to an aldehyde while retaining the carbon-carbon double bond:



Controlled, anhydrous conditions prevent further oxidation of the aldehyde to the carboxylic acid.

Step 2: Control the extent of oxidation The starting compound is prop-2-en-1-ol and the product is prop-2-enal. Only the terminal alcohol group changes to CHO. PCC in anhydrous dichloromethane supplies the required mild oxidation conditions; the alkene remains intact and the aldehyde is isolated without further oxidation to an acid.

Step 3: Conclusion Use pyridinium chlorochromate (PCC) in anhydrous dichloromethane.

Quick Tip to Solve: For an unsaturated primary alcohol, choose PCC to retain the double bond and stop at the aldehyde.

12(d)(i). An alcohol 'A' ($\text{C}_3\text{H}_8\text{O}$) on oxidation gives compound 'B'. 'B' gives negative Tollens' test and reacts with hydrazine to give compound 'C'. 'B' reacts with NaOH and I_2 to give yellow precipitate of 'D'. Identify 'A', 'B', 'C' and 'D'.

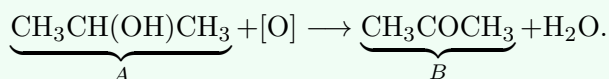
[2 marks]

Solution:

Concept:

- Controlled oxidation converts a primary alcohol to an aldehyde and a secondary alcohol to a ketone. A carbonyl group reacts with hydrazine, H_2NNH_2 , to form a hydrazone.
- A methyl ketone, RCOCH_3 , gives yellow iodoform, CHI_3 , with iodine and aqueous sodium hydroxide.

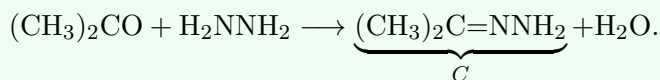
Step 1: (d)(i) Identify the alcohol and its oxidation product Since B gives a negative Tollens' test, the carbonyl product is a ketone. The three-carbon ketone is propanone, CH_3COCH_3 , so its parent alcohol A, with formula $\text{C}_3\text{H}_8\text{O}$, is propan-2-ol:



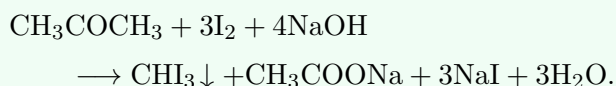
Propan-1-ol would instead give propanal, which gives a positive Tollens' test, so it is excluded.

Step 2: (d)(i) Identify the hydrazone and yellow precipitate Hydrazine condenses with propanone,

eliminating water to form propanone hydrazone, *C*:



Propanone contains the $\text{CH}_3\text{CO}-$ group, so it also undergoes the iodoform reaction. The yellow precipitate *D* is iodoform (triiodomethane):



Step 3: Conclusion *A*: propan-2-ol; *B*: propanone; *C*: propanone hydrazone, $(\text{CH}_3)_2\text{C}=\text{NNH}_2$; *D*: iodoform, CHI_3 .

Quick Tip to Solve: Combine the negative Tollens' test with the positive iodoform test: the three-carbon oxidation product must be propanone, which immediately identifies its parent secondary alcohol.

OR

12(d)(ii). Write the chemical reactions for the following:

(I) Clemmensen reduction

(II) HVZ reaction

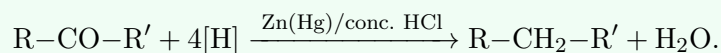
[2 marks]

Solution:

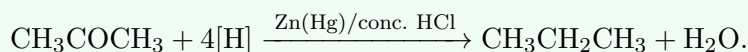
Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam, Zn(Hg) , and concentrated hydrochloric acid.
- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an α -hydrogen of a carboxylic acid by a halogen in the presence of red phosphorus; the acid must possess an α -hydrogen.

Step 1: (I) Clemmensen reduction On heating an aldehyde or ketone with zinc amalgam and concentrated hydrochloric acid, its carbonyl oxygen is removed and the carbonyl carbon gains hydrogen. For a ketone, the general reaction is



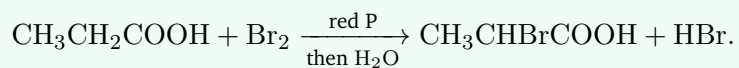
For example, propanone gives propane:



Here $[\text{H}]$ represents reducing hydrogen; an aldehyde similarly gives RCH_3 .

Step 2: (II) Hell-Volhard-Zelinsky reaction A carboxylic acid containing an α -hydrogen reacts with bromine in the presence of a small quantity of red phosphorus, followed by hydrolysis, to give an

α -bromocarboxylic acid. An example is



Thus, propanoic acid gives 2-bromopropanoic acid. Bromination occurs at the carbon immediately next to the carboxyl group, while the carboxyl group is retained.

Step 3: Conclusion Clemmensen reduction: $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Zn(Hg)/conc. HCl}} \text{CH}_3\text{CH}_2\text{CH}_3$. HVZ reaction: $\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{then H}_2\text{O}]{\text{Br}_2, \text{red P}} \text{CH}_3\text{CHBrCOOH}$.

Quick Tip to Solve: Associate Clemmensen with carbonyl-to-methylene reduction in acid; for HVZ, locate an alpha hydrogen and replace it by bromine while retaining COOH.