CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-2-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 2 hours **Maximum Marks: 35**

General Instructions

(i) This question paper contains **12** questions. **All** questions are compulsory.

(ii) This question paper is divided into **three** Sections – **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. How will you carry out the following conversions : (Any two)

(i) Propanal to Propane

(ii) Ethanal to But-2-enal

(iii) Ethanoic acid to ethanamide [2 marks]

Solution:

Concept:

- Clemmensen reduction converts an aldehyde carbonyl into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- An aldehyde with alpha hydrogen undergoes aldol addition in dilute alkali; heating removes water to form an unsaturated aldehyde.
- A carboxylic acid forms an ammonium salt with ammonia; heating this salt produces an amide.

Step 1: Reduce propanal completely (i) Use zinc amalgam and concentrated hydrochloric acid for Clemmensen reduction. The three-carbon chain is retained:

$$CH_3CH_2CHO + 4\,[H] \xrightarrow{Zn(Hg),\,conc\cdot HCl} CH_3CH_2CH_3 + H_2O.$$

Ordinary reduction with $NaBH_4$ would give propan-1-ol, so complete reduction to the hydrocarbon is required here.

Step 2: Condense ethanal and dehydrate the aldol (ii) Treat ethanal with dilute $NaOH$. Two molecules undergo aldol addition, giving 3-hydroxybutanal; heating then removes water:

$$2\,CH_3CHO \xrightarrow{dil\cdot NaOH} CH_3CH(OH)CH_2CHO$$

$$CH_3CH(OH)CH_2CHO \xrightarrow{heat} CH_3CH{=}CHCHO + H_2O.$$

The resulting four-carbon unsaturated aldehyde is but-2-enal.

Step 3: Heat ammonium ethanoate (iii) React ethanoic acid with ammonia to form ammonium ethanoate, then heat the salt:

$$CH_3COOH + NH_3 \longrightarrow CH_3COONH_4$$

$$CH_3COONH_4 \xrightarrow{heat} CH_3CONH_2 + H_2O.$$

Heating is essential for dehydration to ethanamide; acid and ammonia alone produce the salt.

Step 4: Conclusion Use Clemmensen reduction for (i), aldol addition followed by heating for (ii), and ammonium-salt formation followed by heating for (iii). Any two conversions answer the question.

Quick Tip to Solve: Carbonyl to hydrocarbon requires complete reduction; doubling the carbon chain suggests aldol condensation; acid to amide requires heating its ammonium salt.

2. In the given reaction

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

the rate of formation of NH_3 is 3.6×10^{-4} mol L^{-1} s^{-1}.

Calculate the

(i) rate of reaction, and

(ii) rate of disappearance of $H_2(g)$. [2 marks]

Solution:

Concept:

- The reaction rate is the concentration change per unit time divided by the corresponding stoichiometric coefficient.
- For $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$, $r = -d[N_2]/dt = -(1/3)d[H_2]/dt = (1/2)d[NH_3]/dt$. Negative signs for reactants make their disappearance rates positive.

Step 1: Normalize the ammonia formation rate (i) The given quantity is the rate of formation of ammonia, not the stoichiometrically normalized reaction rate. Since the coefficient of ammonia is 2, divide the stated rate by 2:

$$r = \frac{1}{2}\frac{d[NH_3]}{dt} = \frac{3.6 \times 10^{-4}}{2} = 1.8 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}.$$

Step 2: Use the hydrogen coefficient (ii) Three moles of hydrogen disappear for every two moles of ammonia formed. Therefore the disappearance rate of hydrogen is three times the reaction rate:

$$-\frac{d[H_2]}{dt} = 3r = 3(1.8 \times 10^{-4}) = 5.4 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}.$$

Equivalently, multiply the ammonia formation rate by $3/2$. The concentration derivative for hydrogen is negative because it is consumed; its requested disappearance rate is positive.

Step 3: Conclusion (i) The rate of reaction is $1.8 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$. (ii) The rate of disappearance of hydrogen is $5.4 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Quick Tip to Solve: Divide a species rate by its balanced coefficient to find the reaction rate, then multiply by the coefficient of the species whose rate is required.

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

(ii) Calculate the degree of dissociation (α) of CH_3COOH if Λ_m and Λ_m^0 of CH_3COOH are 48 S cm^2 mol^{-1} and 400 S cm^2 mol^{-1} respectively. [2 marks]

Solution:

Concept:

- Kohlrausch's law applies at infinite dilution: each ion contributes independently to the limiting molar conductivity of an electrolyte, irrespective of the other ion present.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda_m^0$, where Λ_m is its molar conductivity

Quick Tip to Solve: For a weak electrolyte, divide the given molar conductivity by its limiting value; keep the fraction dimensionless and multiply by 100 only when expressing a percentage.

at the given concentration and Λ_m^0 is its limiting molar conductivity.

Step 1: State the law and apply it to ethanoic acid (i) At infinite dilution, the molar conductivity of an electrolyte is the sum of the independent contributions of its constituent ions, each multiplied by the number of those ions per formula unit. In general,

$$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0,$$

where ν_+ and ν_- are ion counts and λ_+^0, λ_-^0 are limiting ionic molar conductivities. Thus for CH_3COOH,

$$\Lambda_m^0 = \lambda^0(H^+) + \lambda^0(CH_3COO^-).$$

Step 2: Calculate the dissociated fraction (ii) Ethanoic acid is a weak electrolyte and dissociates according to

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-.$$

Using the ratio of its measured and limiting molar conductivities,

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{48\,\mathrm{S\,cm^2\,mol^{-1}}}{400\,\mathrm{S\,cm^2\,mol^{-1}}} = 0.12.$$

The conductivity units cancel, so the degree of dissociation is dimensionless. As a percentage, it is $0.12 \times 100 = 12\%$.

Step 3: Conclusion Kohlrausch's law states that ions contribute independently to limiting molar conductivity at infinite dilution. The degree of dissociation of ethanoic acid is $\boxed{\alpha = 0.12}$, or 12%.

Quick Tip to Solve: For a weak electrolyte, divide the given molar conductivity by its limiting value; keep the fraction dimensionless and multiply by 100 only when expressing a percentage.

Section B (24 marks)

4(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 determine the metal oxidation state, then count its d electrons. Transition-metal ions lose their $4s$ electrons before their $3d$ electrons.
- Tetrahedral complexes use sp^3 hybridisation; octahedral complexes use inner-orbital d^2sp^3 or outer-orbital sp^3d^2 hybridisation.
- Unpaired electrons cause paramagnetism. When all electrons are paired, the complex is diamag-

Quick Tip to Solve: Determine metal charge before counting d electrons: the ions here are nickel(II), cobalt(III) and iron(III). Ammonia pairs cobalt(III), whereas chloride and fluoride leave these complexes high spin.

netic. Pairing depends on both ligand strength and the metal ion.

Step 1: Determine the nickel configuration in part (i) For $[NiCl_4]^{2-}$, the metal oxidation-state equation is $x - 4 = -2$, giving $x = +2$. Nickel has configuration $[Ar]3d^8 4s^2$; hence Ni^{2+} is $3d^8$. Chloride is a weak-field ligand and does not cause the pairing needed for a square-planar inner-orbital complex. Four ligands occupy a tetrahedral arrangement using sp^3 hybridisation. Two d electrons remain unpaired, so the complex is paramagnetic.

Step 2: Determine the cobalt configuration in part (ii) Ammonia is neutral, so cobalt in $[Co(NH_3)_6]^{3+}$ has oxidation state $+3$. Cobalt has configuration $[Ar]3d^7 4s^2$, making Co^{3+} a $3d^6$ ion. In this cobalt(III) complex, ammonia causes pairing of the d electrons. Two vacant $3d$ orbitals combine with the $4s$ and three $4p$ orbitals to form d^2sp^3 hybrids. The octahedral inner-orbital complex has low-spin configuration $t_{2g}^6 e_g^0$, with no unpaired electrons. It is diamagnetic.

Step 3: Determine the iron configuration in part (iii) For $[FeF_6]^{3-}$, $x - 6 = -3$, giving iron the oxidation state $+3$. Iron has configuration $[Ar]3d^6 4s^2$, so Fe^{3+} is $3d^5$. Fluoride is a weak-field ligand and does not pair the five d electrons. The octahedral complex uses two outer $4d$ orbitals, one $4s$ and three $4p$ orbitals, giving sp^3d^2 hybridisation. Its high-spin configuration is $t_{2g}^3 e_g^2$, with five unpaired electrons; consequently it is paramagnetic.

Step 4: Conclusion (i) $[NiCl_4]^{2-}$: sp^3, paramagnetic (two unpaired electrons). (ii) $[Co(NH_3)_6]^{3+}$: d^2sp^3, diamagnetic (no unpaired electrons). (iii) $[FeF_6]^{3-}$: sp^3d^2, paramagnetic (five unpaired electrons).

Quick Tip to Solve: Determine metal charge before counting d electrons: the ions here are nickel(II), cobalt(III) and iron(III). Ammonia pairs cobalt(III), whereas chloride and fluoride leave these complexes high spin.

OR

4(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:

- Name ligands alphabetically, ignoring multiplicative prefixes. State the central metal oxidation state in Roman numerals and name the counter-ion after the complex cation.
- Denticity is the number of donor atoms of one ligand bonded simultaneously to the same metal. Ambidentate ligands offer alternative donor atoms; bidentate ligands bind through two donor atoms together.
- Chelating ligands form rings with the metal. Their complexes generally have greater thermodynamic stability than corresponding complexes with comparable monodentate ligands; this is the chelate effect.

Step 1: Name the complex in part (i) In $[Co(NH_3)_4(H_2O)Cl]Cl_2$, the two chloride counter-ions show

Quick Tip to Solve: Use the two external chlorides to find cobalt(III). For the ligand distinction, ask whether two donor atoms attach together (bidentate) or offer alternative attachment sites (ambidentate).

that the complex cation has charge $+2$. Ammonia and water are neutral ligands, while coordinated chloride has charge -1. Thus the cobalt oxidation state satisfies $x-1=+2$, giving $x=+3$. The ligand names are ammine, aqua and chlorido. Alphabetical ordering places ammine first (the prefix tetra does not determine alphabetical order), followed by aqua and chlorido. Since the complex is cationic, the metal retains the name cobalt. The complete name is **tetraammineaquachloridocobalt(III) chloride**.

Step 2: Distinguish the ligand types in part (ii) An ambidentate ligand has two possible donor atoms but coordinates through only one of them at a time to a given metal centre. For example, NO_2^- can bind through nitrogen or oxygen, and SCN^- can bind through sulfur or nitrogen. Its alternative attachment modes can produce linkage isomerism. A bidentate ligand coordinates through two donor atoms simultaneously to the same metal ion. For example, ethane-1,2-diamine binds through its two nitrogen atoms, and oxalate, $C_2O_4^{2-}$, binds through two oxygen atoms. Such simultaneous attachment forms a chelate ring. Thus two possible donor sites alone do not make a ligand bidentate.

Step 3: Apply the chelate effect in part (iii) In $[Fe(NH_3)_6]^{3+}$, each ammonia is monodentate and supplies one donor nitrogen, so no chelate rings form. In $[Fe(C_2O_4)_3]^{3-}$, each oxalate is bidentate and supplies two donor oxygen atoms. Three oxalate ligands therefore occupy six coordination positions and form three chelate rings with iron(III). The ring formation gives the oxalate complex enhanced stability through the chelate effect. Hence the oxalate complex is more stable than the corresponding ammonia complex. This comparison concerns chelation, rather than merely the sign of the complex charge.

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

Quick Tip to Solve: Use the two external chlorides to find cobalt(III). For the ligand distinction, ask whether two donor atoms attach together (bidentate) or offer alternative attachment sites (ambidentate).

5. 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:

- Oxidation occurs at the anode and reduction at the cathode. Using standard reduction potentials, $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At $298\,\text{K}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$. Here n is the electron count and Q the reaction quotient; pure solids are omitted.

Quick Tip to Solve: Balance the reaction first: two silver ions accept zinc's two electrons, so use $n=2$ and square the silver-ion concentration in Q.

Step 1: Balance the cell reaction Zinc undergoes oxidation and silver ions undergo reduction:

$$\mathrm{Zn\,(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Ag\,(s)}.$$

Adding them gives

$$\mathrm{Zn\,(s)} + 2\,\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Ag\,(s)}.$$

Thus $n = 2$; electrode potentials are not multiplied when balancing electrons.

Step 2: Find the standard potential and reaction quotient Using the given reduction potentials,

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

The coefficient of silver ions gives their concentration a power of two:

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

The given $\log 10 = 1$ gives $\log Q = 4$.

Step 3: Calculate the emf Using the standard room-temperature form of the Nernst equation,

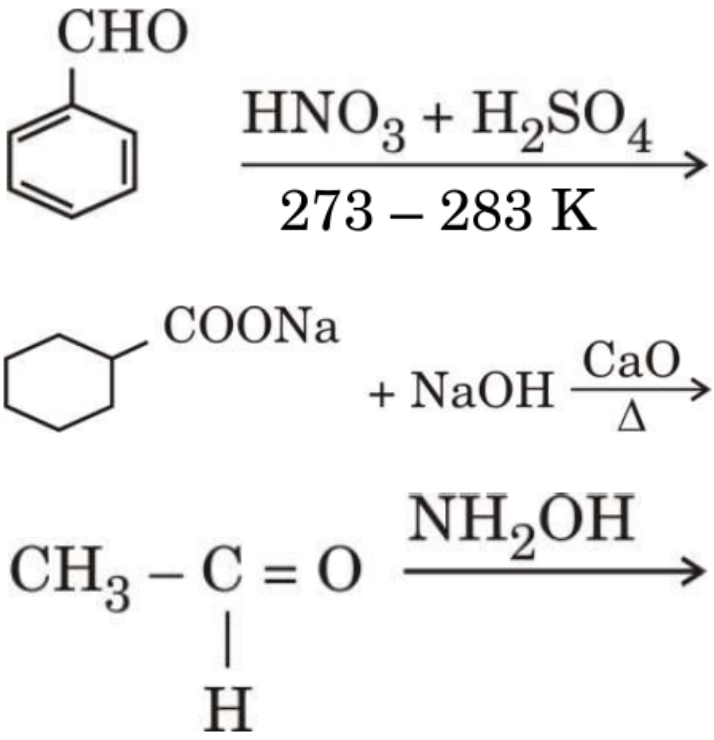
$$\begin{aligned} E_{\text{cell}} &= 1.56 - \frac{0.0591}{2}\log(10^4) \\ &= 1.56 - \frac{0.0591}{2} \times 4 \\ &= 1.56 - 0.1182 = 1.4418\,\text{V}. \end{aligned}$$

Since $Q > 1$, the emf is below its standard value.

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

Quick Tip to Solve: Balance the reaction first: two silver ions accept zinc's two electrons, so use $n = 2$ and square the silver-ion concentration in Q.

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



Solution:

Concept:

- The aldehyde group, $-CHO$, withdraws electron density from a benzene ring and directs electrophilic substitution predominantly to the meta position.
- Heating a sodium carboxylate with soda lime (NaOH and CaO) removes the carboxyl carbon by decarboxylation: $RCOONa + NaOH \longrightarrow RH + Na_2CO_3$.
- Hydroxylamine, NH_2OH, condenses with an aldehyde or ketone to form an oxime, replacing the carbonyl oxygen with $=NOH$ and eliminating water.

Step 1: (i) Locate the nitration position in benzaldehyde The starting compound is benzaldehyde, C_6H_5CHO. The mixture of concentrated nitric and sulphuric acids supplies the nitrating electrophile, $NO_2{}^+$. Since $-CHO$ is a deactivating, meta-directing group, the incoming nitro group enters predominantly at the position meta to $-CHO$; the aldehyde group remains present.

$$C_6H_5CHO + HNO_3 \xrightarrow[273\text{-}283\,K]{H_2SO_4} 3\text{-}NO_2{-}C_6H_4{-}CHO + H_2O$$

This is ring nitration, so the product is neither an ortho/para major product nor replacement of the aldehyde group by a nitro group.

Step 2: (ii) Remove the carboxylate carbon with soda lime The printed structure is a saturated six-membered ring bearing $-COONa$, namely sodium cyclohexanecarboxylate. It is not sodium benzoate: the ring has no alternating double bonds. On heating with soda lime, the $-COONa$ substituent is

Quick Tip to Solve: Check the ring bonds before naming a decarboxylation product: this saturated ring gives cyclohexane. For an oxime, retain the carbon substituents and replace only $=O$ by $=NOH$.

replaced by hydrogen while the saturated ring is retained.

$$C_6H_{11}COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_{12} + Na_2CO_3$$

The inorganic product is sodium carbonate, and the organic product has one fewer carbon atom than the starting salt.

Step 3: (iii) Condense ethanal with hydroxylamine The third carbonyl compound is ethanal, CH_3CHO, because the carbonyl carbon is bonded to one methyl group and one hydrogen. Reaction with hydroxylamine eliminates water and changes C=O into C=NOH, keeping both original carbon substituents.

$$CH_3CHO + NH_2OH \longrightarrow CH_3CH{=}NOH + H_2O$$

The hydrogen on the carbonyl carbon remains bonded to that carbon; the product is an aldoxime rather than a ketoxime.

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

Quick Tip to Solve: Check the ring bonds before naming a decarboxylation product: this saturated ring gives cyclohexane. For an oxime, retain the carbon substituents and replace only =O by =NOH.

OR

6(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:

- Aldehydes oxidise readily to carboxylic acids; ordinary ketone oxidation requires carbon-carbon bond cleavage.
- The iodoform test detects a methyl ketone group, CH_3CO^-, by formation of yellow CHI_3.
- 2,4-Dinitrophenylhydrazine condenses with a carbonyl group to form a hydrazone and water.

Step 1: (i) Compare the oxidation pathways Propanal has a hydrogen directly attached to its carbonyl carbon. It oxidises without breaking a carbon-carbon bond:

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

Propanone has no aldehydic hydrogen. Its oxidation needs stronger conditions and carbon-carbon bond cleavage, so propanal is more easily oxidised.

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

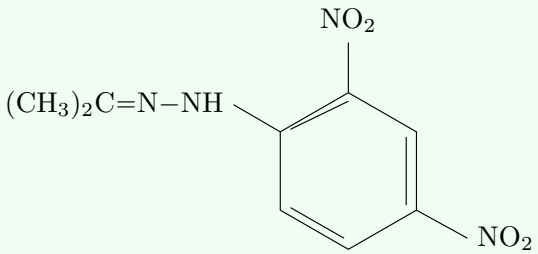
Quick Tip to Solve: Locate $COCH_3$ for the iodoform test. In the hydrazone, keep both methyl groups and put ring nitro groups ortho and para to the nitrogen attachment.

sodium hydroxide. Acetophenone contains $COCH_3$ and gives yellow 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 this group and gives no yellow precipitate. A general carbonyl test cannot distinguish them, since both are ketones.

Step 3: (iii) Construct the hydrazone derivative Replace propanone's oxygen by $N-NH-Ar$, retaining both methyl groups. Water is eliminated in this condensation. Here Ar is the 2,4-dinitrophenyl group: relative to the ring carbon bonded to nitrogen (position 1), the nitro groups are ortho (2) and para (4).



2,4-Dinitrophenylhydrazone of propanone

Step 4: Conclusion Propanal oxidises more readily; acetophenone gives the positive iodoform test while benzophenone does not. The drawn derivative is $(CH_3)_2C{=}N{-}NH{-}C_6H_3(NO_2)_2$.

Quick Tip to Solve: Locate $COCH_3$ for the iodoform test. In the hydrazone, keep both methyl groups and put ring nitro groups ortho and para to the nitrogen attachment.

7. 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 process, the integrated rate law is $k = \dfrac{2.303}{t}\log\dfrac{a}{a-x}$, where a is the initial amount, x is the amount decomposed after time t, and k is the rate constant.
- The first order half-life is $t_{1/2} = \dfrac{0.693}{k} = \dfrac{2.303\log 2}{k}$. It does not depend on the initial concentration.
- Percent decomposition refers to the amount consumed. The amount remaining is found by subtracting that percentage from 100 before substituting into the integrated rate law.

Step 1: Find the fraction remaining after 30 minutes The time given is for 75% decomposition, so the fraction still present is $100\% - 75\% = 25\%$. If the initial amount is a, the remaining amount is $a - x = 0.25a$. Hence the ratio needed in the rate law is

$$\frac{a}{a-x} = \frac{a}{0.25a} = 4.$$

This ratio uses the unreacted amount in the denominator; using the decomposed fraction would give

Quick Tip to Solve: For first order decomposition, 75% consumed means 25% remaining: this is two successive halvings. Divide the stated time by two to obtain the half-life.

an incorrect rate constant.

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

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

The time was expressed in minutes, so the rate constant has units of inverse minutes. These units ensure the calculated half-life will also be in minutes.

Step 3: Substitute into the half-life relation and check Using the supplied logarithms consistently gives

$$t_{1/2} = \frac{2.303\log 2}{k} = \frac{2.303 \times 0.3}{2.303 \times 0.6/30} = 30 \times \frac{0.3}{0.6} = 15\,\text{min}.$$

As an independent check, after one half-life the amount remaining is $a/2$, and after two half-lives it is $a/4$. Thus 75% decomposition corresponds to exactly two half-lives. The given 30 minutes must therefore equal $2t_{1/2}$, agreeing with the rate-law calculation.

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

Quick Tip to Solve: For first order decomposition, 75% consumed means 25% remaining: this is two successive halvings. Divide the stated time by two to obtain the half-life.

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

Solution:

Concept:

- A sol contains solid colloidal particles dispersed in a liquid. The distinction between lyophilic and lyophobic sols depends on the affinity of the particles for the dispersion medium.
- Strong particle–medium attraction produces a protective solvation layer in a lyophilic sol. Lyophobic particles have little affinity for the medium and are stabilised mainly by their charge.

Step 1: Compare affinity and preparation Lyophobic sols have little or no affinity between the dispersed phase and the dispersion medium. They cannot usually be prepared merely by mixing the two phases and require special dispersion or condensation methods. In contrast, lyophilic sols have considerable affinity for the medium and can be prepared by directly mixing a suitable substance with it, sometimes with heating. For example, starch forms a lyophilic sol in water, whereas a gold sol is lyophobic.

Step 2: Compare stability towards electrolytes Lyophobic sols are relatively unstable: a small quantity of a suitable electrolyte can neutralise their stabilising charge and cause coagulation. Lyophilic sols are much more stable because their particles are strongly solvated. Coagulating a lyophilic sol generally requires a much larger quantity of electrolyte, which reduces the protective solvation layer.

Step 3: Compare reversibility Lyophobic sols are irreversible. Once their dispersed phase is precipitated, simply adding the dispersion medium does not regenerate the original sol. Lyophilic sols are reversible: after removal of the dispersion medium, the residue can ordinarily form the sol again

Quick Tip to Solve: Use affinity, electrolyte stability and reversibility as three comparison headings; state the property of both sols under each heading.

when the medium is added. This follows from the strong attraction of the dispersed material for that medium.

Step 4: Conclusion The three differences are: little affinity and special preparation versus strong affinity and direct preparation; low stability and easy coagulation versus high stability and difficult coagulation; and irreversible versus reversible behaviour, respectively, for lyophobic and lyophilic sols.

Quick Tip to Solve: Use affinity, electrolyte stability and reversibility as three comparison headings; state the property of both sols under each heading.

OR

8(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 colloidal dispersion of one liquid in another immiscible liquid. The dispersed phase consists of droplets, while the dispersion medium is the continuous surrounding liquid.
- Brownian movement is the continuous, irregular zigzag motion of colloidal particles caused by the thermal motion of molecules of the dispersion medium.
- Physisorption is adsorption through weak van der Waals forces and is exothermic. Raising the temperature favours desorption, the reverse process.

Step 1: Identify the two phases in milk Milk is an oil-in-water emulsion. Liquid fat droplets are distributed throughout an aqueous continuous phase. Thus the dispersed phase is liquid fat (oil), and the dispersion medium is water. The phase present as separate droplets is named first when identifying the dispersed phase; the continuous phase is the medium.

Step 2: Explain the cause of Brownian movement Molecules of the dispersion medium are in constant thermal motion and strike a colloidal particle from different directions. At any instant the impacts on its different sides are unequal, so their resultant force does not cancel. Successive unbalanced collisions repeatedly change the particle's direction, producing its random zigzag movement. The cause is therefore unequal bombardment by molecules of the dispersion medium, rather than an organised flow of the liquid.

Step 3: Explain the temperature dependence of physisorption Physical adsorption releases heat when an adsorbate attaches to an adsorbent surface. It can 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 heat-consuming reverse process, desorption. Hence fewer molecules remain adsorbed and the extent of physisorption decreases. Increased thermal motion also helps molecules overcome the weak van der Waals attraction to the surface.

Quick Tip to Solve: For milk remember fat droplets in water; for Brownian motion identify unequal molecular impacts; for adsorption first check whether the forward process releases heat.

Step 4: Conclusion (i) Milk has liquid fat as the dispersed phase and water as the dispersion medium. (ii) Brownian movement arises from unequal collisions of medium molecules with colloidal particles. (iii) Physisorption decreases on heating because it is exothermic and higher temperature favours desorption.

Quick Tip to Solve: For milk remember fat droplets in water; for Brownian motion identify unequal molecular impacts; for adsorption first check whether the forward process releases heat.

9. 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 reduction potential refers to $\mathrm{M}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \rightarrow \mathrm{M}(\mathrm{s})$. A more negative value means reduction of the aqueous ion is less favourable relative to the standard hydrogen electrode.
- Formation of $\mathrm{M}^{2+}(\mathrm{aq})$ from the metal involves atomisation, the first two ionisation enthalpies, and hydration of the gaseous ion. Their combined effect controls the electrode potential; no single energy term alone determines the trend.
- Electronic configurations with half-filled or completely filled subshells have extra stability and influence ionisation and hydration energetics.

Step 1: (i) Explain the highly negative manganese value Manganese has configuration $[\mathrm{Ar}]3d^5 4s^2$, while Mn^{2+} has the especially stable half-filled configuration $[\mathrm{Ar}]3d^5$. Formation of this aqueous ion is favoured, whereas its reduction back to manganese metal is comparatively difficult. Thus the reduction potential $E^{\circ}_{\mathrm{Mn}^{2+}/\mathrm{Mn}} = -1.18\,\mathrm{V}$ is highly negative. The stability of the $3d^5$ ion is the characteristic reason for this anomaly.

Step 2: (ii) Explain the irregular pattern Across the series, atomisation enthalpy, the sum of the first and second ionisation enthalpies, and hydration enthalpy do not vary uniformly. Differences in the electronic configurations of the metals and their divalent ions also affect these quantities. Since the electrode potential depends on their combined thermodynamic effect, the tabulated values show an irregular pattern rather than a smooth change with atomic number.

Step 3: (iii) Explain the positive copper value For copper, the energy needed for atomisation and removal of two electrons is high. In particular, the second ionisation breaks the stable $3d^{10}$ configuration of Cu^{+}. The hydration enthalpy of Cu^{2+} does not compensate for these energy requirements. Oxidation of copper to the aqueous divalent ion is therefore unfavourable relative to hydrogen, and the reverse reduction has an exceptionally positive value, $E^{\circ}_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = +0.34\,\mathrm{V}$.

Quick Tip to Solve: Read every value as a reduction potential: stable aqueous ions favour metal oxidation, while costly ion formation favours reduction back to the metal.

Step 4: Conclusion (i) The stable half-filled $3d^5$ configuration of Mn^{2+} accounts for the highly negative manganese value. (ii) Nonuniform atomisation, ionisation and hydration energetics produce the irregular trend. (iii) Copper's high atomisation and ionisation requirements are not offset by hydration, giving its positive reduction potential.

Quick Tip to Solve: Read every value as a reduction potential: stable aqueous ions favour metal oxidation, while costly ion formation favours reduction back to the metal.

10(a). Write the equation involved in the following reactions :

(i) Rosenmund reduction

(ii) Etard reaction

(iii) Stephen reaction [3 marks]

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over a poisoned palladium catalyst supported on barium sulphate.
- The Etard reaction oxidises the benzylic methyl group of toluene to an aldehyde with chromyl chloride, followed by hydrolysis.
- Stephen reduction converts a nitrile into an iminium salt using $SnCl_2/HCl$; hydrolysis of that intermediate gives an aldehyde.

Step 1: (i) Rosenmund reduction A representative equation is the conversion of benzoyl chloride into benzaldehyde:

$$C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl.$$

The supported palladium is poisoned to lower its activity and stop the reduction at the aldehyde stage. In general, the same transformation is $RCOCl + H_2 \rightarrow RCHO + HCl$; the carbon skeleton is retained.

Step 2: (ii) Etard reaction Toluene is treated with chromyl chloride in a nonaqueous solvent such as carbon disulphide, and the resulting Etard complex is hydrolysed:

$$C_6H_5CH_3 \xrightarrow[CS_2]{CrO_2Cl_2} \text{Etard complex} \xrightarrow{H_2O} C_6H_5CHO.$$

Thus the side-chain methyl group becomes $-CHO$, while the benzene ring remains intact. The displayed sequence states the reagent-controlled transformation and work-up, rather than treating water as the oxidising reagent.

Step 3: (iii) Stephen reaction A nitrile first undergoes partial reduction to an iminium chloride and then hydrolysis:

$$RCN + 2[H] + HCl \xrightarrow{SnCl_2} RCH{=}NH \cdot HCl.$$

$$RCH{=}NH \cdot HCl + H_2O \longrightarrow RCHO + NH_4Cl.$$

Here $[H]$ denotes reducing hydrogen equivalents supplied by the $SnCl_2/HCl$ system. The nitrile carbon becomes the aldehyde carbon; hydrolysis releases the nitrogen as ammonium chloride.

Quick Tip to Solve: Match the starting group to the reagent: acyl chloride uses poisoned Pd, benzylic methyl uses chromyl chloride, and nitrile uses SnCl2/HCl followed by hydrolysis.

Step 4: Conclusion The required transformations are acyl chloride → aldehyde by Rosenmund reduction, toluene → benzaldehyde by the Etard reaction, and nitrile → iminium salt → aldehyde by the Stephen reaction, with the reagents shown above.

Quick Tip to Solve: Match the starting group to the reagent: acyl chloride uses poisoned Pd, benzylic methyl uses chromyl chloride, and nitrile uses SnCl2/HCl followed by hydrolysis.

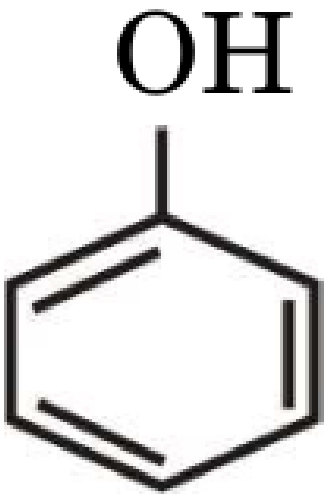
OR

10(b). (i) Which acid of each pair would you expect to be stronger? Give reason.

(I) CH_3COOH or F–CH_2–COOH

(II) Phenol (structure shown below) or CH_3COOH

(ii) Distinguish between Pentan-2-one and Pentan-3-one. [3 marks]



Solution:

Concept:

- An acid is stronger when its conjugate base is better stabilised. Electron-withdrawing groups stabilise a carboxylate ion through the negative inductive effect.
- The iodoform test detects a methyl ketone group, CH_3CO^-, using iodine and aqueous alkali. A positive test gives yellow CHI_3.

Step 1: Compare fluoroacetic acid and acetic acid Fluoroacetic acid, FCH_2COOH, is stronger than acetic acid, CH_3COOH. Fluorine is highly electronegative and withdraws electron density through sigma bonds (the $-I$ effect). It stabilises the negative charge of the conjugate base FCH_2COO^-, making loss of H^+ easier. By contrast, the methyl group in acetic acid has a $+I$ effect and tends to destabilise the carboxylate anion.

Step 2: Compare phenol and acetic acid Acetic acid is stronger than phenol, C_6H_5OH. In acetate, the negative charge is delocalised equally over two oxygen atoms through two equivalent resonance

Quick Tip to Solve: For acid comparisons, inspect conjugate-base stabilisation. For these ketones, look directly for a methyl group bonded to the carbonyl carbon before applying the iodoform test.

structures. In phenoxide, although resonance occurs, some contributing structures place negative charge on less electronegative carbon atoms of the ring; these are less stabilising and are not equivalent to the oxygen-bearing structure. Thus acetate is more stabilised than phenoxide, so acetic acid releases a proton more readily.

Step 3: Apply the iodoform test to the two ketones Warm separate samples with iodine and aqueous sodium hydroxide. Pentan-2-one, $CH_3COCH_2CH_2CH_3$, contains the methyl ketone group and produces a yellow precipitate of iodoform. Its balanced reaction is

$$CH_3COCH_2CH_2CH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3\downarrow + CH_3CH_2CH_2COONa + 3\,NaI + 3\,H_2O.$$

Pentan-3-one, $CH_3CH_2COCH_2CH_3$, has ethyl groups on both sides of the carbonyl and no CH_3CO^- group. It therefore gives no yellow iodoform precipitate under the same conditions.

Step 4: Conclusion The stronger acids are FCH_2COOH in pair (I) and CH_3COOH in pair (II). Pentan-2-one gives a yellow iodoform precipitate; pentan-3-one does not.

Quick Tip to Solve: For acid comparisons, inspect conjugate-base stabilisation. For these ketones, look directly for a methyl group bonded to the carbonyl carbon before applying the iodoform test.

11. 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 their atoms or in at least one of their oxidation states. A d-block position alone does not make an element a transition element.
- Variable oxidation states aid catalytic redox cycles; surface adsorption can bring reactants together and lower the activation barrier.
- Lanthanoid contraction is the gradual decrease in size across the lanthanoid series because 4f electrons shield the increasing nuclear charge poorly.

Step 1: Explain catalytic activity Transition metals and their compounds commonly exhibit variable oxidation states. They can form intermediate compounds with reactants and then regenerate their original state, providing a reaction pathway with lower activation energy. Their available d orbitals also facilitate interactions with reactants. On a solid metal surface, adsorption brings reactant molecules close together and weakens their bonds, making reaction easier. For example, iron catalyses ammonia synthesis, while vanadium(V) oxide catalyses oxidation of sulphur dioxide in the Contact process. The catalyst is regenerated rather than consumed overall.

Step 2: Apply the definition to zinc, cadmium and mercury The relevant outer configurations are $Zn : 3d^{10}4s^2$, $Cd : 4d^{10}5s^2$ and $Hg : 5d^{10}6s^2$. Their common divalent ions lose the two outer s electrons

Quick Tip to Solve: Check d occupancy in both the atom and its usual ions. When comparing a 4d element with its 5d counterpart, check whether lanthanoid contraction offsets the extra shell.

and retain $3d^{10}$, $4d^{10}$ and $5d^{10}$, respectively. Thus the d subshell remains completely filled in these atoms and their usual ions. They do not satisfy the requirement of a partially filled d subshell, so they are classified as non-transition elements despite lying in the d block.

Step 3: Explain the nearly equal radii of zirconium and hafnium Hafnium lies below zirconium and would ordinarily be expected to be larger because it has an additional electron shell. However, the lanthanoid series occurs before hafnium. Across that series, added 4f electrons shield the increasing nuclear charge poorly, so the effective nuclear attraction increases and atomic size contracts. This lanthanoid contraction largely compensates for the expected increase in size on moving from zirconium to hafnium, leaving their atomic radii almost identical.

Step 4: Conclusion Catalytic activity follows from variable oxidation states and reactant interactions; Zn, Cd and Hg have filled d subshells; lanthanoid contraction accounts for the almost equal radii of Zr and Hf.

Quick Tip to Solve: Check d occupancy in both the atom and its usual ions. When comparing a 4d element with its 5d counterpart, check whether lanthanoid contraction offsets the extra shell.

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 use a Lewis acid catalyst, commonly anhydrous $AlCl_3$, to generate an electrophile.
- The nitrogen lone pair of aniline can coordinate to a Lewis acid, reducing electron donation from the amino group into the benzene ring.

Step 1: Identify the interaction with the catalyst In aniline, $C_6H_5NH_2$, nitrogen has an unshared electron pair. Anhydrous $AlCl_3$ accepts this pair and forms a Lewis acid–base complex (often described in the textbook as salt formation). Thus the amino group reacts with the catalyst required for the Friedel–Crafts reaction.

Step 2: Explain the effect on the aromatic ring Coordination ties up the nitrogen lone pair and gives

Quick Tip to Solve: Before predicting Friedel–Crafts substitution on an amine, check whether the nitrogen lone pair binds the Lewis acid catalyst.

nitrogen positive character. The amino group can no longer activate the ring by donating its lone pair in the usual way; the complex strongly deactivates the ring towards electrophilic substitution. Hence the expected Friedel–Crafts alkylation or acylation does not occur. It is the interaction with the Lewis acid catalyst, rather than absence of an aromatic ring, that prevents the reaction.

Step 3: Conclusion Aniline does not give the Friedel–Crafts reaction because its amino group forms a complex or salt with $AlCl_3$, strongly deactivating the benzene ring towards electrophilic substitution.

Quick Tip to Solve: Before predicting Friedel–Crafts substitution on an amine, check whether the nitrogen lone pair binds the Lewis acid catalyst.

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:

- Basic strength measures the availability of the nitrogen lone pair for accepting a proton. In aqueous solution, inductive effects and hydration both influence this availability.
- $pK_b = -\log_{10} K_b$; therefore, a stronger base has a larger K_b and a smaller pK_b.

Step 1: Compare the basic strengths The electron-releasing ethyl group increases the basicity of $C_2H_5NH_2$ relative to ammonia. In water, ethylamine is also more basic than trimethylamine because its conjugate acid is better hydrated. Trimethylamine remains more basic than NH_3. Aniline is the weakest because the nitrogen lone pair is delocalised into the benzene ring by resonance.

Step 2: Reverse the order for pKb Thus, aqueous basic strength decreases as ethylamine, trimethylamine, ammonia, aniline. Since pK_b varies inversely with basic strength, this same sequence gives the increasing pK_b order.

Step 3: Conclusion The required increasing order is

$$C_2H_5NH_2 < (CH_3)_3N < NH_3 < C_6H_5NH_2 \quad \text{(increasing } pK_b\text{)}.$$

Quick Tip to Solve: First rank aqueous basic strength using hydration and resonance, then reverse it for increasing pK_b.

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

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$, used with aqueous alkali to distinguish primary and secondary amines.
- A sulphonamide containing an acidic N–H hydrogen dissolves in alkali by salt formation; a sulphonamide without N–H does not.

Quick Tip to Solve: Count N–H bonds in the sulphonamide product: one remaining N–H allows alkali solubility, while none means insolubility.

Step 1: Test ethylamine Shake each sample with Hinsberg reagent and aqueous $NaOH$. Primary ethylamine forms N-ethylbenzenesulphonamide:

$$C_2H_5NH_2 + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2NHC_2H_5 + HCl.$$

This product retains one N–H hydrogen and dissolves in excess alkali as its salt. Acidifying the alkaline solution precipitates the sulphonamide again.

Step 2: Test diethylamine Secondary diethylamine forms N,N-diethylbenzenesulphonamide:

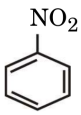
$$(C_2H_5)_2NH + C_6H_5SO_2Cl \longrightarrow C_6H_5SO_2N(C_2H_5)_2 + HCl.$$

This product has no N–H hydrogen and cannot form the corresponding salt, so it remains insoluble in alkali. The alkali also neutralises the acid produced in each reaction.

Step 3: Conclusion Ethylamine gives a sulphonamide soluble in alkali and precipitated by acidification; diethylamine gives a sulphonamide insoluble in alkali.

Quick Tip to Solve: Count N–H bonds in the sulphonamide product: one remaining N–H allows alkali solubility, while none means insolubility.

12(iv)(a). Write the structures of A and B in the following reactions: [2 marks]

(I)  $\xrightarrow{Sn + HCl}$ 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

Solution:

Concept:

- Tin and hydrochloric acid reduce the nitro group of nitrobenzene to the amino group. The amine so obtained activates its ring and directs substitution to the ortho and para positions.
- Bromine water reacts with aniline to substitute all three available ortho/para positions, giving 2,4,6-tribromoaniline.
- Hofmann bromamide degradation converts $RCONH_2$ to RNH_2, with loss of the carbonyl carbon. Acetyl chloride then acylates a primary amine to a secondary amide.

Step 1: (I) Reduce the nitro group, then brominate the ring Reduction of nitrobenzene with Sn/HCl converts $-NO_2$ into $-NH_2$. Thus A is aniline, $C_6H_5NH_2$, represented as the free amine after isolation.

$$C_6H_5NO_2 + 6\,[H] \longrightarrow C_6H_5NH_2 + 2\,H_2O$$

The unprotected amino group strongly activates positions 2, 4 and 6, so bromine water gives:

$$C_6H_5NH_2 + 3\,Br_2 \longrightarrow 2,4,6\text{–}Br_3\text{–}C_6H_2\text{–}NH_2 + 3\,HBr.$$

Quick Tip to Solve: In sequence (II), remove the carbonyl carbon before counting the amine chain. In sequence (I), unprotected aniline with bromine water gives three bromine substituents, at positions 2, 4 and 6.

B is therefore 2,4,6-tribromoaniline, which appears as a white precipitate.

Step 2: (II) Shorten the amide chain, then acetylate nitrogen Propanamide undergoes Hofmann bromamide degradation with Br_2/KOH. Loss of the carbonyl carbon gives A, ethylamine, $CH_3CH_2NH_2$.

$$CH_3CH_2CONH_2 + Br_2 + 4\,KOH \longrightarrow$$

$$CH_3CH_2NH_2 + 2\,KBr + K_2CO_3 + 2\,H_2O.$$

Acetyl chloride acylates nitrogen; pyridine absorbs the hydrogen chloride formed.

$$CH_3CH_2NH_2 + CH_3COCl \xrightarrow{\text{pyridine}} CH_3CONHCH_2CH_3 + HCl.$$

B is N-ethylethanamide (N-ethylacetamide), retaining the ethyl group and one N–H bond.

Step 3: Conclusion (I) $A = C_6H_5NH_2$; $B = 2,4,6\text{–}Br_3\text{–}C_6H_2\text{–}NH_2$, with $-NH_2$ at ring position 1. (II) $A = CH_3CH_2NH_2$; $B = CH_3\text{–}C(=O)\text{–}NH\text{–}CH_2\text{–}CH_3$.

Quick Tip to Solve: In sequence (II), remove the carbonyl carbon before counting the amine chain. In sequence (I), unprotected aniline with bromine water gives three bromine substituents, at positions 2, 4 and 6.

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 into a primary amine with one fewer carbon atom, using Br_2 and aqueous NaOH.
- Protecting the amino group of aniline by acetylation moderates its ring activation, permitting controlled bromination mainly at the para position. Hydrolysis then restores the amino group.

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

$$C_6H_5COOH + NH_3 \longrightarrow C_6H_5COONH_4$$

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

Step 2: Degrade benzamide to aniline Heat benzamide with bromine and aqueous sodium hydroxide:

$$C_6H_5CONH_2 + Br_2 + 4\,NaOH \longrightarrow C_6H_5NH_2 + 2\,NaBr + Na_2CO_3 + 2\,H_2O.$$

The carbonyl carbon is lost in this reaction, so the product is aniline rather than benzylamine.

Quick Tip to Solve: Use Hofmann degradation to remove the carboxyl carbon; protect aniline as acetanilide before bromination to avoid the tribromo product.

Step 3: Protect aniline and brominate Acetylate aniline with acetic anhydride to form acetanilide:

$$C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH.$$

Bromination with Br_2 in glacial acetic acid gives predominantly p-bromoacetanilide. The protected amino group directs substitution to ortho and para positions, with the less hindered para product predominant:

$$C_6H_5NHCOCH_3 + Br_2 \xrightarrow{CH_3COOH} \text{p-}BrC_6H_4NHCOCH_3 + HBr.$$

Step 4: Remove the protecting group Hydrolyse p-bromoacetanilide by heating with dilute acid, then neutralise to obtain the free amine. The net hydrolysis is

$$\text{p-}BrC_6H_4NHCOCH_3 + H_2O \longrightarrow \text{p-}BrC_6H_4NH_2 + CH_3COOH.$$

Direct bromination of unprotected aniline with bromine water would instead yield 2,4,6-tribromoaniline.

Step 5: Conclusion (I) Benzoic acid is converted to benzamide and then to aniline by Hofmann degradation. (II) Aniline is acetylated, brominated to p-bromoacetanilide, and hydrolysed to p-bromoaniline.

Quick Tip to Solve: Use Hofmann degradation to remove the carboxyl carbon; protect aniline as acetanilide before bromination to avoid the tribromo product.