CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-2-3

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. Predict the products formed when CH_3CHO reacts with the following reagents: (Any two)

(i) CH_3MgBr and then H_3O^+

(ii) Zn(Hg)/Conc. HCl

(iii) Tollens' reagent [2 marks]

Solution:

Concept:

- Ethanal, CH_3CHO, undergoes nucleophilic addition with a Grignard reagent, reduction with Zn(Hg)/concentrated HCl, and oxidation with Tollens' reagent.
- Acidic hydrolysis protonates the magnesium alkoxide formed by Grignard addition. Tollens' reagent is alkaline, so the immediate organic oxidation product is a carboxylate ion.

Step 1: (i) Addition of methylmagnesium bromide followed by hydrolysis The methyl group from CH_3MgBr adds to the carbonyl carbon of ethanal. The intermediate magnesium alkoxide gives a secondary alcohol on treatment with H_3O^+:

$$CH_3CHO \xrightarrow{CH_3MgBr} CH_3CH(OMgBr)CH_3 \xrightarrow{H_3O^+} CH_3CH(OH)CH_3.$$

The organic product is propan-2-ol; the added methyl group increases the carbon count from two to three.

Step 2: (ii) Clemmensen reduction Zn(Hg) and concentrated HCl reduce the aldehyde carbonyl group to a methylene group without changing the carbon skeleton:

$$CH_3CHO \xrightarrow{Zn(Hg)/\text{conc. HCl}} CH_3CH_3.$$

The product is ethane, not ethanol; this reagent removes the carbonyl oxygen completely.

Step 3: (iii) Oxidation by Tollens' reagent Ethanal reduces the silver(I) complex to metallic silver and is oxidised to ethanoate in the alkaline medium:

$$CH_3CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Metallic silver forms the silver mirror. Acidification of the ethanoate gives ethanoic acid, CH_3COOH.

Step 4: Conclusion (i) Propan-2-ol, $CH_3CH(OH)CH_3$; (ii) ethane, CH_3CH_3; (iii) ethanoate, CH_3COO^-, giving ethanoic acid on acidification, with a silver mirror. Any two reactions may be written as requested.

Quick Tip to Solve: Track the carbonyl group: Grignard addition adds a carbon group, Clemmensen reduction removes oxygen, and Tollens' oxidation retains the carbon count.

2. The resistance and conductivity of a conductivity cell containing 0.001 M KCl solution at 298 K are 1200 Ω and 1.5 $\times$ 10^{-4} S cm^{-1}. Calculate its cell constant and molar conductivity. [2 marks]

Solution:

Concept:

- Conductance is the reciprocal of resistance: $G = 1/R$. Conductivity is related to conductance by $\kappa = G(l/A)$, where l/A is the cell constant.
- For concentration c in $\mathrm{mol\,L^{-1}}$ and conductivity in $\mathrm{S\,cm^{-1}}$, molar conductivity is $\Lambda_m = 1000\kappa/c$, expressed in $\mathrm{S\,cm^2\,mol^{-1}}$.

Step 1: Calculate the cell constant The given values are $R = 1200\,\Omega$, $\kappa = 1.5 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$, and $c = 0.001\,\mathrm{mol\,L^{-1}}$, all for the same solution at $298\,\mathrm{K}$. Since $\kappa = (1/R)(l/A)$,

$$\begin{aligned}\frac{l}{A} &= \kappa R \\ &= (1.5 \times 10^{-4})(1200) \\ &= 0.18\,\mathrm{cm^{-1}}.\end{aligned}$$

The unit is inverse length because the cell constant is electrode separation divided by electrode area; $\mathrm{S} \times \Omega = 1$.

Step 2: Calculate the molar conductivity Substitute the concentration in molarity, keeping the conductivity in centimetre-based units:

$$\begin{aligned}\Lambda_m &= \frac{1000\kappa}{c} \\ &= \frac{1000(1.5 \times 10^{-4})}{0.001} \\ &= 150\,\mathrm{S\,cm^2\,mol^{-1}}.\end{aligned}$$

The factor 1000 converts one litre to $1000\,\mathrm{cm^3}$; it must be included when c is given in $\mathrm{mol\,L^{-1}}$.

Step 3: Conclusion The cell constant is $\boxed{0.18\,\mathrm{cm^{-1}}}$ and the molar conductivity is $\boxed{150\,\mathrm{S\,cm^2\,mol^{-1}}}$ at $298\,\mathrm{K}$.

Quick Tip to Solve: Multiply conductivity by resistance for the cell constant; then use 1000 times conductivity divided by molarity for molar conductivity.

3. A reaction is first order in X and second order in Y.

(i) How is the rate affected on increasing the concentration of Y three times?

(ii) How is the rate affected when the concentrations of both X and Y are doubled? [2 marks]

Solution:

Concept:

- The order with respect to a reactant is its concentration exponent in the rate law. First order in X and second order in Y give $r = k[X][Y]^2$, where k is the rate constant.

Quick Tip to Solve: Raise each concentration multiplier to its own reaction order, then multiply the resulting factors: here use a times b squared.

- At a fixed temperature, k remains unchanged. If the concentrations are multiplied by factors a and b, then the rate is multiplied by ab^2.

Step 1: (i) Triple the concentration of Y Keep the concentration of X and the temperature fixed. Initially, $r = k[X][Y]^2$. After increasing Y three times, $[Y]' = 3[Y]$, so

$$\begin{aligned} r' &= k[X](3[Y])^2 \\ &= 9k[X][Y]^2, \\ \frac{r'}{r} &= 9. \end{aligned}$$

The concentration multiplier is squared because the reaction is second order in Y; a threefold change in Y therefore produces a ninefold rate.

Step 2: (ii) Double the concentrations of both X and Y Now $[X]' = 2[X]$ and $[Y]' = 2[Y]$. Substituting both changes in the same rate law gives

$$\begin{aligned} r'' &= k(2[X])(2[Y])^2 \\ &= 2 \times 4\, k[X][Y]^2, \\ \frac{r''}{r} &= 8. \end{aligned}$$

X contributes a factor of two, while Y contributes a factor of four. These independent factors multiply, rather than add, because the concentrations occur as a product in the rate law.

Step 3: Conclusion (i) The rate becomes $\boxed{9}$ times the original rate. (ii) The rate becomes $\boxed{8}$ times the original rate when both concentrations are doubled.

Quick Tip to Solve: Raise each concentration multiplier to its own reaction order, then multiply the resulting factors: here use a times b squared.

Section B (24 marks)

4(a). Predict the products in the following reactions:

(i) $CH_3MgBr + CO_2 \xrightarrow{H_3O^+}$

(ii) $CH_3CN \xrightarrow[\text{(b) } H_2O]{\text{(a) DIBAL-H}}$

(iii)

[3 marks]



Solution:

Concept:

- Grignard reagents react with carbon dioxide to form magnesium carboxylates; acidic hydrolysis gives a carboxylic acid containing one carbon more than the original alkyl group.
- DIBAL-H is a selective reducing agent. Controlled reduction of a nitrile followed by hydrolysis gives the corresponding aldehyde, retaining the nitrile carbon as the carbonyl carbon.
- An amide undergoes hydrolysis on heating with aqueous acid. Its $-CONH_2$ group becomes $-COOH$, while the nitrogen is released as ammonium ion in the acidic medium.

Step 1: (i) Carboxylation of methylmagnesium bromide The methyl group of CH_3MgBr attacks the electrophilic carbon of CO_2, producing magnesium acetate. Acidic work-up protonates the carboxylate:

$$CH_3MgBr + CO_2 \longrightarrow CH_3COOMgBr$$

$$CH_3COOMgBr \xrightarrow{H_3O^+} CH_3COOH.$$

Thus the carbon chain increases from one carbon to two, and the product is ethanoic acid (acetic acid).

Step 2: (ii) Controlled reduction of ethanenitrile DIBAL-H partially reduces CH_3CN to an aluminium-bound imine intermediate. Hydrolysis in the second stage converts that intermediate into the aldehyde:

$$CH_3CN \xrightarrow[\text{2. H2O}]{\text{1. DIBAL-H}} CH_3CHO.$$

The two-carbon skeleton is retained. The specified selective reagent and hydrolytic work-up give ethanal (acetaldehyde), rather than the primary amine obtained by complete nitrile reduction.

Step 3: (iii) Acidic hydrolysis of benzamide The printed aromatic substrate is benzamide, $C_6H_5CONH_2$. Heating with hydronium ions hydrolyses its amide linkage:

$$C_6H_5CONH_2 + H_2O + H^+ \xrightarrow{\Delta} C_6H_5COOH + NH_4{}^+.$$

The benzene ring remains intact. The organic product is benzoic acid; the nitrogen-containing product is ammonium ion because ammonia is protonated in the acidic medium.

Quick Tip to Solve: Track the functional-group carbon: CO2 adds one carbon, whereas nitrile reduction and amide hydrolysis retain the original carbon skeleton.

Step 4: Conclusion The organic products are (i) CH_3COOH, ethanoic acid; (ii) CH_3CHO, ethanal; and (iii) C_6H_5COOH, benzoic acid.

Quick Tip to Solve: Track the functional-group carbon: CO2 adds one carbon, whereas nitrile reduction and amide hydrolysis retain the original carbon skeleton.

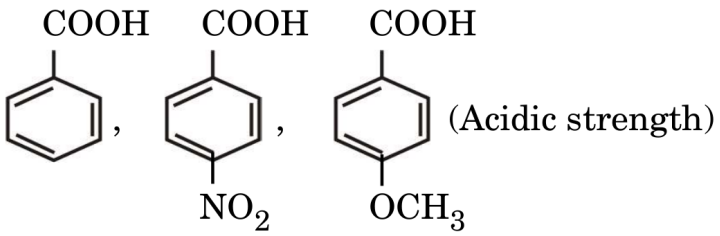
OR

4(b). Arrange the following compounds in increasing order of their property as indicated:

(i) $CH_3CHO,\ CH_3CH_2CHO,\ CH_3COCH_2CH_3,\ CH_3COCH_3$ **(Reactivity towards HCN)**

(ii) $CH_3COOH,\ ClCH_2COOH,\ (CH_3)_2CHCOOH$ **(Acidic strength)**

(iii) [3 marks]



(Acidic strength)

Solution:

Concept:

- Cyanide attacks the carbonyl carbon. Low steric hindrance and high electrophilicity favour HCN addition.
- Alkyl groups donate electrons and hinder attack: aldehydes are generally more reactive than ketones.
- Acid strength increases with carboxylate stability. Electron withdrawal increases acidity; electron donation generally decreases it.

Step 1: (i) Increasing reactivity towards HCN Aldehydes are less crowded and less electron-rich than ketones. Within each class, ethyl causes greater crowding and electron donation than methyl. Therefore:

$$CH_3COCH_2CH_3 < CH_3COCH_3 < CH_3CH_2CHO < CH_3CHO.$$

Step 2: (ii) Increasing acidity of the aliphatic acids Isopropyl donates electrons more strongly than methyl, reducing acidity. Chlorine withdraws electrons and stabilises the carboxylate anion, increasing acidity:

$$(CH_3)_2CHCOOH < CH_3COOH < ClCH_2COOH.$$

Step 3: (iii) Increasing acidity of the aromatic acids Para-nitro withdraws electrons by induction and resonance, stabilising the conjugate base. Para-methoxy resonance donation outweighs its inductive withdrawal, reducing acidity:

$$p\text{-}CH_3OC_6H_4COOH < C_6H_5COOH < p\text{-}NO_2C_6H_4COOH.$$

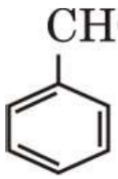
Quick Tip to Solve: For HCN addition compare crowding and alkyl donation; for acidity compare how each substituent stabilises the negatively charged conjugate base.

Here p means para to the carboxyl group.

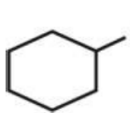
Step 4: Conclusion Increasing orders are: (i) butan-2-one < propanone < propanal < ethanal; (ii) 2-methylpropanoic acid < ethanoic acid < chloroethanoic acid; (iii) para-methoxybenzoic acid < benzoic acid < para-nitrobenzoic acid.

Quick Tip to Solve: For HCN addition compare crowding and alkyl donation; for acidity compare how each substituent stabilises the negatively charged conjugate base.

5(a). Write the major products in the following: [3 marks]

(i) 

$\xrightarrow[273-283\ \text{K}]{\text{HNO}_3 + \text{H}_2\text{SO}_4}$

(ii) 

$+ \text{NaOH} \xrightarrow[\Delta]{\text{CaO}}$

(iii) $\text{CH}_3 - \underset{\displaystyle \text{H}}{\underset{|}{\text{C}}} = \text{O} \xrightarrow{\text{NH}_2\text{OH}}$

Solution:

Concept:

- The aldehyde group $-\text{CHO}$ withdraws electrons and is a meta-directing group in electrophilic aromatic substitution. Nitration therefore gives predominantly the meta product.
- Heating a sodium carboxylate with soda lime, NaOH/CaO, removes its carboxyl carbon: $\text{RCOONa} + \text{NaOH} \longrightarrow \text{RH} + \text{Na}_2\text{CO}_3$.
- Hydroxylamine, NH_2OH, reacts with the carbonyl group of an aldehyde or ketone to form an oxime by elimination of water.

Step 1: (i) Nitrate benzaldehyde The mixture of concentrated nitric acid and sulphuric acid generates the electrophile $\text{NO}_2{}^+$. The $-\text{CHO}$ group deactivates the ring and directs substitution mainly to the meta position. Thus the major product at 273–283 K is 3-nitrobenzaldehyde:

$$\text{C}_6\text{H}_5\text{CHO} + \text{HNO}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{3-NO}_2\text{–C}_6\text{H}_4\text{–CHO} + \text{H}_2\text{O}.$$

The aldehyde group remains attached to the ring; nitration substitutes a ring hydrogen.

Step 2: (ii) Decarboxylate the sodium salt The printed reactant is sodium cyclohexanecarboxylate: its six-membered ring is saturated. On heating with soda lime, the $-\text{COONa}$ group is replaced by

Quick Tip to Solve: Check the ring bonds before decarboxylation: this saturated ring gives cyclohexane. For hydroxylamine, replace C=O by C=N-OH.

hydrogen. Therefore the product is cyclohexane, not benzene:

$$C_6H_{11}COONa + NaOH \xrightarrow{CaO,\ \Delta} C_6H_{12} + Na_2CO_3.$$

The ring retains all six carbon atoms, while the carboxyl carbon enters sodium carbonate.

Step 3: (iii) Form the oxime of ethanal The reactant CH_3CHO is ethanal. Condensation with hydroxylamine replaces the carbonyl oxygen with the $=N-OH$ group, giving ethanal oxime (acetaldoxime):

$$CH_3CHO + NH_2OH \longrightarrow CH_3CH{=}N{-}OH + H_2O.$$

The carbonyl carbon retains its methyl group and its hydrogen; hence the product is an aldoxime.

Step 4: Conclusion The major products are (i) 3-nitrobenzaldehyde, $3\text{-}NO_2{-}C_6H_4{-}CHO$; (ii) cyclohexane, C_6H_{12}; and (iii) ethanal oxime, $CH_3CH{=}N{-}OH$.

Quick Tip to Solve: Check the ring bonds before decarboxylation: this saturated ring gives cyclohexane. For hydroxylamine, replace C=O by C=N-OH.

OR

5(b). (i) Oxidation of propanal is easier than propanone. Why?
(ii) How can you distinguish between Acetophenone and Benzophenone?
(iii) Draw the structure of the following derivative : 2,4-Dinitrophenylhydrazone of Propanone.

[3 marks]

Solution:

Concept:

- An aldehyde contains a hydrogen attached directly to its carbonyl carbon. Oxidation converts $-CHO$ to $-COOH$ without breaking a carbon-carbon bond.
- The iodoform test detects the methyl ketone group CH_3CO^-: warming with iodine and aqueous sodium hydroxide gives a yellow precipitate of CHI_3.
- A carbonyl compound condenses with 2,4-dinitrophenylhydrazine to give a hydrazone containing $C{=}N{-}NH{-}C_6H_3(NO_2)_2$; the nitro groups occupy positions 2 and 4 relative to the hydrazine attachment.

Step 1: (i) Compare oxidation of propanal and propanone Propanal, CH_3CH_2CHO, has an aldehydic hydrogen. It is readily oxidised to propanoic acid without breaking the carbon skeleton:

$$CH_3CH_2CHO + [O] \longrightarrow CH_3CH_2COOH.$$

Propanone, CH_3COCH_3, has two carbon groups attached to the carbonyl carbon and no aldehydic hydrogen. Its oxidation requires cleavage of a carbon-carbon bond, which is harder and requires strong oxidising conditions. Hence propanal is oxidised more easily.

Step 2: (ii) Apply the iodoform test Warm each compound separately with iodine and aqueous

Quick Tip to Solve: Identify COCH3 for a positive iodoform test. In the hydrazone, retain both methyl groups and write C=N-NH, with NO2 at ring positions 2 and 4.

sodium hydroxide. Acetophenone, $C_6H_5COCH_3$, contains the $-COCH_3$ group and gives a yellow precipitate of iodoform:

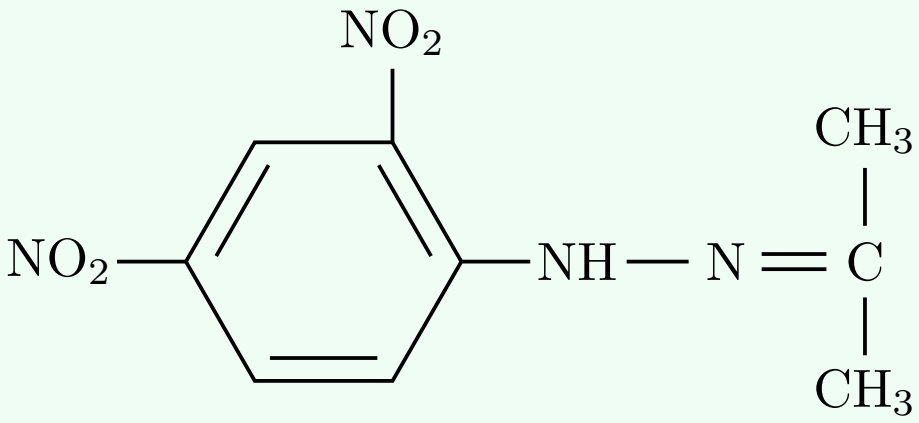
$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow C_6H_5COONa + CHI_3\downarrow + 3\,NaI + 3\,H_2O.$$

Benzophenone, $C_6H_5COC_6H_5$, lacks a methyl ketone group, so it does not give the yellow precipitate under this test. Both are ketones, so a general carbonyl test alone does not distinguish them.

Step 3: (iii) Draw the 2,4-dinitrophenylhydrazone of propanone Propanone condenses with the terminal $-NH_2$ group of 2,4-dinitrophenylhydrazine, eliminating one molecule of water:

$$(CH_3)_2CO + H_2N{-}NH{-}C_6H_3(NO_2)_2 \longrightarrow (CH_3)_2C{=}N{-}NH{-}C_6H_3(NO_2)_2 + H_2O.$$

Both methyl groups remain attached to the former carbonyl carbon. The structure below shows the $C{=}N{-}NH$ linkage and the nitro groups ortho and para to the ring's $-NH-$ attachment.



Structure of the 2,4-dinitrophenylhydrazone of propanone

Step 4: Conclusion (i) Propanal oxidises more easily because it has an aldehydic hydrogen and needs no carbon-carbon bond cleavage. (ii) Acetophenone gives yellow CHI_3 with $I_2/NaOH$, whereas benzophenone does not. (iii) The derivative is $(CH_3)_2C{=}N{-}NH{-}C_6H_3(NO_2)_2$, with nitro groups at positions 2 and 4.

Quick Tip to Solve: Identify COCH3 for a positive iodoform test. In the hydrazone, retain both methyl groups and write C=N-NH, with NO2 at ring positions 2 and 4.

6. Calculate the emf of the following cell :

Zn(s) | Zn^{2+} (0.01 M) || (0.001 M) Ag^{+} | Ag(s)

Given : $E^{\circ}_{Zn^{2+}/Zn} = -0.76\,V$ **and** $E^{\circ}_{Ag^{+}/Ag} = +0.80\,V$

[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1] [3 marks]

Solution:

Concept:

- A galvanic cell oxidises the metal at the anode and reduces the ion at the cathode. Standard cell potential is $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$, using both values as reduction potentials.
- At $298\,\text{K}$, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Activities of pure solids equal unity; dilute ionic concentrations may be used for the aqueous species.

Step 1: Balance the electrode reactions Zinc is oxidised at the left electrode, while silver ions are reduced at the right electrode:

$$\text{Anode: } \text{Zn(s)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{e}^{-},$$
$$\text{Cathode: } 2\text{Ag}^{+}\text{(aq)} + 2\text{e}^{-} \rightarrow 2\text{Ag(s)}.$$

Thus the overall cell reaction is $\text{Zn(s)} + 2\text{Ag}^{+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{Ag(s)}$, and $n = 2$. The coefficient of silver ions must also appear as an exponent in the reaction quotient.

Step 2: Calculate the standard potential and reaction quotient The supplied potentials give

$$E^{\circ}_{\text{cell}} = 0.80 - (-0.76) = 1.56\,\text{V}.$$

Omitting the pure solid zinc and silver, the reaction quotient is

$$Q = \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^2} = \frac{0.01}{(0.001)^2} = 10^4.$$

Therefore $\log Q = 4\log 10 = 4$; the given values of $\log 2$ and $\log 3$ are not needed for these concentrations.

Step 3: Substitute in the Nernst equation Using the usual $298\,\text{K}$ form of the equation,

$$E_{\text{cell}} = 1.56 - \frac{0.0591}{2} \times 4$$
$$= 1.56 - 0.1182 = 1.4418\,\text{V}.$$

Since $Q > 1$, the concentration correction lowers the potential below its standard value, consistent with the calculation.

Step 4: Conclusion The emf of the cell at $298\,\text{K}$ is $\boxed{E_{\text{cell}} = 1.4418\,\text{V} \approx 1.44\,\text{V}}$.

Quick Tip to Solve: Balance the cell reaction first: two silver ions are reduced per zinc atom, so square the silver-ion concentration in Q and use $n = 2$.

7(a). Write three differences between Lyophobic sol and Lyophilic sol. [3 marks]

Solution:

Concept:

- A sol is a colloidal system with a solid dispersed phase and a liquid dispersion medium. The distinction between lyophilic and lyophobic sols concerns the affinity of the dispersed substance for that medium.
- Lyophilic means solvent-loving: appreciable attraction between the dispersed phase and solvent produces solvation. Lyophobic means solvent-hating: the dispersed phase has little affinity for the solvent, so its particles are weakly solvated.

Step 1: Compare affinity for the dispersion medium **Lyophobic sol:** The dispersed particles have little or no affinity for the dispersion medium and undergo little solvation. Metal sols such as gold sol in water illustrate this class.

Lyophilic sol: The dispersed particles have strong affinity for the dispersion medium and become extensively solvated. Starch or gum dispersed in water illustrates this class. This interaction with the solvent is the fundamental difference underlying the contrasting behaviour of the two sols.

Step 2: Compare ease of preparation **Lyophobic sol:** Simply mixing the substance with the dispersion medium does not normally produce the sol. Special dispersion or condensation methods are needed to obtain particles of colloidal size and keep them dispersed.

Lyophilic sol: The sol is formed readily by bringing the dispersed substance into contact with a suitable dispersion medium, sometimes with warming. Its affinity for the medium makes direct formation comparatively easy.

Step 3: Compare stability towards electrolytes **Lyophobic sol:** It is relatively less stable and is readily coagulated by adding a small amount of a suitable electrolyte. Its stability relies chiefly on the electrical charge on its particles; neutralising this charge allows aggregation.

Lyophilic sol: It is comparatively more stable and requires a much larger amount of electrolyte for coagulation. The surrounding solvation layer, in addition to any charge, helps prevent its particles from aggregating.

Step 4: Conclusion Three differences are: lyophobic sols have little solvent affinity, need special preparation methods and coagulate readily with small electrolyte additions; lyophilic sols have strong solvent affinity, form readily in a suitable solvent and resist such coagulation because of extensive solvation.

Quick Tip to Solve: Use three matching comparison headings: solvent affinity, preparation and electrolyte stability. Link the greater stability of a lyophilic sol to its solvation layer.

OR

7(b). (i) Write the dispersed phase and dispersion medium of 'milk'.
(ii) What is the cause of Brownian movement in colloidal particles?
(iii) Why does physisorption decrease with increase in temperature? [3 marks]

Solution:

Concept:

- An emulsion is a colloid in which both phases are liquids. The dispersed phase consists of small droplets; the dispersion medium is the continuous liquid surrounding them.
- Brownian movement is the continuous, random zigzag motion of colloidal particles caused by collisions with the molecules of the dispersion medium.
- Physisorption involves weak van der Waals forces and is exothermic. Raising the temperature favours desorption and lowers the equilibrium amount adsorbed.

Step 1: (i) Identify the two phases of milk Milk is an oil-in-water emulsion. Tiny droplets of liquid fat are distributed throughout the aqueous phase. Therefore, its dispersed phase is liquid fat (oil), and its dispersion medium is water. Both phases are liquids, but water forms the continuous phase; the fat droplets form the discontinuous phase.

Step 2: (ii) Explain Brownian movement Molecules of the dispersion medium are in constant thermal motion. They collide with a colloidal particle from different directions. At any instant, these impacts are unequal and unbalanced, giving the particle a resultant push. As the direction of this push changes continually, the particle follows a random zigzag path. Thus Brownian movement arises from the uneven bombardment of colloidal particles by molecules of the dispersion medium.

Step 3: (iii) Explain the temperature dependence of physisorption In physisorption, an adsorbate adheres to a surface through weak van der Waals forces, and heat is released. The process may be represented as

$$\text{Gas} + \text{surface} \rightleftharpoons \text{adsorbed gas} + \text{heat}.$$

By Le Chatelier's principle, an increase in temperature shifts this equilibrium towards the reverse, heat-absorbing process, namely desorption. The increased thermal motion also helps molecules overcome the weak attraction to the surface. Hence fewer molecules remain adsorbed at higher temperature, at the same pressure.

Step 4: Conclusion (i) Dispersed phase: liquid fat (oil); dispersion medium: water. (ii) Brownian movement is caused by unequal collisions of medium molecules with colloidal particles. (iii) Physisorption decreases with temperature because it is exothermic and heating favours desorption.

Quick Tip to Solve: For milk, remember oil-in-water: fat is the droplets and water surrounds them. For physisorption, write heat on the product side to predict the temperature effect.

8. A first order reduction takes 30 minutes for 75% decomposition. Calculate $t_{1/2}$.

Given : [log 2 = 0.3, log 3 = 0.48, log 4 = 0.6, log 5 = 0.7] [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$, where k is the rate constant, $[A]_0$ is the initial concentration and $[A]_t$ is the concentration remaining at time t.
- The half-life of a first-order reaction is $t_{1/2} = \dfrac{2.303\log 2}{k}$. It is independent of the initial concentration.

Step 1: Find the fraction of reactant remaining After $30\,\text{min}$, 75% of the reactant has decomposed. Thus only $100 - 75 = 25\%$ remains. Taking the initial amount as 100 units, the remaining amount is 25 units. Since concentration is proportional to amount at constant volume,

$$\frac{[A]_0}{[A]_t} = \frac{100}{25} = 4.$$

The integrated rate law uses the amount remaining, rather than the amount decomposed.

Step 2: Calculate the rate constant Substituting $t = 30\,\text{min}$ and the supplied value $\log 4 = 0.6$ into the first-order equation gives

$$\begin{aligned} k &= \frac{2.303}{30}\log 4 \\ &= \frac{2.303 \times 0.6}{30} \\ &= 0.04606\,\text{min}^{-1}. \end{aligned}$$

The unit is inverse minutes because the time was substituted in minutes.

Step 3: Use the half-life relation and check the result Using the given $\log 2 = 0.3$,

$$\begin{aligned} t_{1/2} &= \frac{2.303\log 2}{k} \\ &= \frac{2.303 \times 0.3}{0.04606} \\ &= 15\,\text{min}. \end{aligned}$$

As an independent check, the fraction remaining after two half-lives is $(1/2)^2 = 1/4$, corresponding to 75% decomposition. The stated duration therefore represents two equal first-order half-lives: $30 = 2t_{1/2}$, consistent with the calculation.

Step 4: Conclusion The half-life of the first-order reduction is $\boxed{t_{1/2} = 15\,\text{min}}$.

Quick Tip to Solve: Convert decomposition to the fraction remaining first: 75% decomposed means one-quarter remains, which is exactly two first-order half-lives.

9. Account for the following :

(i) Transition metals and their compounds show catalytic activities.

(ii) Zn, Cd and Hg are non-transition elements.

(iii) Zr and Hf are of almost identical atomic radii. [3 marks]

Solution:

Concept:

- Transition elements have a partially filled d subshell in the atom or in at least one of their common oxidation states.
- Catalysts provide an alternative reaction pathway of lower activation energy; variable oxidation states and adsorption help transition metals do this.
- Lanthanoid contraction is the gradual decrease in size across the lanthanoid series because 4f electrons shield the nuclear charge poorly.

Step 1: (i) Explain catalytic activity Transition metals and their compounds can adopt several oxidation states. They can therefore form intermediate compounds with the reactants and undergo oxidation and reduction during the reaction, returning to their original state at the end. These intermediate stages provide a pathway of lower activation energy. In heterogeneous catalysis, their surfaces also adsorb reactant molecules; this brings reactants together and weakens bonds, facilitating reaction. Thus both variable oxidation states and surface adsorption account for their catalytic activity.

Step 2: (ii) Examine the d subshells of Zn, Cd and Hg The configurations of the atoms are Zn : $[Ar]3d^{10}4s^2$, Cd : $[Kr]4d^{10}5s^2$ and Hg : $[Xe]4f^{14}5d^{10}6s^2$. Their usual divalent ions lose the two outer s electrons and retain completely filled d^{10} subshells. Hence neither the atoms nor their common ions have an incompletely filled d subshell, so these d-block metals do not satisfy the definition of transition elements.

Step 3: (iii) Apply lanthanoid contraction to Zr and Hf Hf follows the lanthanoid series, whereas Zr is in the preceding transition series. Normally an additional electron shell would make Hf larger. However, the intervening 4f electrons shield the increasing nuclear charge poorly, causing contraction across the lanthanoids. This lanthanoid contraction largely offsets the expected increase in size, so Hf and Zr have almost identical atomic radii.

Step 4: Conclusion (i) Variable oxidation states, intermediate formation and adsorption explain catalytic activity. (ii) Zn, Cd and Hg have filled d subshells in their atoms and common ions. (iii) Lanthanoid contraction makes the radii of Zr and Hf almost equal.

Quick Tip to Solve: Link the three reasons to three keywords: variable oxidation states, filled d subshells and lanthanoid contraction.

10(a). Write the hybridisation and magnetic character of the following complexes :

(i) $[NiCl_4]^{2-}$

(ii) $[Co(NH_3)_6]^{3+}$

(iii) $[FeF_6]^{3-}$

[Atomic number : Ni = 28, Co = 27, Fe = 26] [3 marks]

Solution:

Concept:

- First find the metal oxidation state from the total complex charge, then determine its d-electron configuration by removing outer s electrons first.
- In valence bond theory, four-coordinate tetrahedral complexes use sp^3 hybridisation; octahedral complexes use d^2sp^3 for inner-orbital or sp^3d^2 for outer-orbital bonding.
- Unpaired electrons cause paramagnetism; a complex with all electrons paired is diamagnetic. Ligand strength and the metal ion determine whether pairing occurs.

Step 1: (i) Analyse the nickel complex In $[NiCl_4]^{2-}$, four chloride ligands contribute a charge of -4, so nickel has oxidation state $+2$. Nickel has atomic number 28 and Ni^{2+} has configuration $[Ar]3d^8$. Chloride is a weak-field ligand and does not cause the pairing needed to leave a vacant 3d orbital for square-planar bonding. The metal uses one 4s and three 4p orbitals for sp^3 hybridisation, giving tetrahedral geometry. The d^8 ion has two unpaired electrons, so the complex is paramagnetic.

Step 2: (ii) Analyse the cobalt complex Ammonia is neutral, so cobalt in $[Co(NH_3)_6]^{3+}$ has oxidation state $+3$. With atomic number 27, Co^{3+} has configuration $[Ar]3d^6$. In this cobalt(III) complex the ligand-field splitting is sufficient to pair the six d electrons in the lower-energy orbitals. Two inner 3d orbitals are thereby available for bonding along with one 4s and three 4p orbitals. Thus the hybridisation is d^2sp^3, the geometry is octahedral and all the electrons are paired. The complex is diamagnetic.

Step 3: (iii) Analyse the iron complex In $[FeF_6]^{3-}$, six fluoride ligands contribute -6, so iron is in oxidation state $+3$. Iron has atomic number 26, giving Fe^{3+} : $[Ar]3d^5$. Fluoride is a weak-field ligand, so it does not pair the five 3d electrons. Each of the five 3d orbitals retains one electron. The metal therefore uses outer 4d orbitals together with 4s and 4p orbitals, giving sp^3d^2 hybridisation and octahedral geometry. Five unpaired electrons make this complex paramagnetic.

Step 4: Conclusion (i) $[NiCl_4]^{2-}$: sp^3, paramagnetic (two unpaired electrons). (ii) $[Co(NH_3)_6]^{3+}$: d^2sp^3, diamagnetic. (iii) $[FeF_6]^{3-}$: sp^3d^2, paramagnetic (five unpaired electrons).

Quick Tip to Solve: Calculate the metal charge first: these three ions are Ni(II), Co(III) and Fe(III), with d counts 8, 6 and 5 respectively.

OR

10(b). (i) Write the IUPAC name of the following complex :

$[Co(NH_3)_4(H_2O)Cl]Cl_2$

(ii) What is the difference between an Ambidentate ligand and a Bidentate ligand?

(iii) Out of $[Fe(NH_3)_6]^{3+}$ and $[Fe(C_2O_4)_3]^{3-}$, which complex is more stable and why? [3 marks]

Solution:

Concept:

- In naming a coordination compound, name ligands alphabetically before the metal, then give the metal oxidation state in Roman numerals. Neutral ammine and aqua ligands do not contribute to the charge.
- Denticity is the number of donor atoms of one ligand that bind simultaneously to a metal ion; chelate rings form when a multidentate ligand binds through more than one donor atom.

Step 1: (i) Determine the oxidation state and name the complex In $[Co(NH_3)_4(H_2O)Cl]Cl_2$, the two chloride counter-ions show that the complex ion has charge $+2$. The four ammine ligands and one aqua ligand are neutral, while the coordinated chlorido ligand has charge -1. If the cobalt oxidation state is x,

$$x + 4(0) + 0 - 1 = +2, \qquad x = +3.$$

Alphabetical order is ammine, aqua, chlorido; the prefix tetra does not affect that order. Because the complex ion is cationic, retain the metal name cobalt. The IUPAC name is tetraammineaquachlorido-cobalt(III) chloride.

Step 2: (ii) Distinguish the two kinds of ligand An ambidentate ligand has two alternative donor atoms, but coordinates to a given metal through only one of them at a time. For example, NO_2^- can bind through nitrogen or oxygen. A bidentate ligand binds to the same metal simultaneously through two donor atoms. For example, ethane-1,2-diamine uses both nitrogen atoms, and oxalate, $C_2O_4^{2-}$, uses two oxygen atoms. Thus alternative coordination sites must not be confused with simultaneous two-point attachment.

Step 3: (iii) Apply the chelate effect In $[Fe(NH_3)_6]^{3+}$, each ammine is monodentate. In $[Fe(C_2O_4)_3]^{3-}$, each oxalate is bidentate, so the three ligands form three chelate rings around iron. Both complexes have iron in oxidation state $+3$ and coordination number six. The oxalate complex is more stable owing to the chelate effect: simultaneous attachment through two donor atoms and ring formation stabilise the complex relative to comparable monodentate-ligand complexes.

Step 4: Conclusion (i) Tetraammineaquachloridocobalt(III) chloride. (ii) An ambidentate ligand binds through either of two alternative donor atoms; a bidentate ligand binds through both donor atoms simultaneously. (iii) $[Fe(C_2O_4)_3]^{3-}$ is more stable because of chelation.

Quick Tip to Solve: Count chloride ions outside the brackets first to find the complex charge; for ligand type, ask whether its two donor atoms bind alternatively or simultaneously.

11. From the given E° values of the first row transition elements, answer the following questions :

(i) Why is $E^{\circ}_{Mn^{2+}/Mn}$ value highly negative as compared to other elements?

(ii) What is the reason for the irregularity in the above E° values?

(iii) Why is $E^{\circ}_{Cu^{2+}/Cu}$ value exceptionally positive? [3 marks]

$E^{\ominus}_{M^{2+}/M}$	Cr	Mn	Fe	Co	Ni	Cu	Zn
	− 0·91	− 1·18	− 0·44	− 0·28	− 0·25	+ 0·34	− 0·76

Solution:

Concept:

- The standard potential $E^{\circ}_{\mathrm{M^{2+}/M}}$ refers to the reduction $\mathrm{M^{2+}(aq) + 2\,e^{-} \longrightarrow M(s)}$. A more negative value means this reduction is less favourable relative to the standard hydrogen electrode.
- Formation of an aqueous divalent metal ion involves atomisation of the solid, the first two ionisation enthalpies and hydration of the ion. Electrode potentials depend on the combined thermodynamic effects of these processes.

Step 1: (i) Explain the highly negative value for manganese Manganese has the configuration $[\mathrm{Ar}]\,3d^5 4s^2$, whereas $\mathrm{Mn^{2+}}$ has the especially stable half-filled $3d^5$ configuration. Formation of this stable divalent ion favours oxidation of the metal; conversely, reduction of $\mathrm{Mn^{2+}}$ to manganese is relatively unfavourable. Consequently, the reduction potential is highly negative, $-1.18\,\mathrm{V}$, compared with the neighbouring metals in the table. The stability of the ion, rather than an unusually unstable ion, explains the sign.

Step 2: (ii) Identify the competing contributions The energy needed to atomise the metal and remove two electrons opposes formation of $\mathrm{M^{2+}(aq)}$, while hydration releases energy and favours it. These contributions do not vary uniformly across the series. Atomisation enthalpies, successive ionisation enthalpies and hydration enthalpies show variations associated with electronic configuration and metallic bonding. Their combined effect therefore gives an irregular sequence of standard electrode potentials instead of a smooth trend with atomic number.

Step 3: (iii) Explain the positive value for copper For copper, the relatively high energy needed for atomisation and ionisation to $\mathrm{Cu^{2+}}$ is not sufficiently compensated by the hydration enthalpy of $\mathrm{Cu^{2+}}$. In particular, the second ionisation removes an electron from the stable filled $3d^{10}$ configuration of $\mathrm{Cu^{+}}$. Thus conversion of copper metal into aqueous divalent ions is energetically unfavourable relative to hydrogen oxidation. The reverse reduction is favoured, giving the exceptionally positive value $E^{\circ}_{\mathrm{Cu^{2+}/Cu}} = +0.34\,\mathrm{V}$.

Step 4: Conclusion (i) The stable half-filled $3d^5$ configuration of $\mathrm{Mn^{2+}}$ makes its reduction potential highly negative. (ii) Irregular variations in atomisation, ionisation and hydration enthalpies cause the irregular potentials. (iii) Copper's high atomisation and ionisation energy requirements are not compensated by hydration, producing its positive reduction potential.

Quick Tip to Solve: Read the table as reduction potentials: a stable aqueous divalent ion makes reduction harder; for copper, compare the energy cost of forming the ion with the energy released on hydration.

Section C (5 marks)

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

Amines constitute an important class of organic compounds derived by replacing one or more hydrogen atoms of ammonia molecule by alkyl/aryl groups. Amines are usually formed from nitro compounds, halides, amides, etc. They exhibit hydrogen bonding which influences their physical properties. Alkyl amines are found to be stronger bases than ammonia. In aromatic amines, electron releasing and withdrawing groups, respectively increase and decrease their basic character. Reactions of amines are governed by availability of the unshared pair of electrons on nitrogen. Influence of the number of hydrogen atoms at nitrogen atom on the type of reactions and nature of products is responsible for identification and distinction between primary, secondary and tertiary amines. Reactivity of aromatic amines can be controlled by acylation process.

Why does aniline not give Friedel-Crafts reaction? [1 mark]

Solution:

Concept:

- Friedel-Crafts alkylation and acylation require a Lewis acid catalyst such as anhydrous $AlCl_3$.
- The nitrogen lone pair of aniline can bind to a Lewis acid; the resulting salt or complex strongly deactivates the aromatic ring.

Step 1: Identify the interaction with the catalyst Aniline, $C_6H_5NH_2$, acts as a Lewis base through its nitrogen lone pair. It reacts with the Lewis acid $AlCl_3$ used in the Friedel-Crafts reaction, forming a salt or complex in which nitrogen acquires positive character.

Step 2: Explain the effect on ring reactivity This positively charged nitrogen group withdraws electron density and strongly deactivates the benzene ring towards electrophilic substitution. Therefore the ring does not undergo the required Friedel-Crafts alkylation or acylation under these conditions. The availability of the free amine lone pair is the reason for reaction with the catalyst.

Step 3: Conclusion Aniline does not give the Friedel-Crafts reaction because it forms a salt or complex with $AlCl_3$, making nitrogen positively charged and strongly deactivating the ring.

Quick Tip to Solve: When an aromatic amine meets a Lewis acid catalyst, check lone-pair binding to the catalyst before applying the usual activating effect of the amino group.

12(ii). Arrange the following in the increasing order of their pK_b values :

$C_6H_5NH_2$, NH_3, $C_2H_5NH_2$, $(CH_3)_3N$ [1 mark]

Solution:

Concept:

- The base dissociation constant K_b measures the ability of an amine to accept a proton in water; $pK_b = -\log_{10} K_b$.
- A stronger base has a larger K_b and hence a smaller pK_b. Inductive effects, resonance and solvation together determine aqueous basicity.

Quick Tip to Solve: Rank aqueous basic strength first, accounting for solvation; then place the strongest base at the smallest pKb end.

Step 1: Compare the basic strengths Ethylamine, $C_2H_5NH_2$, has an electron-releasing ethyl group and its protonated ion is well solvated in water. It is more basic than trimethylamine, $(CH_3)_3N$, whose protonated ion is less effectively solvated. Both alkylamines are stronger bases than NH_3. Aniline, $C_6H_5NH_2$, is weakest because its nitrogen lone pair is delocalised into the benzene ring and is less available for protonation.

Step 2: Reverse the basicity order for pKb The aqueous basicity order is $C_2H_5NH_2 > (CH_3)_3N > NH_3 > C_6H_5NH_2$. Since the negative logarithm decreases as K_b increases, the strongest base must appear first when listing increasing pK_b, and the weakest must appear last.

Step 3: Conclusion The increasing order of pK_b is

$$C_2H_5NH_2 < (CH_3)_3N < NH_3 < C_6H_5NH_2.$$

Quick Tip to Solve: Rank aqueous basic strength first, accounting for solvation; then place the strongest base at the smallest pKb end.

12(iii). How can you distinguish between $CH_3CH_2NH_2$ and $(CH_3CH_2)_2NH$ by Hinsberg test? [1 mark]

Solution:

Concept:

- Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$, used in aqueous alkali to distinguish primary and secondary amines.
- A primary amine forms a sulphonamide retaining an acidic $N-H$ bond; a secondary amine forms a sulphonamide without such a bond.

Step 1: Test ethylamine with Hinsberg's reagent Shake $CH_3CH_2NH_2$ with benzenesulphonyl chloride and aqueous $NaOH$. It forms $C_6H_5SO_2NHCH_2CH_3$, N-ethylbenzenesulphonamide. Its remaining hydrogen on nitrogen is acidic because of the electron-withdrawing sulphonyl group, so it forms a salt soluble in alkali. Acidifying this alkaline solution regenerates the sulphonamide as a precipitate.

Step 2: Compare diethylamine under the same conditions $(CH_3CH_2)_2NH$ gives $C_6H_5SO_2N(CH_2CH_3)_2$, N,N-diethylbenzenesulphonamide. This product has no hydrogen attached to nitrogen and cannot form the corresponding salt with alkali; it remains insoluble in the alkaline mixture.

Step 3: Conclusion Ethylamine gives a sulphonamide soluble in aqueous alkali and precipitated on acidification; diethylamine gives a sulphonamide insoluble in aqueous alkali. This solubility difference distinguishes the two amines.

Quick Tip to Solve: Check whether the sulphonamide retains an N-H bond: its presence makes the primary-amine product soluble in alkali.

12(iv)(a). Write the structures of A and B in the following reactions:

(I) $C_6H_5NO_2 \xrightarrow{Sn+HCl} A \xrightarrow{Br_2 \text{ water}} B$

(II) $CH_3CH_2CONH_2 \xrightarrow{Br_2/\text{alc. KOH}} A \xrightarrow[\text{Pyridine}]{CH_3COCl} B$ [2 marks]

Solution:

Concept:

- Tin and hydrochloric acid reduce an aromatic nitro group to an amino group. Aniline strongly activates the benzene ring towards bromination at both ortho positions and the para position.
- Hofmann bromamide degradation converts $RCONH_2$ into RNH_2, losing the carbonyl carbon. Acetyl chloride acylates an amine to form an amide; pyridine removes the hydrogen chloride produced.

Step 1: Identify both products in reaction I Reduction of the $-NO_2$ group of nitrobenzene gives aniline, so $A = C_6H_5NH_2$. On treatment with bromine water, the strongly activating amino group directs substitution to positions 2, 4 and 6. Therefore B is 2,4,6-tribromoaniline, with NH_2 at position 1 and Br at positions 2, 4 and 6.

$$C_6H_5NH_2 + 3\,Br_2 \longrightarrow 2,4,6-C_6H_2Br_3NH_2 + 3\,HBr.$$

Step 2: Identify both products in reaction II Propanamide, $CH_3CH_2CONH_2$, undergoes Hofmann bromamide degradation. Removal of its carbonyl carbon leaves the ethyl group bonded to nitrogen, so $A = CH_3CH_2NH_2$, ethylamine. Acetylation with CH_3COCl in pyridine replaces one nitrogen-bound hydrogen with an acetyl group:

$$CH_3CH_2NH_2 + CH_3COCl \longrightarrow CH_3CONHCH_2CH_3 + HCl.$$

Pyridine binds the released HCl. Thus $B = CH_3CONHCH_2CH_3$, N-ethylethanamide.

Step 3: Conclusion (I) $A = C_6H_5NH_2$; $B = 2,4,6-C_6H_2Br_3NH_2$, 2,4,6-tribromoaniline.
(II) $A = CH_3CH_2NH_2$; $B = CH_3CONHCH_2CH_3$, N-ethylethanamide.

Quick Tip to Solve: For Hofmann degradation delete the amide carbonyl carbon; for bromine water with unprotected aniline fill both ortho sites and the para site.

OR

12(iv)(b). How will you convert the following :

(I) Benzoic acid to aniline

(II) Aniline to p-bromoaniline [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into RNH_2, with loss of the carbonyl carbon.
- Acetylation protects aniline's strongly activating amino group. The resulting acetamido group still directs bromination mainly to the para position; hydrolysis then restores $-NH_2$.

Step 1: Convert benzoic acid into aniline Treat benzoic acid with ammonia to form ammonium benzoate, then heat the salt to obtain benzamide:

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4$$

$$C_6H_5COONH_4 \xrightarrow{\Delta} C_6H_5CONH_2 + H_2O.$$

Treat benzamide with bromine and aqueous potassium hydroxide. Hofmann degradation removes its carbonyl carbon, producing aniline:

$$C_6H_5CONH_2 + Br_2 + 4\,KOH \longrightarrow C_6H_5NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O.$$

The benzene ring is retained throughout; the carboxyl carbon is lost during the final step.

Step 2: Convert aniline into p-bromoaniline First acetylate aniline using acetic anhydride to obtain acetanilide, $C_6H_5NHCOCH_3$. Brominate acetanilide with Br_2 in glacial acetic acid; the para product predominates because the ortho positions are more hindered. Finally hydrolyse the acetyl group with aqueous acid on heating, then neutralise to obtain the free amine:

$$\begin{aligned} C_6H_5NH_2 &\xrightarrow{(CH_3CO)_2O} C_6H_5NHCOCH_3 \\ &\xrightarrow{Br_2/CH_3COOH} \text{p-}BrC_6H_4NHCOCH_3 \\ &\xrightarrow[\text{then neutralise}]{H_3O^+,\,\Delta} \text{p-}BrC_6H_4NH_2. \end{aligned}$$

Direct use of bromine water on aniline gives 2,4,6-tribromoaniline, so protection and subsequent removal of the acetyl group are needed for the required monobromo product.

Step 3: Conclusion (I) Benzoic acid $\rightarrow$ ammonium benzoate $\rightarrow$ benzamide $\rightarrow$ aniline, using NH_3, heat, then Br_2/KOH.

(II) Aniline $\rightarrow$ acetanilide $\rightarrow$ p-bromoacetanilide $\rightarrow$ p-bromoaniline, using acetylation, controlled bromination and hydrolysis.

Quick Tip to Solve: Use the amide route to remove one carbon from benzoic acid; protect aniline before bromination to avoid substitution at all three activated positions.