

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-6-3 - 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.

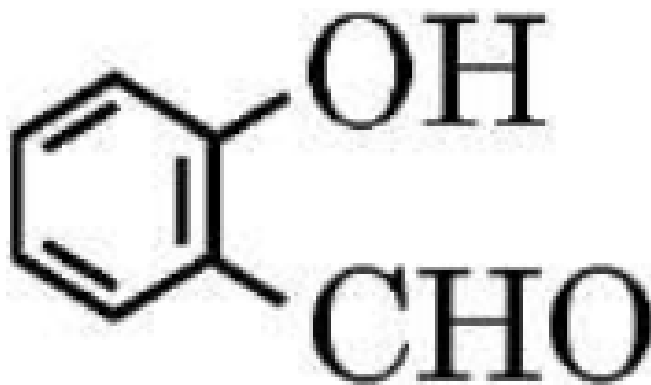
Section A (6 marks)

1. (a) Arrange the following compounds in the increasing order of their boiling points:

CH_3COCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3COOH

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

[2 marks]



Solution:

Concept:

- Boiling point rises with intermolecular attraction. Hydrogen bonding is stronger than ordinary dipole-dipole attraction for these comparable small molecules.
- In substituted benzaldehyde, the ring carbon bearing the aldehyde group is numbered 1; a neighbouring substituent is at position 2.

Step 1: (a) Compare the intermolecular forces Acetone, CH_3COCH_3 , is polar but lacks an O – H bond, so its molecules cannot hydrogen-bond to one another. Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, forms intermolecular hydrogen bonds and consequently boils at a higher temperature. Acetic acid, CH_3COOH , forms strongly associated hydrogen-bonded dimers, producing the greatest intermolecular attraction here. Hence the increasing order is



Step 2: (b) Identify the parent and locate the hydroxy group The structure contains a benzene ring bearing –CHO and –OH on adjacent carbons. The aldehyde is the principal functional group, so benzaldehyde is the parent name. Numbering its attached ring carbon as 1 places the hydroxy substituent at carbon 2. Therefore its IUPAC name is 2-hydroxybenzaldehyde.

Step 3: Conclusion (a) $\text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CH}_2\text{OH} < \text{CH}_3\text{COOH}$. (b) 2-hydroxybenzaldehyde.

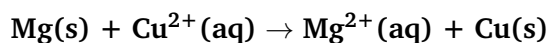
Quick Tip to Solve: Look for an O-H bond when comparing boiling points; for the name, count from the ring carbon attached to CHO.

2. 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:

- Direct current can cause electrolysis and electrode polarisation; alternating current reverses direction rapidly, suppressing these effects during resistance measurement.
- At infinite dilution, ions contribute independently to the limiting molar conductivity of an electrolyte.
- In a galvanic cell oxidation occurs at the negative anode and reduction at the positive cathode. The salt bridge maintains electrical neutrality.

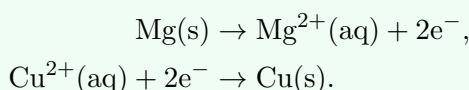
Step 1: (a) Explain the use of alternating current With direct current, ions undergo sustained discharge at electrodes and products can accumulate there. The resulting polarisation and change in ionic concentration alter the measured resistance. Alternating current rapidly reverses electrode polarity, avoiding appreciable electrolysis and polarisation, so the resistance of the solution can be measured reliably.

Step 2: (b) State Kohlrausch's law At infinite dilution, each ion makes a definite contribution to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present. Thus

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ,$$

where λ_+° and λ_-° are limiting ionic molar conductivities and ν_+ , ν_- are the numbers of the respective ions per formula unit.

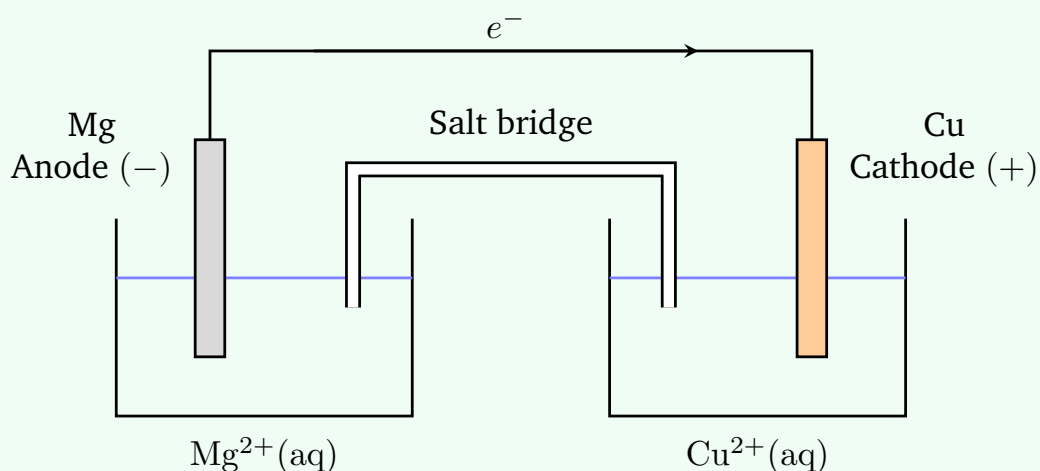
Step 3: (c) Depict the magnesium-copper cell Magnesium is oxidised at the anode and copper ions are reduced at the cathode:



The cell notation is



Electrons flow from Mg to Cu through the external circuit. Anions from the salt bridge migrate towards the Mg compartment; cations migrate towards the Cu compartment.



Magnesium-copper galvanic cell with electron flow from the anode to the cathode.

Step 4: Conclusion AC prevents appreciable electrolysis and polarisation; Kohlrausch's law expresses independent limiting ionic contributions; the cell is $\text{Mg}|\text{Mg}^{2+}||\text{Cu}^{2+}|\text{Cu}$, with Mg as anode and Cu as cathode. Any two parts may be attempted.

Quick Tip to Solve: Use the given reaction to place the oxidised metal on the left of the cell notation and the reduced ion on the right.

3. (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:

- The half-life, $t_{1/2}$, is the time required for the reactant concentration to fall to half its initial value. For a first-order reaction, $t_{1/2} = \ln 2/k$, where k is the rate constant.
- Order is the sum of the concentration exponents in the experimentally determined rate law. Molecularity counts the reacting species participating in a single elementary reaction step.

Step 1: (a) Identify the reaction order For a first-order reaction, the integrated rate equation is

$$kt = \ln \frac{[R]_0}{[R]_t}$$

At the half-life, $[R]_t = [R]_0/2$. Substitution gives $kt_{1/2} = \ln 2$, or $t_{1/2} = 0.693/k$. Since the initial concentration cancels, the given concentration-independent half-life identifies a first-order reaction.

Step 2: (b) Distinguish order from molecularity Order can be zero, fractional or an integer because it is obtained from the observed rate law. Molecularity is always a positive integer because it counts actual reacting species in an elementary step; it can never be zero or fractional. For example, an experimentally measured order of $1/2$ is possible, whereas a molecularity of $1/2$ is impossible.

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

Quick Tip to Solve: If half-life remains unchanged when initial concentration changes, immediately use the first-order relation $t_{1/2} = 0.693/k$.

Section B (24 marks)

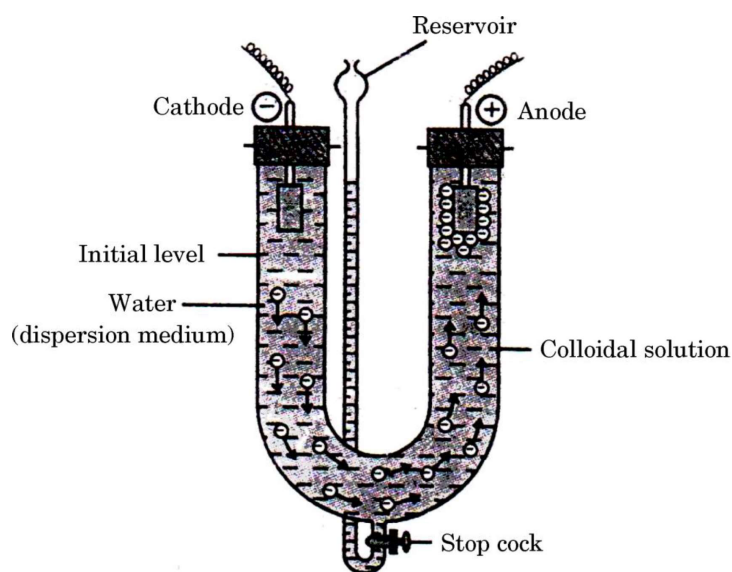
4(a). Answer the following questions on the basis of the given figure:

(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 bearing the opposite charge; this movement is electrophoresis.
- Like charges on sol particles produce mutual electrostatic repulsion and help keep a lyophobic sol stable. Discharge of the particles removes this repulsion and permits aggregation.

Step 1: (a) Identify and define the illustrated process The process is electrophoresis: the movement of charged colloidal particles towards the oppositely charged electrode under the influence of an applied electric field. In the figure, negatively charged colloidal particles move towards the positive electrode, the anode. The direction of particle motion therefore also indicates the sign of the charge on the sol particles.

Step 2: (b) Explain its use for coagulating lyophobic sols Yes. When a suitable electric field is applied for a sufficiently long time, the charged particles migrate to the oppositely charged electrode and lose their charge there. The loss of charge removes the repulsive force that had kept the particles

separated. They can then come together, form larger aggregates and precipitate. Thus persistent electrophoresis can bring about coagulation of a lyophobic sol.

Step 3: (c) Define coagulation Coagulation is the precipitation of colloidal particles by their aggregation into larger particles, usually following neutralisation of their charge. These larger aggregates no longer remain dispersed as a stable sol and separate out. The process is also called flocculation; addition of an electrolyte is another common way of producing it in lyophobic sols.

Step 4: Conclusion (a) The figure shows electrophoresis. (b) Yes; particles lose their charge at the opposite electrode and coagulate. (c) Coagulation is the aggregation and precipitation of colloidal particles.

Quick Tip to Solve: Follow the particle arrows towards the anode: motion of charged particles identifies electrophoresis, and their discharge explains coagulation.

OR

4(b). Define the following terms:

(a) Adsorption

(b) Lyophobic sol

(c) Multimolecular colloid

[3 marks]

Solution:

Concept:

- A surface phenomenon involves accumulation at an interface, whereas a colloid contains a dispersed phase distributed through a dispersion medium.
- Colloids can be classified by the affinity between the two phases and by the nature of the particles forming the dispersed phase.

Step 1: (a) Adsorption Adsorption is the accumulation of molecules or ions of a substance on the surface of a solid or liquid, so that their concentration at the surface is greater than in the bulk. The substance accumulated is the adsorbate and the material on whose surface accumulation occurs is the adsorbent. For example, gases are adsorbed on activated charcoal. Adsorption is a surface phenomenon; absorption involves penetration throughout the bulk.

Step 2: (b) Lyophobic sol A lyophobic sol is a colloidal system in which the dispersed phase has little or no affinity for the dispersion medium. Such sols require special methods of preparation and are comparatively unstable: a small amount of a suitable electrolyte can coagulate them. Their formation is generally irreversible, since simply mixing the separated phase with the medium does not restore the sol. Gold sol in water is an example.

Step 3: (c) Multimolecular colloid A multimolecular colloid is formed when a large number of atoms or small molecules aggregate together to produce particles of colloidal dimensions, approximately 1 to 1000 nm. The constituent atoms or molecules are held together by van der Waals forces. Gold sol, containing aggregates of gold atoms, and sulphur sol, containing aggregates of S_8 molecules, are examples. Each colloidal particle is therefore an aggregate rather than one giant molecule.

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

Quick Tip to Solve: Classify by the defining feature: surface concentration for adsorption, phase affinity for lyophobic sols, and aggregated small units for multimolecular colloids.

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:

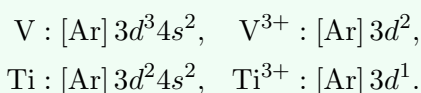
Concept:

- Oxidation states depend on the electrons lost from the outer orbitals; the most common lanthanoid oxidation state is +3.
- Atomic size depends on effective nuclear attraction. Across a transition series, added d -electrons only partly shield the increasing nuclear charge.
- For transition-metal cations, remove $4s$ -electrons before $3d$ -electrons. By Hund's rule, electrons occupy different degenerate d -orbitals singly before pairing.

Step 1: (i) Common oxidation state of lanthanoids The most common oxidation state of lanthanoids is +3. They generally form trivalent ions by losing the two outer $6s$ -electrons and one more electron from the $5d$ or $4f$ subshell. Although some lanthanoids also exhibit +2 or +4, these are not the oxidation states common to the series.

Step 2: (ii) Explain the decrease in atomic size On moving across a transition series, the nuclear charge increases by one at each successive element, while the added electron enters the inner $(n-1)d$ subshell. The shielding provided by these added d -electrons does not completely offset the increasing nuclear charge. Consequently, the effective nuclear attraction on the outer electrons increases and pulls the electron cloud closer to the nucleus. This produces the gradual decrease in atomic size across the series. The decrease is relatively small because the additional d -electrons do provide some shielding.

Step 3: (iii) Count the unpaired electrons in the gaseous ions For vanadium, $Z = 23$, and for titanium, $Z = 22$. Their configurations and those of the trivalent ions are



In each case, first remove the two $4s$ -electrons and then one $3d$ -electron. The two d -electrons of gaseous V^{3+} occupy separate orbitals and are unpaired; the sole d -electron of gaseous Ti^{3+} is also unpaired. Thus their numbers of unpaired electrons are 2 and 1, respectively.

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

Quick Tip to Solve: Write the neutral configuration first, remove both $4s$ electrons before any $3d$ electron, then use Hund's rule to count unpaired electrons.

5(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 a partially filled d subshell in its atom or in at least one of its ions. Colour in aqueous transition-metal ions commonly arises from d-d electronic transitions.

Step 1: (i) Obtain the configuration and moment of cerium(III) On forming Ce^{3+} , neutral cerium loses its two 6s electrons and its one 5d electron. Thus



Its single 4f electron is unpaired, so $n = 1$. Substitution in the spin-only expression gives

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

This is the spin-only value specifically requested in the question.

Step 2: (ii) Apply the transition-element definition to copper Copper has the ground-state configuration $[\text{Ar}]3d^{10}4s^1$, so the atom has a full d subshell. However, it forms Cu^{2+} with configuration $[\text{Ar}]3d^9$. This ion has an incompletely filled d subshell and therefore copper satisfies the definition of a transition element. A filled d subshell in the neutral atom alone does not exclude an element from this category.

Step 3: (iii) Compare the aqueous ions Sc^{3+} has configuration $[\text{Ar}]3d^0$. It has no d electron available for a d-d transition and is colourless in aqueous solution. In contrast, Ti^{3+} is $[\text{Ar}]3d^1$. Water ligands split its d orbitals into sets of different energies; the d electron absorbs visible light to move to a higher set. The remaining transmitted light gives the solution its colour.

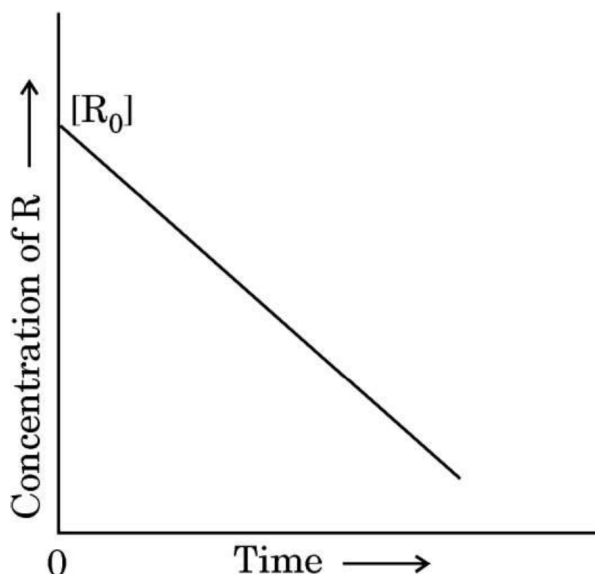
Step 4: Conclusion (i) $\mu_{\text{spin-only}}(\text{Ce}^{3+}) = 1.73 \mu_B$. (ii) Copper is a transition element because Cu^{2+} is $3d^9$. (iii) Sc^{3+} is d^0 and has no d-d transition, whereas Ti^{3+} is d^1 and absorbs visible light by a d-d transition.

Quick Tip to Solve: Remove outer 6s electrons before 5d electrons when forming Ce^{3+} ; then count unpaired electrons in the ion, not the atom.

6(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:

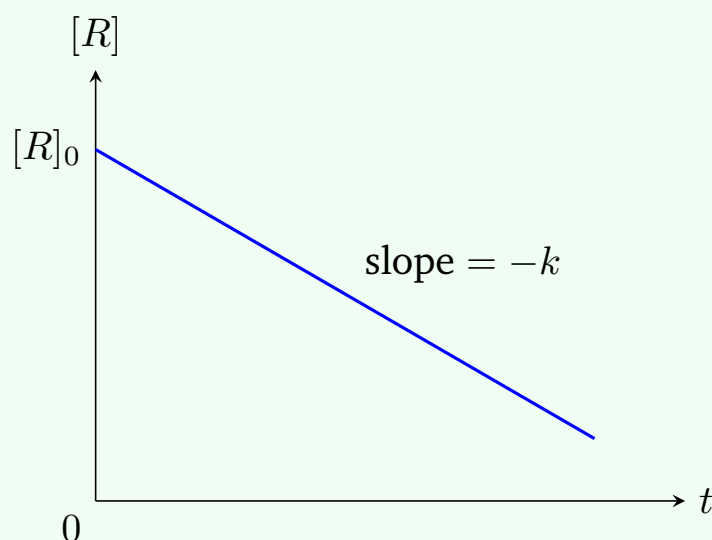
Concept:

- For a zero-order reaction, $-d[R]/dt = k$, where $[R]$ is the reactant concentration, t is time and k is the rate constant.
- Integration gives $[R] = [R]_0 - kt$. Comparing this with $y = c + mx$, a concentration-time plot has intercept $[R]_0$ and slope $-k$.

Step 1: (i) Identify the order from the plotted variables The given graph plots concentration directly against time and is a straight line with a negative slope. The reactant concentration therefore falls by equal amounts in equal time intervals. This matches the integrated zero-order rate law,

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

Hence the reaction is zero order. For a first-order reaction, it is the logarithm of concentration, rather than concentration itself, that decreases linearly with time.



Zero-order concentration-time plot: vertical intercept $[R]_0$ and slope $-k$.

Step 2: (ii) Read the slope of the line Write the integrated equation in the straight-line form $y = mx + c$, taking $y = [R]$ and $x = t$. The coefficient of time is $-k$, so

$$\text{slope} = \frac{[R]_2 - [R]_1}{t_2 - t_1} = -k.$$

The negative sign indicates consumption of reactant. The rate constant k itself is positive; the intercept on the concentration axis is $[R]_0$. No numerical slope can be calculated because the supplied axes have no numerical scale.

Step 3: (iii) Determine the units of the rate constant From $kt = [R]_0 - [R]$, the product kt must have units of concentration. Therefore

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

when concentration is measured in mol L^{-1} and time in seconds. The equivalent SI units are $\text{mol m}^{-3} \text{s}^{-1}$. The units s^{-1} apply to a first-order rate constant and do not apply to this graph.

Step 4: Conclusion (i) The reaction is zero order. (ii) The slope of the concentration-time line is $-k$. (iii) The units of k are $\text{mol L}^{-1} \text{s}^{-1}$, for concentration in molarity and time in seconds.

Quick Tip to Solve: First inspect the vertical-axis variable: a straight line of concentration against time identifies zero order and has slope $-k$.

6(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 satisfies $t_{1/2} = \frac{2.303 \log 2}{k}$. The fraction remaining, rather than the fraction decomposed, enters the logarithm.

Step 1: Obtain the rate constant from the half-life Fifty per cent decomposition leaves half the original reactant. Thus the given time is the half-life, $t_{1/2} = 24$ min. From the given logarithm,

$$\log 2 = \frac{1}{2} \log 4 = 0.30105, \quad k = \frac{2.303(0.30105)}{24} = 0.02889 \text{ min}^{-1}.$$

The rate constant is independent of the initial concentration for this first order reaction.

Step 2: Use the fraction remaining after 25 per cent decomposition Take an initial amount of 100 units. When 25 units have decomposed, 75 units remain, so $[R]_t = 0.75[R]_0$. Substitution in the integrated rate law gives

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{100}{75} = \frac{2.303}{k} (\log 4 - \log 3) \\ &= 24 \frac{0.6021 - 0.4771}{0.30105} = \frac{3.0000}{0.30105} = 9.965 \text{ min.} \end{aligned}$$

This is less than the half-life, as expected because less than half the reactant has decomposed. The time is not proportional to percentage decomposition because the rate decreases as reactant is consumed.

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

Quick Tip to Solve: For 25% decomposition use 75% remaining: divide the two time expressions to cancel both k and 2.303.

7. The conductivity of 2.5×10^{-4} M methanoic acid is $5.25 \times 10^{-5} \text{ S cm}^{-1}$ and its Λ_m^0 has a value $400 \text{ S cm}^2 \text{ mol}^{-1}$. Calculate its molar conductivity and degree of dissociation.

[3 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa \frac{1000}{c}$ when conductivity κ is in S cm^{-1} and concentration c is in mol L^{-1} .

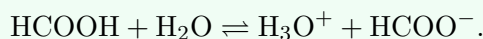
- For a weak electrolyte, the degree of dissociation is $\alpha = \frac{\Lambda_m}{\Lambda_m^0}$, where Λ_m^0 is the limiting molar conductivity at infinite dilution.

Step 1: Convert conductivity into molar conductivity The given concentration is $c = 2.5 \times 10^{-4} \text{ mol L}^{-1}$ and the conductivity is $\kappa = 5.25 \times 10^{-5} \text{ S cm}^{-1}$. One litre is 1000 cm^3 , so the volume containing one mole of solute is $1000/c$ in cubic centimetres. Hence

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{5.25 \times 10^{-5} \times 1000}{2.5 \times 10^{-4}} \\ &= 210 \text{ S cm}^2 \text{ mol}^{-1}.\end{aligned}$$

The factor 1000 is essential because the concentration is specified per litre while conductivity uses centimetres.

Step 2: Calculate the fraction of acid dissociated Methanoic acid is a weak electrolyte and dissociates according to



At infinite dilution it is effectively completely dissociated. Therefore, comparing its molar conductivity at the stated concentration with the limiting value gives

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{210}{400} = 0.525.$$

Both conductivities have the same units, so their ratio is dimensionless. The percentage dissociation is $100\alpha = 52.5\%$. The value lies between zero and one, consistent with partial dissociation of the acid.

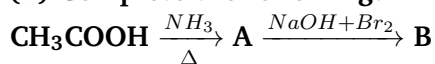
Step 3: Conclusion The molar conductivity is $210 \text{ S cm}^2 \text{ mol}^{-1}$, and the degree of dissociation is $\alpha = 0.525$, or 52.5%.

Quick Tip to Solve: With conductivity in S cm^{-1} and concentration in molarity, include 1000 before taking $\Lambda_m/400$.

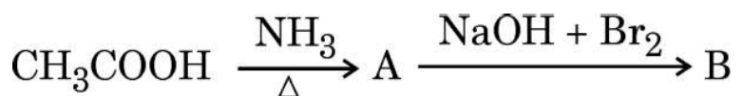
8. (a) Choose the tertiary amine from the following compounds:

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

(b) Complete the following:



[3 marks]



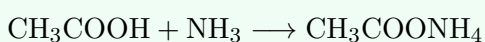
Solution:

Concept:

- Amines are classified by the number of carbon groups directly attached to nitrogen: primary has one, secondary has two, and tertiary has three.
- A carboxylic acid reacts with ammonia to form an ammonium carboxylate, which loses water on heating to give an amide.
- Hofmann bromamide degradation converts a primary amide into a primary amine containing one carbon atom fewer, using bromine and aqueous sodium hydroxide.

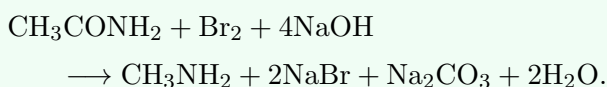
Step 1: (a) Count the groups attached to nitrogen In $\text{CH}_3\text{NHCH}(\text{CH}_3)\text{CH}_3$, nitrogen is bonded to two carbon groups and one hydrogen, so this is a secondary amine. In $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, nitrogen is bonded to one carbon group and two hydrogens, so this is a primary amine. The third compound, $\text{CH}_3\text{N}(\text{CH}_3)\text{C}_2\text{H}_5$, has two methyl groups and one ethyl group directly attached to nitrogen, with no N-H bond. It is therefore the tertiary amine.

Step 2: (b) Identify the amide A Ethanoic acid first forms ammonium ethanoate with ammonia. Heating dehydrates this salt to ethanamide (acetamide):



Hence A is CH_3CONH_2 . The carbonyl carbon is retained in this first conversion.

Step 3: (b) Apply Hofmann bromamide degradation to find B Bromine and sodium hydroxide convert ethanamide into methanamine (methylamine). The carbonyl carbon leaves the organic product and appears in carbonate:



Thus B is CH_3NH_2 , with one carbon atom compared with the two in A.

Step 4: Conclusion (a) The tertiary amine is $\text{CH}_3\text{N}(\text{CH}_3)\text{C}_2\text{H}_5$. (b) $\boxed{\text{A} = \text{CH}_3\text{CONH}_2, \quad \text{B} = \text{CH}_3\text{NH}_2}$.

Quick Tip to Solve: Count carbon groups directly bonded to N, then remember that Hofmann degradation removes the amide carbonyl carbon.

9. (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:

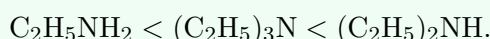
Concept:

- Gabriel phthalimide synthesis requires nucleophilic substitution of a halide by the phthalimide anion, followed by hydrolysis to release a primary amine.
- Basicity measures the tendency to accept a proton through the nitrogen lone pair. Electron donation increases its availability; resonance delocalisation decreases it.
- In water, amine basicity depends on the inductive effect as well as hydration and steric effects in the protonated amine.

Step 1: (a) Explain the limitation of Gabriel synthesis Aromatic primary amines would require an aryl halide, ArX , to react with potassium phthalimide. Aryl halides do not undergo the required nucleophilic substitution under the usual Gabriel conditions. Resonance gives the aryl carbon–halogen bond partial double-bond character, making it stronger; moreover, the carbon bearing the halogen is sp^2 -hybridised, preventing the ordinary backside displacement used for alkyl halides. Consequently the required N-arylpthalimide is not obtained by this route, so hydrolysis cannot furnish the aromatic primary amine.

Step 2: (b) Compare aniline with alkyl amines In aniline, the lone pair on nitrogen is delocalised into the benzene ring by resonance. It is therefore less available to accept H^+ . Alkyl amines have a localised lone pair and their alkyl groups exert an electron-releasing $+I$ effect, increasing electron density at nitrogen. The phenyl group's electron-withdrawing inductive effect also favours lower basicity of aniline. Thus aniline accepts a proton less readily and is a weaker base than alkyl amines.

Step 3: (c) Balance electron donation and hydration in water For these ethylamines in aqueous solution, the observed basicity increases in the sequence



Ethyl groups donate electron density towards nitrogen, favouring protonation. However, hydration stabilises the conjugate acid, and crowding around nitrogen affects this stabilisation. Diethylamine provides the most favourable balance of electron donation and hydration, so it is the strongest of these three bases. For ethyl groups, triethylamine remains more basic than ethylamine, although its conjugate acid is less effectively hydrated than the less crowded ions. Counting alkyl groups alone would therefore give the wrong aqueous order.

Step 4: Conclusion (a) Aryl halides do not undergo the substitution required in Gabriel synthesis. (b) Aniline's nitrogen lone pair is delocalised into the ring and is less available for protonation. (c) Increasing aqueous basic strength: $\text{C}_2\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_3\text{N} < (\text{C}_2\text{H}_5)_2\text{NH}$.

Quick Tip to Solve: For aqueous ethylamines remember primary < tertiary < secondary; include hydration instead of using only the inductive effect.

10(a). The elements of 3d transition series are given below:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

Answer the following questions:

(a) Which element is a strong reducing agent in +2 oxidation state, and why?

(b) Which element has the highest melting point, and why?

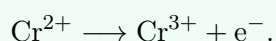
(c) Which element of the first transition series has the highest third ionisation enthalpy? [3 marks]

Solution:

Concept:

- The reducing strength of a metal ion depends on how readily it loses an electron. Formation of a more stable electronic configuration favours oxidation.
- Strong metallic bonding gives high melting points in the middle of the transition series. Ionisation enthalpy is especially high when an electron must be removed from a filled subshell.

Step 1: (a) Strong reducing agent in the +2 state Chromium is the required element. Its ion has the configuration $\text{Cr}^{2+} : [\text{Ar}]3d^4$. It readily loses one electron to form $\text{Cr}^{3+} : [\text{Ar}]3d^3$:



The $3d^3$ configuration of chromium(III) is particularly stable in aqueous solution. Thus chromium(II) readily undergoes oxidation and reduces another species.

Step 2: (b) Highest melting point Chromium has the highest melting point in the usual CBSE trend for the first transition series. Its atomic configuration is $[\text{Ar}]3d^54s^1$, with six unpaired valence electrons. Extensive participation of these electrons in metallic bonding produces strong interatomic attraction and a high enthalpy of atomisation. A large amount of thermal energy is therefore needed to overcome the metallic bonding.

Step 3: (c) Highest third ionisation enthalpy Zinc has the highest third ionisation enthalpy. The first two electrons removed from Zn, with configuration $[\text{Ar}]3d^{10}4s^2$, are the two 4s electrons. Hence Zn^{2+} has the stable, completely filled $3d^{10}$ subshell. The third ionisation, $\text{Zn}^{2+}(\text{g}) \longrightarrow \text{Zn}^{3+}(\text{g}) + e^{-}$, must remove an electron from this filled subshell, so it requires especially high energy.

Step 4: Conclusion (a) Chromium, because Cr^{2+} is readily oxidised to stable Cr^{3+} ; (b) chromium, due to strong metallic bonding; (c) zinc, because the third electron must be removed from its filled $3d^{10}$ subshell.

Quick Tip to Solve: For the third ionisation enthalpy, first write the configuration of the doubly charged ion, not that of the neutral atom.

10(b). Define transition elements. Write two characteristics of transition elements.

[3 marks]

Solution:**Concept:**

- A transition element has an incompletely filled d subshell in its atom or in at least one of its oxidation states.
- The similar energies of the ns and $(n-1)d$ orbitals and the presence of unpaired d electrons explain many characteristic properties.

Step 1: Define transition elements Transition elements are elements whose atoms have an incompletely filled d subshell, or which form at least one ion with an incompletely filled d subshell. Both parts of this definition matter. For example, copper qualifies because Cu^{2+} is $3d^9$, even though the neutral copper atom has a filled $3d^{10}$ subshell. Zinc has $3d^{10}$ in both its atom and its usual $+2$ state, so it is not a transition element.

Step 2: Characteristic 1: Variable oxidation states Transition elements commonly exhibit variable oxidation states. The ns and $(n-1)d$ electrons have comparable energies, so different numbers of these electrons can take part in bonding or be removed. For example, iron forms Fe^{2+} and Fe^{3+} , corresponding to the $+2$ and $+3$ oxidation states.

Step 3: Characteristic 2: Paramagnetic behaviour Many transition elements and their ions are paramagnetic because they contain one or more unpaired d electrons. The magnetic moments associated with these electrons cause attraction towards an applied magnetic field. For example, Fe^{3+} has the configuration $[\text{Ar}]3d^5$ with five unpaired electrons in its usual high-spin state. This is a common characteristic, not a claim that every transition-metal ion is paramagnetic: ions with no unpaired electrons are diamagnetic.

Step 4: Conclusion Transition elements have an incompletely filled d subshell in their atoms or in at least one oxidation state. Two characteristics are variable oxidation states and paramagnetism due to unpaired electrons.

Quick Tip to Solve: Use the atom-or-ion definition: a filled d subshell in the neutral atom alone does not rule out a transition element.

11. (a) Write the hybridisation, shape and magnetic character of $[\text{CoF}_6]^{3-}$. [Atomic number of Co = 27]**(b) Write the formula of Pentaamminechloridocobalt(III) chloride.**

[3 marks]

Solution:**Concept:**

- The oxidation state of the central metal determines its d -electron count. Neutral cobalt has configuration $[\text{Ar}]3d^74s^2$; electrons are removed from $4s$ before $3d$ when forming its cation.
- Fluoride is a weak-field ligand. In an octahedral complex it gives a high-spin arrangement when the crystal-field splitting is smaller than the electron-pairing energy. Unpaired electrons produce

paramagnetism.

- In a coordination formula, ligands named within the coordination entity are written inside square brackets, while counter-ions are written outside. Ammine is neutral and chlorido has charge -1 .

Step 1: (a) Determine the cobalt ion and its electron configuration Let the oxidation state of cobalt in $[\text{CoF}_6]^{3-}$ be x . Since each fluoride ligand has charge -1 ,

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

Thus the central ion is Co^{3+} , with configuration $[\text{Ar}]3d^6$. The six fluoride ligands give coordination number six.

Step 2: (a) Establish hybridisation, shape and magnetic character The weak-field F^- ligands do not cause pairing of the $3d$ electrons to produce two vacant inner d orbitals. The high-spin octahedral configuration is



containing four unpaired electrons: two in the t_{2g} set and two in the e_g set. In valence-bond terminology, the metal uses one $4s$, three $4p$ and two $4d$ orbitals to form six sp^3d^2 hybrid orbitals. This is an outer-orbital complex with octahedral geometry. Its four unpaired electrons make it paramagnetic, rather than diamagnetic. Using d^2sp^3 here would incorrectly describe an inner-orbital arrangement.

Step 3: (b) Balance the coordination entity and counter-ions Pentaammine specifies five neutral NH_3 ligands, and chlorido specifies one coordinated Cl^- ligand. Cobalt(III) has charge $+3$, so the charge on the coordination entity is

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

Two chloride counter-ions are therefore needed outside the brackets to make the compound electrically neutral. The coordinated chloride remains inside the brackets; it is distinct from these counter-ions.

Step 4: Conclusion (a) $[\text{CoF}_6]^{3-}$ has sp^3d^2 hybridisation, octahedral shape and paramagnetic character with four unpaired electrons. (b) The formula is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

Quick Tip to Solve: For the named cobalt salt, calculate the charge inside the brackets first: five ammines are neutral and one chlorido reduces cobalt(III)'s charge to $+2$.

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]

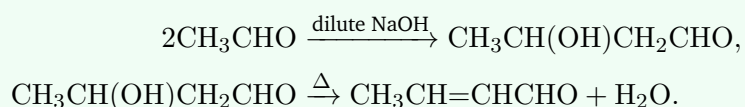
Solution:

Concept:

- Aldol condensation requires at least one α -hydrogen, a hydrogen attached to the carbon adjacent to the carbonyl group. Dilute base produces an enolate which adds to another carbonyl molecule.
- An aldehyde must have a hydrogen on an adjacent carbon to form the enolate required for self-aldol condensation.

Step 1: Check the three aldehydes Ethanal, CH_3CHO , has three hydrogens on the carbon adjacent to its carbonyl group 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 its adjacent ring carbon. Neither has an α -hydrogen.

Step 2: Write the aldol condensation For ethanal, the reaction proceeds through 3-hydroxybutanal:



Step 3: Conclusion Ethanal undergoes aldol condensation; methanal and benzaldehyde do not.

Quick Tip to Solve: Inspect the carbon next to the carbonyl carbon: ethanal alone has alpha-hydrogens.

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

[1 mark]

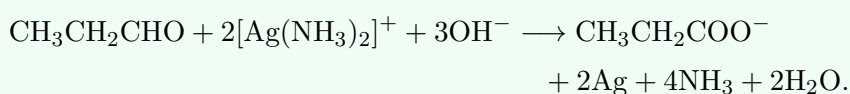
Solution:

Concept:

- Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver(I) is reduced to metallic silver. An ordinary ketone does not give this test.
- A silver mirror is the positive observation in Tollens' test; compare both samples under the same gentle warming conditions.

Step 1: Perform the test Warm separate samples gently with freshly prepared Tollens' reagent. Propanal gives a silver mirror on the inner wall of the test tube, whereas propanone gives no silver mirror.

Step 2: Explain the observation The aldehyde group of propanal is oxidised to propanoate in the alkaline medium:

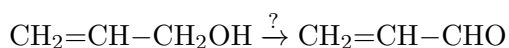


Propanone is a ketone and is not oxidised by this mild reagent.

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

Quick Tip to Solve: Use freshly prepared Tollens reagent and state the observation for both compounds.

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



[1 mark]

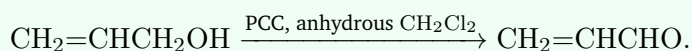
Solution:

Concept:

- Controlled oxidation changes a primary alcohol group, $-\text{CH}_2\text{OH}$, into an aldehyde group, $-\text{CHO}$.
- Pyridinium chlorochromate (PCC) is a mild oxidant used in anhydrous dichloromethane; the carbon-carbon double bond remains intact.

Step 1: Compare the functional groups The reactant is prop-2-en-1-ol and the product is prop-2-enal. Only the primary alcohol group is oxidised; the alkene group must be retained.

Step 2: Choose the reagent Use PCC in anhydrous dichloromethane, CH_2Cl_2 . It oxidises the primary alcohol group of prop-2-en-1-ol to the aldehyde group without changing the carbon-carbon double bond:



These controlled, nonaqueous conditions stop the oxidation at prop-2-enal instead of continuing to the carboxylic acid.

Step 3: Conclusion The required reagent is PCC in anhydrous CH_2Cl_2 .

Quick Tip to Solve: Choose a controlled nonaqueous oxidant when a primary alcohol must stop at an aldehyde.

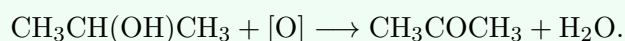
12(d)(i). An alcohol 'A', ($\text{C}_3\text{H}_8\text{O}$) on oxidation gives compound 'B'. 'B' gives negative Tollens' test and reacts with hydrazine to give compound 'C'. 'B' reacts with NaOH and I_2 to give yellow precipitate of 'D'. Identify 'A', 'B', 'C' and 'D'. [2 marks]

Solution:

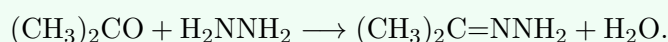
Concept:

- A secondary alcohol oxidises to a ketone, which gives a negative Tollens' test.
- Ketones condense with hydrazine to form hydrazones; methyl ketones give yellow iodoform with iodine and aqueous sodium hydroxide.

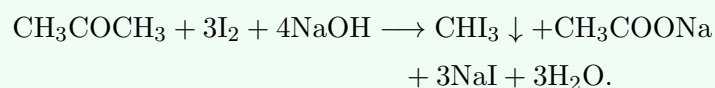
Step 1: (d)(i) Identify the alcohol and its oxidation product The formula $\text{C}_3\text{H}_8\text{O}$ and oxidation to a carbonyl compound with a negative Tollens' test identify A as the secondary alcohol propan-2-ol and B as propanone. Propan-1-ol would instead produce propanal, which gives a positive Tollens' test.



Step 2: Identify the hydrazone and the yellow precipitate Propanone condenses with hydrazine through its carbonyl group, eliminating water. Thus C is propanone hydrazone, $(\text{CH}_3)_2\text{C}=\text{NNH}_2$:



B also contains the methyl ketone group, $\text{CH}_3\text{CO}-$, so iodine and sodium hydroxide produce the yellow precipitate D, iodoform (triiodomethane), CHI_3 :



Step 3: Conclusion A: propan-2-ol, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$; B: propanone, CH_3COCH_3 ; C: propanone hydrazone, $(\text{CH}_3)_2\text{C}=\text{NNH}_2$; D: iodoform, CHI_3 .

Quick Tip to Solve: For the identification chain, combine the negative Tollens' test with the positive iodoform test first: together they identify B as a methyl ketone, fixing the three-carbon alcohol as propan-2-ol.

Write the chemical reactions for the following:

12(d)(ii)(I). Clemmensen reduction

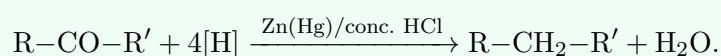
[1 mark]

Solution:

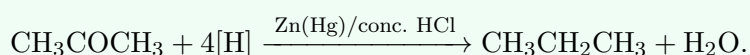
Concept:

- Clemmensen reduction converts the carbonyl group of an aldehyde or ketone into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- The reagent and the reacting functional group together identify the named transformation.

Step 1: State the general reaction On treatment with Zn(Hg) and concentrated HCl , the oxygen of the carbonyl group is removed while the carbon skeleton remains intact. A ketone gives the corresponding hydrocarbon:



Step 2: Give a representative equation For example, propanone gives propane:



Here $[\text{H}]$ represents reducing equivalents; the reaction takes place in an acidic medium.

Step 3: Conclusion Clemmensen reduction: $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{Zn(Hg)/conc. HCl}} \text{CH}_3\text{CH}_2\text{CH}_3$.

Quick Tip to Solve: Remember the reaction sites: Clemmensen removes carbonyl oxygen, whereas HVZ replaces an α -hydrogen of a carboxylic acid by halogen.

12(d)(ii)(II). HVZ reaction

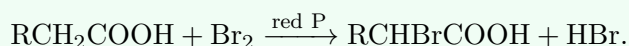
[1 mark]

Solution:

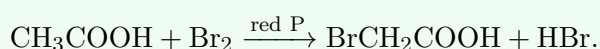
Concept:

- The Hell-Volhard-Zelinsky (HVZ) reaction replaces an α -hydrogen of a carboxylic acid by a halogen, using chlorine or bromine in the presence of red phosphorus.
- The reagent and the reacting functional group together identify the named transformation.

Step 1: State the general reaction A carboxylic acid containing at least one α -hydrogen undergoes bromination at the carbon adjacent to the carboxyl group. With bromine and red phosphorus, followed by hydrolysis, the overall reaction is



Step 2: Give a representative equation For example, ethanoic acid forms bromoethanoic acid:



The carboxyl group is retained; substitution occurs at the α -carbon, rather than at its hydroxyl group.

Step 3: Conclusion HVZ reaction: $\text{CH}_3\text{COOH} + \text{Br}_2 \xrightarrow{\text{red P}} \text{BrCH}_2\text{COOH} + \text{HBr}$.

Quick Tip to Solve: Remember the reaction sites: Clemmensen removes carbonyl oxygen, whereas HVZ replaces an α -hydrogen of a carboxylic acid by halogen.