

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-6-1 - 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.

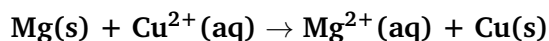
Section A (6 marks)

1. Answer the following questions (Any two):

(a) Why is alternating current used instead of direct current for measuring resistance of an electrolytic solution?

(b) State Kohlrausch's law of independent migration of ions.

(c) Depict the Galvanic cell in which the following reaction takes place:



[2 marks]

Solution:

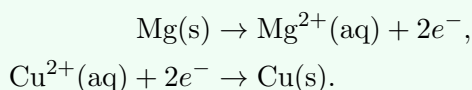
Concept:

- Electrolytic resistance is measured using ionic conduction. Electrode reactions and persistent changes in the concentration near an electrode can alter the measured resistance.
- At infinite dilution, ions migrate independently: $\Lambda_m^{\circ} = \nu_+ \lambda_+^{\circ} + \nu_- \lambda_-^{\circ}$, where the ν 's are the numbers of each type of ion in one formula unit.

Step 1: (a) Explain the use of AC Direct current causes electrolysis and electrode polarisation. Discharge or accumulation of ions changes the solution near the electrodes and affects the measured resistance. Alternating current reverses direction rapidly, minimising electrolysis and polarisation, so the measured resistance represents the solution more reliably.

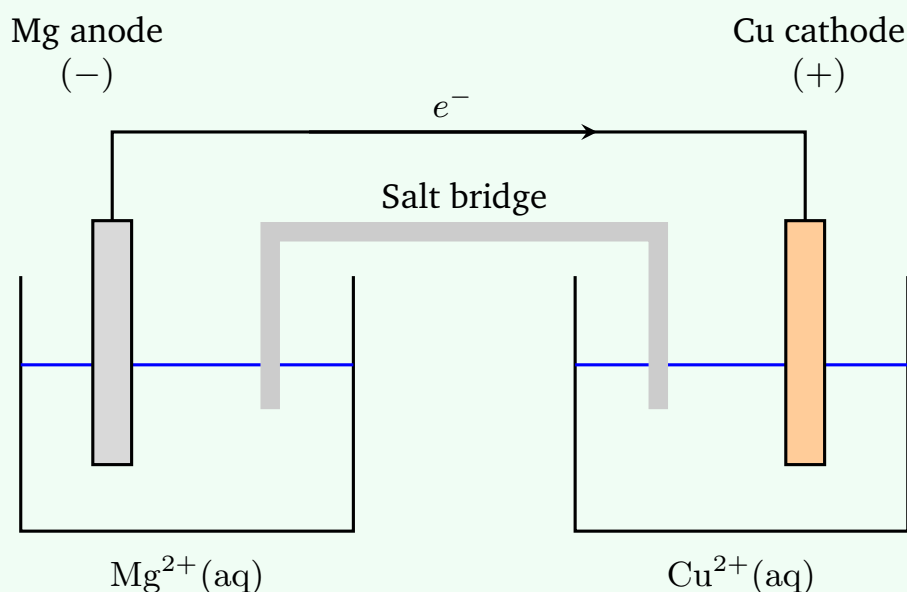
Step 2: (b) State Kohlrausch's law At infinite dilution, each ion contributes a definite amount to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. Thus the limiting molar conductivity equals the sum of the limiting ionic molar conductivities, weighted by the respective stoichiometric numbers of the ions.

Step 3: (c) Identify anode and cathode Magnesium undergoes oxidation at the negative anode; copper(II) ions undergo reduction at the positive cathode:



Electrons flow through the wire from Mg to Cu, while the salt bridge completes the internal circuit and maintains electrical neutrality. The anode is written on the left of the cell notation. A single vertical line indicates a phase boundary and a double line indicates the salt bridge.

Quick Tip to Solve: Identify oxidation first: the metal that loses electrons is written on the left in galvanic cell notation.



Magnesium–copper galvanic cell with external electron flow from Mg to Cu.

Step 4: Conclusion (a) AC minimises electrolysis and polarisation. (b) At infinite dilution, ionic conductivity contributions are independent and additive. (c) The cell is $\text{Mg(s)}|\text{Mg}^{2+}(\text{aq})||\text{Cu}^{2+}(\text{aq})|\text{Cu(s)}$. Any two parts may be attempted.

Quick Tip to Solve: Identify oxidation first: the metal that loses electrons is written on the left in galvanic cell notation.

2. (a) For a reaction $\text{R} \rightarrow \text{P}$, 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:

- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law. It controls how the rate and half-life depend on concentration.
- Molecularity is the number of reacting species that participate in a single elementary step. It follows from that step's mechanism and is a positive integer.

Step 1: (a) Use the half-life relation For a first-order reaction with rate constant k , the integrated rate law gives

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

There is no initial concentration term in this expression. Hence a half-life independent of the initial reactant concentration is the characteristic of a first-order reaction in the standard kinetic rate laws. By contrast, for zero order the half-life is $[R]_0/(2k)$, and for second order it is $1/(k[R]_0)$; both depend on the initial concentration $[R]_0$.

Quick Tip to Solve: If half-life does not change on dilution, recall the concentration-free formula $t_{1/2} = 0.693/k$.

Step 2: (b) Distinguish order from molecularity Order is determined experimentally from the rate law and may be zero, fractional or integral. Molecularity counts the reacting species involved in an elementary step, so it is always a positive integer and is never zero or fractional. Molecularity is defined for an elementary step, whereas an overall complex reaction can have an experimentally measured order.

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

Quick Tip to Solve: If half-life does not change on dilution, recall the concentration-free formula $t_{1/2} = 0.693/k$.

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

$\text{Cl-CH}_2\text{-COOH}$, Cl-CH(Cl)-COOH , $\text{CCl}_3\text{-COOH}$

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

$\text{CH}_3\text{COCH}_2\text{COCH}_3$

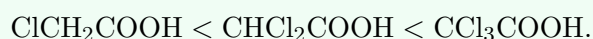
[2 marks]

Solution:

Concept:

- Chlorine exerts a negative inductive effect ($-I$): it withdraws electron density through sigma bonds and stabilises the carboxylate conjugate base.
- The parent chain of a diketone includes both carbonyl carbons; use the suffix “dione” and give the carbonyl groups the lowest possible locants.

Step 1: (a) Compare the inductive effects All three compounds have chlorine attached to the carbon next to the carboxyl group. As the number of chlorine atoms increases from one to two to three, electron withdrawal increases. This stabilises the negative charge of the conjugate base formed by loss of H^+ , so dissociation becomes more favourable. Hence acidic strength increases in the order



Step 2: (b) Identify the parent and the carbonyl positions In $\text{CH}_3\text{COCH}_2\text{COCH}_3$, the continuous chain contains five carbon atoms, so the parent is pentane. Numbering from either end puts the two ketone carbonyl groups at carbons 2 and 4. Replace the terminal “e” of pentane by “2,4-dione” to obtain pentane-2,4-dione.

Step 3: Conclusion (a) $\text{ClCH}_2\text{COOH} < \text{CHCl}_2\text{COOH} < \text{CCl}_3\text{COOH}$. (b) The IUPAC name is pentane-2,4-dione.

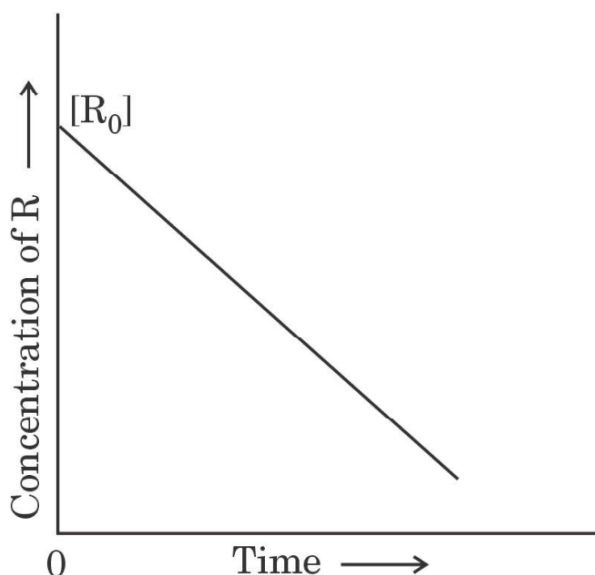
Quick Tip to Solve: When the chlorine atoms are equally close to COOH , count them: more chlorine means a stronger acid.

Section B (24 marks)

4(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:

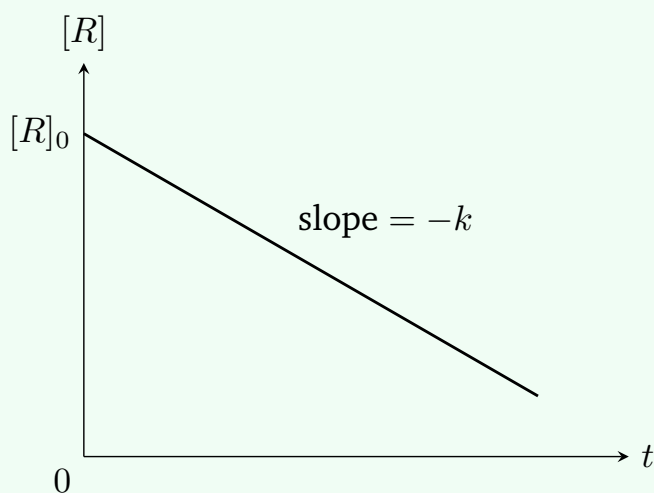
- For a zero-order reaction, the rate is independent of reactant concentration: $-d[R]/dt = k$, where $[R]$ is the reactant concentration and k is the rate constant.
- The integrated equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration. Comparison with $y = c + mx$ gives the intercept and slope of a concentration-time graph.

Step 1: (i) Identify the order from the plotted variables The given graph plots concentration itself against time and shows a straight line sloping downwards. Thus equal intervals of time produce equal decreases in concentration: the rate is constant. The equation matching this graph is

$$[R] = [R]_0 - kt.$$

This is the integrated rate equation of a zero-order reaction. A first-order reaction instead gives a straight line for $\ln[R]$ versus time, not for $[R]$ versus time.

Quick Tip to Solve: Read the vertical-axis variable first: a straight line for concentration itself versus time identifies zero order.



A zero-order concentration-time plot has intercept $[R]_0$ and slope $-k$.

Step 2: (ii) Determine the slope Comparing the equation with $y = c + mx$, take $y = [R]$, $x = t$, and the vertical intercept $c = [R]_0$. The coefficient of time is $-k$, so

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

The negative sign expresses the decrease in reactant concentration; the rate constant itself is positive.

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

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

In SI concentration units the equivalent form is $\text{mol m}^{-3} \text{s}^{-1}$.

Step 4: Conclusion (i) Zero order. (ii) Slope = $-k$. (iii) Units of k : $\boxed{\text{mol L}^{-1} \text{s}^{-1}}$ when time is measured in seconds.

Quick Tip to Solve: Read the vertical-axis variable first: a straight line for concentration itself versus time identifies zero order.

4(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, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$, where $[R]_0$ and $[R]_t$ are the initial and remaining reactant concentrations.
- The half-life is the time for 50% decomposition: $t_{1/2} = 2.303 \log 2/k$. For 25% decomposition, 75% of the reactant remains; the logarithm uses the remaining amount.

Step 1: Identify the half-life and concentration ratio The reaction takes 24 minutes to decompose half of the initial reactant, so $t_{1/2} = 24$ min. If the initial concentration is a , the concentration after 25% decomposition is $a - 0.25a = 0.75a$. Therefore,

$$\frac{[R]_0}{[R]_t} = \frac{a}{0.75a} = \frac{4}{3}.$$

The initial concentration cancels because the required extent of reaction is specified as a fraction.

Step 2: Eliminate the rate constant and substitute the logarithms Apply the same integrated rate law to 50% and 25% decomposition:

$$24 = \frac{2.303}{k} \log 2, \quad t = \frac{2.303}{k} \log \frac{4}{3}.$$

Dividing eliminates both k and 2.303. From the given data, $\log 2 = \frac{1}{2} \log 4 = 0.30105$ and $\log(4/3) = 0.6021 - 0.4771 = 0.1250$. Hence,

$$t = 24 \frac{0.1250}{0.30105} = 9.965 \text{ min.}$$

This is less than the half-life, as expected because only a quarter of the reactant has decomposed. Taking one half of the half-life would be incorrect: the reaction slows as the reactant concentration falls.

Step 3: Conclusion The time required for 25% decomposition is 9.97 min, approximately 10.0 min.

Quick Tip to Solve: Use $t = t_{1/2} \log[1/(1-f)]/\log 2$, with f the fraction decomposed; here $f = 0.25$, so the remaining fraction is 0.75.

5(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:

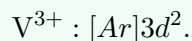
Concept:

- Lanthanoids most commonly form the +3 oxidation state by losing the two outer 6s electrons and one further electron from the 5d or 4f subshell.
- Atomic size depends on the effective nuclear charge: the nuclear attraction remaining after shielding by other electrons. Added d electrons shield incompletely across a transition series.
- For transition-metal cations, remove 4s electrons before 3d electrons. Hund's rule places electrons singly in separate orbitals of a degenerate subshell before pairing.

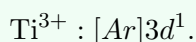
Step 1: State the common oxidation state of lanthanoids (i) The most common oxidation state is +3. The formation of trivalent ions involves removal of the two outer 6s electrons and one additional 5d or 4f electron. Although a few lanthanoids also show +2 or +4 when especially stable configurations result, +3 is characteristic of the series as a whole.

Step 2: Explain the change in atomic size across a transition series (ii) With increasing atomic number, nuclear charge increases, while the added electrons enter the inner $(n - 1)d$ subshell. These electrons do not completely shield the outer electrons from the increasing nuclear charge. Consequently, the effective nuclear charge increases and the electron cloud is drawn closer to the nucleus, causing a gradual decrease in atomic size. The added d-electron shielding partly offsets the increased nuclear attraction, so the overall contraction is relatively small.

Step 3: Obtain the ionic configurations and count unpaired electrons (iii) Vanadium has atomic number 23 and configuration V : $[Ar]3d^34s^2$. Remove the two 4s electrons first and then one 3d electron:



The two d electrons occupy separate orbitals, so V^{3+} has two unpaired electrons. Titanium has atomic number 22 and configuration Ti : $[Ar]3d^24s^2$. Removing two 4s electrons and one 3d electron gives



Its single d electron is unpaired. These are gaseous ions, so no ligand-induced pairing needs to be considered.

Step 4: Conclusion (i) The most common lanthanoid oxidation state is $+3$. (ii) Increasing effective nuclear charge causes the gradual decrease in atomic size. (iii) V^{3+} has 2 unpaired electrons and Ti^{3+} has 1 .

Quick Tip to Solve: Write the neutral atom's configuration, remove 4s before 3d, and then apply Hund's rule: free-ion d^1 and d^2 configurations have one and two unpaired electrons.

5(b). (i) The electronic configuration of Ce is: ${}_{58}\text{Ce} = [\text{Xe}] 4f^1 5d^1 6s^2$. 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?

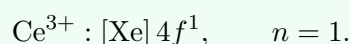
[3 marks]

Solution:

Concept:

- The spin-only magnetic moment is $\mu_{\text{so}} = \sqrt{n(n+2)} \mu_{\text{B}}$, where n is the number of unpaired electrons and μ_{B} denotes the Bohr magneton.
- A transition element has an incompletely filled d subshell in its atom or in at least one of its oxidation states.
- In aqueous transition-metal ions, visible colour commonly arises from d–d transitions between ligand-field-split d orbitals; such a transition requires an occupied d orbital.

Step 1: (i) Obtain the configuration and magnetic moment of cerium(III) From the given configuration Ce : $[\text{Xe}] 4f^1 5d^1 6s^2$, remove the two 6s electrons and the 5d electron to form Ce^{3+} . Thus



Substitution into the spin-only formula gives

$$\mu_{\text{so}} = \sqrt{1(1+2)} \mu_{\text{B}} = \sqrt{3} \mu_{\text{B}} \simeq 1.73 \mu_{\text{B}}.$$

This is the requested spin-only value, based on the one unpaired electron of the ion.

Step 2: (ii) Apply the definition of a transition element to copper A neutral copper atom has the configuration $[\text{Ar}] 3d^{10} 4s^1$, but its common Cu^{2+} ion has the configuration $[\text{Ar}] 3d^9$. The ion therefore has an incompletely filled d subshell. Copper satisfies the definition through this oxidation state even though the ground-state atom has a filled d subshell.

Step 3: (iii) Compare the d-electron configurations in water Scandium has atomic number 21, so Sc^{3+} has configuration $[\text{Ar}] 3d^0$. No d electron is present to undergo a d–d transition; hence its aqueous solution is colourless. Titanium has atomic number 22, so Ti^{3+} has configuration $[\text{Ar}] 3d^1$. In the field of water ligands, its d orbitals split into different energy levels. The d electron can absorb visible light and move to a higher level; the transmitted light gives the solution its colour.

Step 4: Conclusion (i) $\mu_{\text{so}}(\text{Ce}^{3+}) = \sqrt{3} \mu_{\text{B}} \simeq 1.73 \mu_{\text{B}}$. (ii) Copper is a transition element because Cu^{2+} is $3d^9$. (iii) Sc^{3+} is colourless because it is d^0 , whereas Ti^{3+} is coloured because its d^1 electron permits a d–d transition.

Quick Tip to Solve: Write the ion's configuration before counting unpaired electrons: remove outer s electrons first, and test copper using its common +2 ion.

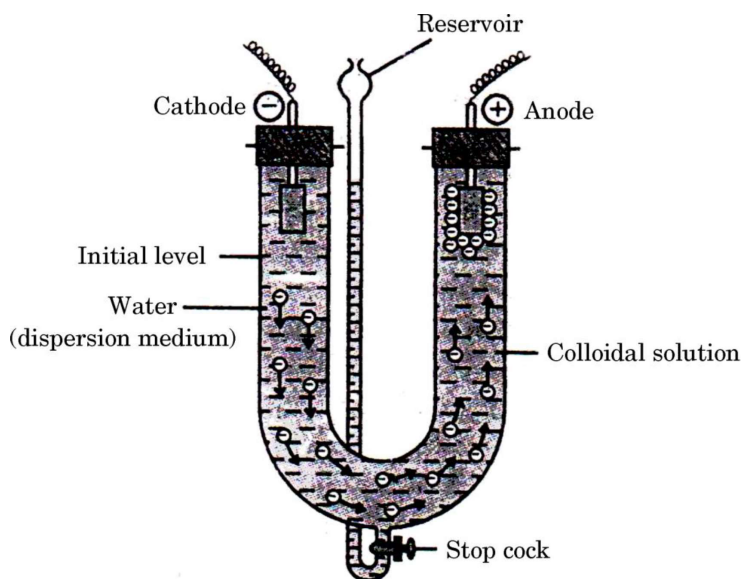
6(a). Answer the following questions on the basis of the given figure:

(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 possess a net electrical charge. In an applied electric field, they move towards the oppositely charged electrode; this motion is called electrophoresis.
- The common charge on particles of a lyophobic sol provides mutual electrostatic repulsion and helps prevent their aggregation. Removing this charge allows the particles to coagulate.

Step 1: (a) Identify and define the process shown The apparatus depicts electrophoresis: the movement of colloidal particles towards the oppositely charged electrode when an electric potential difference is applied across the sol. Positively charged particles move towards the cathode, while negatively charged particles move towards the anode. In the figure, the particles move towards the positively charged anode, showing that the sol particles are negatively charged.

Step 2: (b) Explain how the process causes coagulation Yes. Electrophoresis can be used to coagulate a lyophobic sol. Its particles migrate to the oppositely charged electrode and lose their charge on contact with it. The electrostatic repulsion that had kept the particles apart is then removed. The discharged particles aggregate into larger masses and may settle out.

Step 3: (c) Define coagulation Coagulation is the process in which colloidal particles aggregate to form larger particles that separate out as a precipitate. For a lyophobic sol, neutralisation or removal of the stabilising charge allows this aggregation; the larger particles then settle out.

Step 4: Conclusion (a) Electrophoresis. (b) Yes, by discharge at the electrode. (c) Coagulation is aggregation and precipitation of colloidal particles.

Quick Tip to Solve: Follow the moving particles to identify electrophoresis: migration explains the process, while loss of their charge at the electrode explains coagulation.

6(b). Define the following terms:

(a) Adsorption

(b) Lyophobic sol

(c) Multimolecular colloid

[3 marks]

Solution:

Concept:

- Adsorption is a surface phenomenon: particles accumulate at an interface rather than throughout the bulk.
- A sol has solid dispersed particles in a liquid dispersion medium. Its classification depends on the attraction for the medium and on the constitution of its particles.

Step 1: Define adsorption Adsorption is the accumulation of molecular species at the surface of a solid or liquid rather than in the bulk. The substance accumulating at the surface is the adsorbate, while the material providing the surface is the adsorbent. For example, a gas can accumulate on activated charcoal. The concentration of the adsorbate at the surface is consequently greater than that in the bulk; this distinguishes adsorption from absorption.

Step 2: Define a 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 generally require special methods of preparation and are relatively easily coagulated by adding electrolytes. A gold sol in water is an example. When water is the medium, the term hydrophobic sol is also used.

Step 3: Define a multimolecular colloid A multimolecular colloid is a colloidal system whose particles consist of aggregates of many atoms or small molecules held together by van der Waals forces. The individual atoms or molecules are smaller than colloidal dimensions, but their aggregates have colloidal size. Gold sol and sulphur sol are examples; the aggregate, rather than an isolated small molecule, acts as a colloidal particle.

Step 4: Conclusion (a) Adsorption is surface accumulation of molecular species. (b) A lyophobic sol has little affinity between its dispersed phase and dispersion medium. (c) A multimolecular colloid contains colloidal aggregates of many atoms or small molecules.

Quick Tip to Solve: Separate the three ideas: adsorption describes a surface process, lyophobic describes affinity for the medium, and multimolecular describes the constitution of a colloidal particle.

7. 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 $\Lambda_m = \kappa \times 1000 / c$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} . The factor 1000 converts litres to cubic centimetres.
- For a weak electrolyte such as acetic acid, the degree of dissociation is $\alpha = \Lambda_m / \Lambda_m^0$, where Λ_m^0 is its limiting molar conductivity at infinite dilution.

Step 1: Identify the concentration and conductivity The given values are

$$c = 0.001 \text{ mol L}^{-1}, \quad \kappa = 3.905 \times 10^{-5} \text{ S cm}^{-1}.$$

Since conductivity is expressed per centimetre, the concentration can equivalently be written as $1.0 \times 10^{-6} \text{ mol cm}^{-3}$. Thus the volume containing one mole is 10^6 cm^3 . Keeping these volume units consistent avoids losing the factor of 1000.

Step 2: Calculate the molar conductivity Substitute the concentration in moles per litre into the standard expression:

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

This is the conductivity contribution expressed for one mole of the electrolyte at the specified concentration.

Step 3: Find the fraction dissociated Acetic acid is weak and is only partly ionised at this concentration. Using the given limiting molar conductivity,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{39.05}{390.5} = 0.100.$$

The conductivity units cancel, so α is dimensionless. Its percentage value is $0.100 \times 100 = 10.0\%$, which is consistent with partial dissociation.

Step 4: 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: First include the factor 1000 when the concentration is in mol per litre. Then divide the calculated molar conductivity by 390.5; the ratio, not the percentage, is α .

8(a). Choose the primary amine from the following compounds:

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

[1 mark]

Solution:

Concept:

- The class of an amine depends on the number of carbon groups bonded directly to its nitrogen atom.
- A primary amine has the general formula RNH_2 : nitrogen is bonded to one carbon group and two hydrogen atoms.

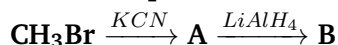
Step 1: Count the groups attached directly to nitrogen In $(\text{C}_2\text{H}_5)_2\text{CHNH}_2$, nitrogen belongs to an $-\text{NH}_2$ group and is bonded to just one carbon atom, the CH carbon. Hence this compound is a primary amine. The two ethyl groups on that carbon do not increase the number of carbon groups directly bonded to nitrogen.

Step 2: Compare the other two compounds In $(\text{C}_2\text{H}_5)_2\text{NH}$, nitrogen is bonded directly to two ethyl groups, so it is a secondary amine. In $(\text{CH}_3)_3\text{N}$, nitrogen is bonded directly to three methyl groups, so it is a tertiary amine.

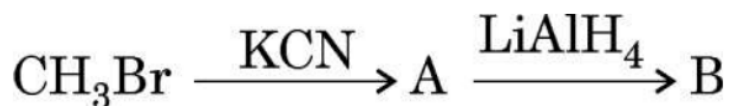
Step 3: Conclusion The primary amine is $(\text{C}_2\text{H}_5)_2\text{CHNH}_2$, because its nitrogen is bonded to one carbon group and two hydrogens.

Quick Tip to Solve: Classify the amine by counting carbon groups attached to nitrogen; branching at the adjacent carbon does not make an $-\text{NH}_2$ group secondary.

8(b). Complete the following:



[2 marks]

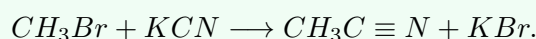


Solution:

Concept:

- With ionic KCN , the carbon end of the cyanide ion attacks an alkyl halide to form a nitrile, $\text{R}-\text{C} \equiv \text{N}$. This reaction increases the carbon chain by one carbon atom.
- Lithium aluminium hydride, LiAlH_4 , reduces the nitrile group to a primary amine: $\text{R}-\text{C} \equiv \text{N} \longrightarrow \text{R}-\text{CH}_2\text{NH}_2$, retaining the nitrile carbon in the chain.

Step 1: Identify intermediate A Cyanide ion replaces bromide in methyl bromide by nucleophilic substitution. Carbon attack gives the carbon-carbon bond in the nitrile:



Therefore, A is ethanenitrile (acetonitrile), CH_3CN . The product has two carbon atoms; KCN gives a nitrile rather than the isocyanide obtained predominantly with AgCN .

Quick Tip to Solve: Count the cyanide carbon: KCN adds one carbon, and nitrile reduction retains it in the resulting primary amine.

Step 2: Identify reduction product B Reduction of the carbon-nitrogen triple bond with $LiAlH_4$, followed by hydrolysis, converts the nitrile carbon into a methylene group and nitrogen into $-NH_2$:



Here $[H]$ denotes reducing hydrogen equivalents. Thus B is ethanamine (ethylamine), a primary amine containing two carbon atoms, rather than methylamine.

Step 3: Conclusion $A = CH_3CN$ (ethanenitrile), $B = CH_3CH_2NH_2$ (ethanamine).

Quick Tip to Solve: Count the cyanide carbon: KCN adds one carbon, and nitrile reduction retains it in the resulting primary amine.

9. (a) Write the hybridisation, shape and magnetic character of $[CoF_6]^{3-}$. [Atomic number of Co = 27]

(b) Write the formula of Pentaamminechloridocobalt(III) chloride.

[3 marks]

Solution:

Concept:

- The oxidation state of the metal follows from the complex charge and ligand charges. The d -electron count of the metal ion is then used with ligand strength to determine pairing and hybridisation.
- Fluoride is a weak-field ligand; an octahedral cobalt(III) fluoride complex is high spin. Unpaired electrons make a complex paramagnetic.
- In a coordination formula, ligands bound to the metal are inside square brackets, while counter-ions are outside; their charges must give an electrically neutral compound.

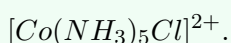
Step 1: Part (a): Find the cobalt ion and its electron count Each fluoride ligand has charge -1 . If the oxidation state of Co is x , then

$$x + 6(-1) = -3 \Rightarrow x = +3.$$

Cobalt has atomic number 27 and ground-state configuration $[Ar]3d^74s^2$. Removing the two $4s$ electrons and one $3d$ electron gives $Co^{3+} : [Ar]3d^6$.

Step 2: Part (a): Determine hybridisation, shape and magnetism The six F^- ligands are weak-field ligands and do not cause pairing of the $3d$ electrons. The high-spin d^6 ion has one doubly occupied and four singly occupied $3d$ orbitals, so there are four unpaired electrons. Two vacant inner $3d$ orbitals are therefore unavailable for d^2sp^3 hybridisation. The metal instead uses its outer $4s$, three $4p$ and two $4d$ orbitals to form six sp^3d^2 hybrid orbitals. Hence the complex is an outer-orbital octahedral complex and is paramagnetic because of its four unpaired electrons. Equivalently, its octahedral occupation is $t_{2g}^4e_g^2$.

Step 3: Part (b): Translate the coordination name into a formula Pentaammine means five neutral NH_3 ligands; chlorido means one coordinated Cl^- ligand. The cobalt(III) ion contributes $+3$, making the charge of the coordination entity $+3 - 1 = +2$:



Quick Tip to Solve: First calculate the metal oxidation state; in the named salt, distinguish the one chlorido ligand inside the brackets from chloride counter-ions outside.

Two chloride counter-ions are required outside the brackets to balance this charge, so the compound is $[Co(NH_3)_5Cl]Cl_2$. The coordinated chloride is included within the bracket and is distinct from the two counter-ions.

Step 4: Conclusion (a) $[CoF_6]^{3-}$: sp^3d^2 hybridisation, octahedral shape and paramagnetic, with four unpaired electrons. (b) Pentaamminechloridocobalt(III) chloride is $[Co(NH_3)_5Cl]Cl_2$.

Quick Tip to Solve: First calculate the metal oxidation state; in the named salt, distinguish the one chlorido ligand inside the brackets from chloride counter-ions outside.

10(a). Account for the following:

(a) Transition elements show variable oxidation states.

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

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

[3 marks]

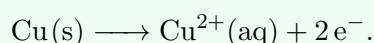
Solution:

Concept:

- Transition elements have closely spaced $(n-1)d$ and ns orbital energies, so electrons from both subshells can participate in bonding.
- The standard electrode potential for Cu^{2+}/Cu depends on the overall energy balance of atomisation, ionisation and hydration.
- Oxidation is loss of electrons; a reducing agent is itself oxidised. A particularly stable product configuration can favour oxidation.

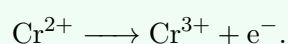
Step 1: Explain variable oxidation states (a) The energy difference between the $(n-1)d$ and ns orbitals is small. Therefore, in addition to the outer ns electrons, different numbers of $(n-1)d$ electrons can take part in bond formation. Loss or sharing of these different numbers of electrons gives several oxidation states. For example, manganese exhibits oxidation states from +2 to +7 in its compounds.

Step 2: Explain the positive copper electrode potential (b) Consider the conversion of solid copper into aqueous copper(II) ions:



Copper has a high enthalpy of atomisation and high ionisation enthalpies. In particular, its second ionisation removes an electron from the stable $3d^{10}$ configuration of Cu^+ . The hydration enthalpy released on forming $Cu^{2+}(aq)$ is insufficient to compensate for these energy requirements. Thus oxidation of copper is unfavourable relative to hydrogen under standard conditions, giving a highly positive standard reduction potential for the reverse Cu^{2+}/Cu process.

Step 3: Relate chromium's reducing action to its configuration (c) Cr^{2+} has the configuration $3d^4$. It readily loses one electron to form Cr^{3+} , which has the more stable $3d^3$ configuration:



Quick Tip to Solve: For these reasons, link variable valency to the small d-s energy gap, copper's potential to the full energy balance, and chromium's reducing action to the product's d3 configuration.

In an octahedral environment the d^3 configuration gives a particularly stable t_{2g}^3 arrangement. Since Cr^{2+} is readily oxidised and supplies an electron to another species, it acts as a strong reducing agent.

Step 4: Conclusion (a) Closely spaced d and s orbital energies permit variable oxidation states. (b) Copper's high atomisation and ionisation energy costs are not compensated by hydration, so $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ is highly positive. (c) Cr^{2+} readily forms stable $3d^3 \text{Cr}^{3+}$, making it a strong reducing agent.

Quick Tip to Solve: For these reasons, link variable valency to the small d-s energy gap, copper's potential to the full energy balance, and chromium's reducing action to the product's d^3 configuration.

OR

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

[3 marks]

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in atomic and ionic radii with increasing atomic number across the lanthanoid series.
- The $4f$ electrons shield the increasing nuclear charge poorly, so the effective nuclear attraction for the outer electrons increases.
- Similar ionic sizes produce similar chemical behaviour, while contraction can also make corresponding $4d$ and $5d$ transition elements nearly equal in size.

Step 1: Define and explain lanthanoid contraction On moving from lanthanum to lutetium, the atomic radii and, more regularly, the radii of the corresponding Ln^{3+} ions decrease gradually. This systematic decrease in size with increasing atomic number is called lanthanoid contraction. Here Ln^{3+} denotes a tripositive lanthanoid ion. Across the series, the nuclear charge increases by one at each successive element and the added electrons enter the inner $4f$ subshell. Since $4f$ electrons do not shield the nuclear charge effectively, the increasing nuclear attraction draws the electron cloud closer to the nucleus.

Step 2: State the difficulty in separating lanthanoids First consequence: the Ln^{3+} ions have very similar radii and the lanthanoids commonly show the same $+3$ oxidation state. Their compounds therefore have closely similar chemical properties. As a result, separating individual lanthanoids from one another is difficult; the small differences in ionic size must be exploited by suitable separation methods.

Step 3: Compare corresponding transition elements Second consequence: the contraction across the lanthanoid series largely compensates for the size increase expected on moving from the $4d$ transition series to the $5d$ series. Thus zirconium and hafnium, Zr and Hf , have nearly equal atomic radii even though hafnium belongs to the next period. Their similar sizes lead to very similar chemical properties.

Step 4: Conclusion Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the lanthanoid series due to poor shielding by $4f$ electrons. Two consequences are the difficult separation of lanthanoids and the nearly equal sizes and similar chemistry of corresponding $4d$ and $5d$ elements

Quick Tip to Solve: Remember two distinct consequences: similar lanthanoid ions are hard to separate, and the Zr-Hf size similarity links the $4d$ and $5d$ series.

such as Zr and Hf.

Quick Tip to Solve: Remember two distinct consequences: similar lanthanoid ions are hard to separate, and the Zr-Hf size similarity links the 4d and 5d series.

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:

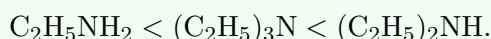
Concept:

- Gabriel phthalimide synthesis forms a carbon–nitrogen bond by nucleophilic substitution of a halide by the phthalimide anion, followed by hydrolysis to give a primary amine.
- Basic strength measures the ability of the nitrogen lone pair to accept a proton. Electron donation increases its availability, whereas resonance delocalisation decreases it.
- In aqueous solution, the basic strength of an alkylamine depends on the electron-releasing inductive effect of alkyl groups and the solvation of its conjugate ammonium ion.

Step 1: (a) Explain the limitation of Gabriel synthesis An aromatic primary amine such as aniline would require the phthalimide anion to replace the halogen of an aryl halide, such as chlorobenzene. In an aryl halide, the carbon bonded to the halogen is sp^2 -hybridised and the carbon–halogen bond has partial double-bond character owing to resonance with the aromatic ring. Consequently, aryl halides do not undergo the nucleophilic substitution required under the usual conditions of Gabriel synthesis. The nitrogen–aryl bond therefore cannot be formed by this route, so aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

Step 2: (b) Compare the availability of the nitrogen lone pair In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance. It is therefore less available to bond to an incoming proton. Protonation also removes this lone pair from conjugation with the ring, so the resonance stabilisation of aniline favours the unprotonated form. In alkylamines, the lone pair is localised on nitrogen and the alkyl groups exert an electron-releasing $+I$ effect, increasing electron density on nitrogen. Thus alkylamines accept a proton more readily than aniline, making aniline the weaker base.

Step 3: (c) Balance the inductive and solvation effects in water Ethyl groups increase basic strength by their $+I$ effect. However, the conjugate ammonium ions are also stabilised by hydration in water; increasing alkyl substitution reduces this hydration and increases steric crowding around nitrogen. For the given ethylamines, the combined effects make diethylamine the strongest base. Triethylamine is stronger than ethylamine because its greater electron donation outweighs its reduced hydration, but it remains weaker than diethylamine. Hence, the increasing order is



Quick Tip to Solve: For ethylamines in water, remember primary < tertiary < secondary; do not use the inductive effect alone to rank aqueous basic strength.

Step 4: Conclusion (a) Aryl halides do not undergo the nucleophilic substitution required in Gabriel synthesis. (b) Resonance makes aniline's nitrogen 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 primary < tertiary < secondary; do not use the inductive effect alone to rank aqueous basic strength.

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 the carbonyl group. Aldehydes are prepared by the oxidation of alcohols. Formaldehyde is sold in an aqueous solution called formalin. Propanone, the 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 at least one α -hydrogen on a carbon adjacent to the aldehyde or ketone carbonyl group.
- A base removes an α -hydrogen to generate the nucleophile that attacks another carbonyl molecule.

Step 1: Check ethanal Ethanal, CH_3CHO , has three α -hydrogens on the methyl carbon next to the CHO group. It therefore undergoes aldol addition in dilute base and condensation on heating.

Step 2: Exclude the other compounds Methanal, HCHO , has no α -carbon and hence no α -hydrogen. Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, also lacks an α -hydrogen; the ring carbon attached to CHO carries no hydrogen. Neither can undergo self-aldol condensation.

Step 3: Conclusion Only ethanal, CH_3CHO , undergoes aldol condensation.

Quick Tip to Solve: Look for a hydrogen on the carbon immediately beside the carbonyl carbon; the aldehydic hydrogen itself does not count.

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

[1 mark]

Solution:

Concept:

- Tollens' reagent is freshly prepared ammoniacal silver nitrate, containing the diamminesilver(I) ion, $[\text{Ag}(\text{NH}_3)_2]^+$.
- An aldehyde reduces silver(I) to metallic silver while being oxidised to a carboxylate ion; an ordinary ketone does not give this reaction.

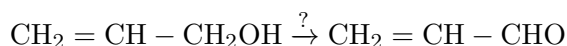
Step 1: Apply the test Add freshly prepared Tollens' reagent separately to propanal and propanone in clean test tubes and warm gently in a water bath.

Step 2: Compare the observations Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, gives a silver mirror on the inner wall of the tube because its aldehyde group reduces the reagent. Propanone, CH_3COCH_3 , gives no silver mirror under the same conditions because its ketone group is not oxidised by Tollens' reagent.

Step 3: Conclusion Tollens' test distinguishes them: propanal gives a silver mirror, whereas propanone does not.

Quick Tip to Solve: Use the silver-mirror observation to distinguish an aldehyde from a ketone; a carbonyl test alone would be positive for both.

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).
- PCC in an anhydrous solvent is a controlled oxidant: it permits isolation of the aldehyde without continued oxidation to the carboxylic acid.

Step 1: Identify the required transformation The starting compound, $\text{CH}_2=\text{CHCH}_2\text{OH}$, is prop-2-en-1-ol, a primary allylic alcohol. The product, $\text{CH}_2=\text{CHCHO}$, is prop-2-enal. Only the terminal CH_2OH group must change to CHO ; the carbon-carbon double bond must remain intact.

Step 2: Choose the reagent Use PCC in dry dichloromethane, CH_2Cl_2 . This reagent oxidises the primary alcohol to the aldehyde under controlled, non-aqueous conditions while retaining the carbon-carbon double bond.

Step 3: Conclusion The required reagent is pyridinium chlorochromate (PCC) in dry CH_2Cl_2 .

Quick Tip to Solve: When a primary alcohol must stop at an aldehyde and retain a $\text{C}=\text{C}$ bond, choose controlled oxidation with PCC.

12(d)(i). An alcohol 'A', (C_3H_8O) 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'.

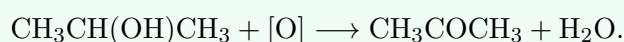
[2 marks]

Solution:

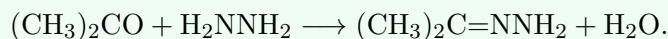
Concept:

- Oxidation of a secondary alcohol produces a ketone, whereas oxidation of a primary alcohol initially produces an aldehyde.
- A methyl ketone gives the iodoform test with $I_2/NaOH$, producing yellow CHI_3 . A carbonyl compound reacts with hydrazine to form a hydrazone.

Step 1: Identify the alcohol and its oxidation product Compound B is a carbonyl compound because it reacts with hydrazine. Its negative Tollens' test indicates a ketone rather than an aldehyde. The three-carbon ketone is propanone, CH_3COCH_3 . Therefore A is the corresponding secondary alcohol, propan-2-ol:



Step 2: Identify the hydrazine product Propanone condenses with hydrazine, H_2NNH_2 , with elimination of water:



Thus C is propanone hydrazone. The product retains one terminal NH_2 group.

Step 3: Identify the yellow precipitate Propanone contains the CH_3CO- group and gives the iodoform reaction:



The yellow precipitate D is iodoform, CHI_3 .

Step 4: Conclusion A: propan-2-ol, $CH_3CH(OH)CH_3$; B: propanone, CH_3COCH_3 ; C: propanone hydrazone, $(CH_3)_2C=NNH_2$; D: iodoform, CHI_3 .

Quick Tip to Solve: Combine the negative Tollens test with the positive iodoform test: a three-carbon carbonyl compound satisfying both is propanone.

OR

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

(I) Clemmensen reduction

(II) HVZ reaction

[2 marks]

Solution:

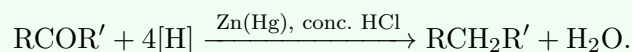
Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using amalgamated zinc, $Zn(Hg)$, and concentrated hydrochloric acid.
- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an α -hydrogen of a carboxylic acid by a halogen.

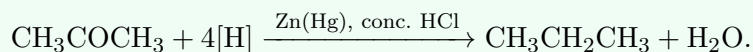
Quick Tip to Solve: For Clemmensen reduction replace $C=O$ by CH_2 ; for HVZ, replace an α -hydrogen next to $COOH$ by bromine.

Bromine in the presence of red phosphorus, followed by hydrolysis, gives an α -bromocarboxylic acid.

Step 1: (I) Clemmensen reduction For a ketone, the general reaction is

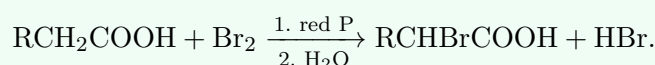


Here R and R' are alkyl or aryl groups, and $[\text{H}]$ denotes reducing hydrogen equivalents. For example, propanone is reduced to propane:

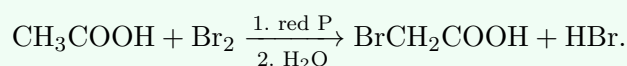


The oxygen of the carbonyl group is removed as water; reduction does not stop at the alcohol stage.

Step 2: (II) Hell-Volhard-Zelinsky reaction An acid containing at least one α -hydrogen undergoes bromination at the carbon adjacent to the carboxyl group:



In this formula R is an alkyl group or hydrogen. Red phosphorus promotes formation of the acid halide, which undergoes α -bromination; hydrolysis restores the carboxyl group. For example, ethanoic acid gives bromoethanoic acid:



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: $\text{CH}_3\text{COOH} \xrightarrow[2. \text{H}_2\text{O}]{1. \text{Br}_2, \text{red P}} \text{BrCH}_2\text{COOH}$.

Quick Tip to Solve: For Clemmensen reduction replace $\text{C}=\text{O}$ by CH_2 ; for HVZ, replace an α -hydrogen next to COOH by bromine.