CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-4-2

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)

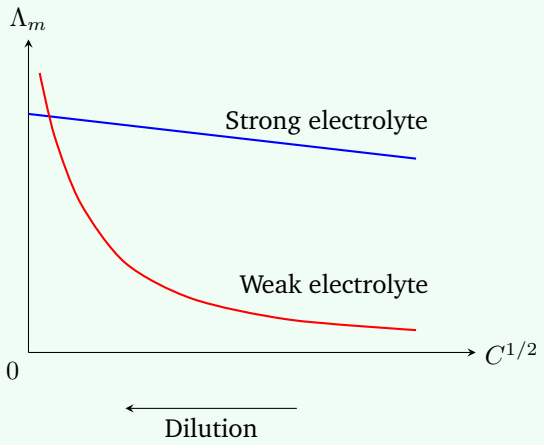
1. In a plot of Λ_m against the square root of concentration $(C^{1/2})$ for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically. Suggest a way to obtain this value. Also state the related law, if any. [2 marks]

Solution:

Concept:

- Limiting molar conductivity, Λ_m°, is the molar conductivity at infinite dilution, where interactions between ions become negligible.
- Kohlrausch's law of independent migration of ions states that, at infinite dilution, each ion contributes independently to the molar conductivity of an electrolyte, irrespective of the nature of the other ion present.

Step 1: Explain why direct extrapolation fails For a strong electrolyte, the low-concentration plot of Λ_m against $C^{1/2}$ is approximately linear, so its intercept gives Λ_m°. A weak electrolyte becomes increasingly ionised on dilution, making its plot strongly curved. Its measured values cannot be extrapolated reliably as a straight line.



Schematic conductivity trends on dilution; no numerical scale is implied.

Step 2: Combine the limiting values of strong electrolytes For ethanoic acid, combine the limiting molar conductivities of three strong electrolytes at the same temperature:

$$\Lambda_m^\circ(\mathrm{CH_3COOH}) = \Lambda_m^\circ(\mathrm{HCl}) + \Lambda_m^\circ(\mathrm{CH_3COONa}) - \Lambda_m^\circ(\mathrm{NaCl}).$$

On adding and subtracting their ionic contributions, those of $\mathrm{Na^+}$ and $\mathrm{Cl^-}$ cancel. Only $\lambda^\circ(\mathrm{H^+}) + \lambda^\circ(\mathrm{CH_3COO^-})$ remains, where λ° denotes the limiting ionic molar conductivity.

Step 3: Conclusion Obtain the weak electrolyte's limiting molar conductivity indirectly using Kohlrausch's law and known limiting values of suitable strong electrolytes. In general, $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$, where ν_+ and ν_- are the numbers of cations and anions per formula unit.

Quick Tip to Solve: Choose strong electrolytes whose ionic sums leave only the weak electrolyte's ions: acid plus its sodium salt minus sodium chloride works for ethanoic acid.

2. Write reasons for the following statements:

(i) Benzoic acid does not undergo Friedel-Crafts reaction.

(ii) Oxidation of aldehydes is easier than that of ketones. [2 marks]

Solution:

Concept:

- Friedel–Crafts alkylation and acylation are electrophilic aromatic substitution reactions, favoured by an electron-rich benzene ring and catalysed by a Lewis acid such as anhydrous $AlCl_3$.
- Aldehydes contain a hydrogen attached directly to the carbonyl carbon. Ketones contain two carbon groups attached to that carbon, so their oxidation generally requires cleavage of a carbon–carbon bond.

Step 1: Explain the unreactivity of benzoic acid In benzoic acid, C_6H_5COOH, the $-COOH$ group withdraws electron density from the benzene ring through both its inductive and resonance effects. The ring is strongly deactivated towards attack by the electrophile used in a Friedel–Crafts reaction. In addition, the carboxyl group coordinates with the Lewis acid catalyst, $AlCl_3$, further hindering the normal catalytic reaction. Consequently, benzoic acid does not undergo the usual Friedel–Crafts alkylation or acylation.

Step 2: Compare oxidation of aldehydes and ketones An aldehyde can be oxidised to a carboxylic acid while retaining its carbon skeleton, because the hydrogen bonded to its carbonyl carbon can be replaced by a hydroxyl group:

$$RCHO + [O] \longrightarrow RCOOH.$$

Thus mild oxidising agents, such as Tollens' reagent, readily oxidise aldehydes. A ketone, $R^1{-}CO{-}R^2$, has no hydrogen on the carbonyl carbon. Its oxidation generally requires breaking a stronger carbon–carbon bond and therefore needs a powerful oxidising agent and vigorous conditions. A hydrogen on an adjacent carbon is not equivalent to the aldehydic hydrogen.

Step 3: Conclusion (i) Benzoic acid resists Friedel–Crafts reaction because its carboxyl group deactivates the ring and interacts with the Lewis acid catalyst. (ii) Aldehydes oxidise more easily because their conversion to acids does not require the carbon–carbon bond cleavage generally needed for ketones.

Quick Tip to Solve: For oxidation, inspect the carbonyl carbon itself: an attached hydrogen identifies the aldehyde's easy oxidation route; hydrogens on neighbouring carbons do not.

3. Give reasons for the following statements: (Any two)

(i) Benzaldehyde is less reactive than propanal in nucleophilic addition reactions.

(ii) Carboxylic acids do not give reactions of carbonyl group.

(iii) 4-nitrobenzoic acid is a stronger acid than benzoic acid. [2 marks]

Solution:

Concept:

- Nucleophilic addition is favoured by a more electrophilic carbonyl carbon and easier access to that carbon.
- Resonance can decrease the positive character of a carbonyl carbon; electron-withdrawing groups increase carboxylic acid strength by stabilising the conjugate base.

Step 1: (i) Compare benzaldehyde with propanal In benzaldehyde, the carbonyl group is conjugated with the benzene ring. Resonance delocalises the carbonyl group with the ring and reduces the positive character on the carbonyl carbon. Hence a nucleophile attacks it less readily than the carbonyl carbon of propanal, which has no such conjugation. The larger phenyl group also offers greater steric hindrance than the ethyl group of propanal.

Step 2: (ii) Examine the carboxyl group In $-\mathrm{COOH}$, a lone pair on the hydroxyl oxygen is delocalised towards the carbonyl group. This resonance reduces the electrophilicity of the carbonyl carbon. Thus carboxylic acids do not undergo the characteristic nucleophilic addition reactions of aldehydes and ketones. Their reactions generally involve the carboxyl group as a whole, such as acid-base reactions and substitution at the acyl carbon.

Step 3: (iii) Compare the stability of the conjugate bases The para nitro group withdraws electron density by both its inductive and resonance effects. It stabilises the negatively charged carboxylate conjugate base of 4-nitrobenzoic acid relative to benzoate. Loss of H^+ is therefore more favourable, making 4-nitrobenzoic acid the stronger acid.

Step 4: Conclusion Benzaldehyde is less reactive because of conjugation and greater steric hindrance; carboxylic acids lack typical carbonyl addition reactions because of resonance within $-\mathrm{COOH}$; and the electron-withdrawing $-\mathrm{NO}_2$ group increases the acidity of 4-nitrobenzoic acid. Any two of these explanations answer the question.

Quick Tip to Solve: For carbonyl addition, check positive character at carbon; for acidity, compare the stability of the carboxylate formed after loss of H^+.

Section B (24 marks)

4(a). (i) Silver atom has completely filled d-orbitals in its ground state, it is still considered to be a transition element. Justify the statement.

(ii) Why are $E^{\circ}_{M^{2+}/M}$ values of Mn and Zn more negative than expected?

(iii) Why do transition metals form alloys? [3 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its oxidation states.
- The standard reduction potential $E^{\circ}_{M^{2+}/M}$ refers to $M^{2+}(aq) + 2\,e^- \longrightarrow M(s)$. Greater stability of the divalent ion can make its reduction less favourable.
- Atoms with similar sizes can replace one another in a metallic crystal lattice to form substitutional alloys.

Step 1: (i) Apply the definition to silver Ground-state silver has the electronic configuration $Ag : [Kr]\,4d^{10}5s^1$, so its d subshell is full. However, silver can exhibit the $+2$ oxidation state, for example in AgF_2. The corresponding configuration is $Ag^{2+} : [Kr]\,4d^9$, which has an incompletely filled d subshell. It therefore satisfies the definition of a transition element even though the neutral atom has a filled d subshell.

Step 2: (ii) Explain the unusually negative reduction potentials The divalent ions have the configurations

$$Mn^{2+} : [Ar]\,3d^5, \qquad Zn^{2+} : [Ar]\,3d^{10}.$$

The half-filled $3d^5$ subshell of Mn^{2+} and the completely filled $3d^{10}$ subshell of Zn^{2+} provide extra stability. Consequently, formation of these ions from the respective metals is favoured relative to the general trend, while their reduction back to metals is less favourable. Their $E^{\circ}_{M^{2+}/M}$ values are therefore more negative than expected from a smooth trend across the series.

Step 3: (iii) Explain alloy formation Transition metals have similar atomic radii and often similar crystal structures. Thus an atom of one transition metal can replace an atom of another in the metallic lattice without causing a large distortion. The resulting mixture retains metallic bonding and forms an alloy, as in nickel-copper alloys.

Step 4: Conclusion Silver is a transition element because Ag^{2+} is $4d^9$. The unusually stable $3d^5$ and $3d^{10}$ divalent ions explain the more negative reduction potentials of Mn and Zn. Similar atomic sizes and lattice structures favour alloy formation by transition metals.

Quick Tip to Solve: Check an element's ions as well as its neutral atom; for Mn and Zn, write the divalent-ion configurations before explaining the reduction potentials.

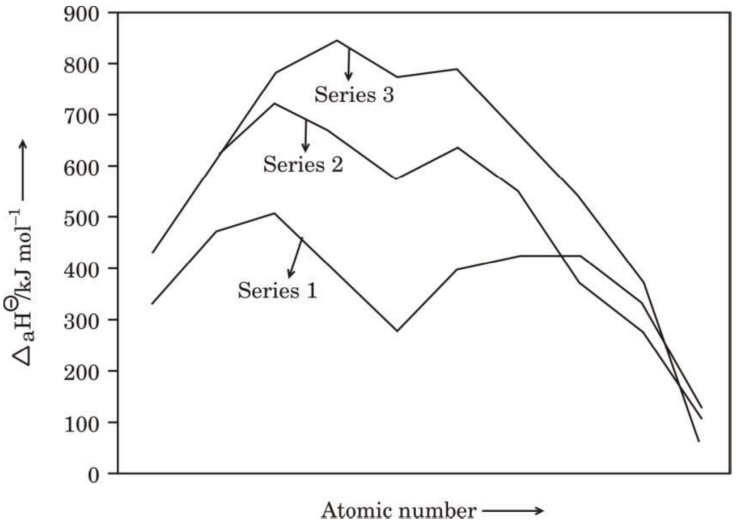
OR

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

(i) Which element in 3d series has lowest enthalpy of atomisation?

(ii) Why do metals of the second and third series have greater enthalpies of atomisation?

(iii) Why are enthalpies of atomisation of transition metals quite high? [3 marks]



Solution:

Concept:

- Enthalpy of atomisation is the energy required to form one mole of separate gaseous atoms from the element in its standard state: $\mathrm{M(s)} \rightarrow \mathrm{M(g)}$. A larger value indicates stronger metallic bonding.
- In transition metals, both the outer s electrons and the available d electrons contribute to metallic bonding. The number of unpaired electrons and the extent of orbital overlap affect its strength.

Step 1: (i) Identify the lowest point of the first series Series 1 represents the $3d$ series. Its lowest point is the final element, zinc, Zn. Zinc has the configuration $[\mathrm{Ar}]3d^{10}4s^2$; its filled $3d$ subshell supplies no unpaired d electrons for strong metal–metal bonding. Its metallic bonds are consequently relatively weak, so less energy is needed to separate its atoms than for the other elements of this series.

Step 2: (ii) Compare the second and third series The $4d$ and $5d$ orbitals are more spatially extended than $3d$ orbitals. This permits more effective overlap between neighbouring metal atoms and stronger metal–metal bonding. Therefore, metals of the second and third transition series generally require more energy for atomisation, as their higher curves in the figure show.

Step 3: (iii) Explain the high values for transition metals Transition-metal atoms generally have several unpaired d electrons in addition to their outer s electrons. The participation of these electrons in bonding gives strong interatomic attraction in the metal crystal. Atomisation breaks these metallic interactions completely, so considerable energy must be supplied. Thus the high enthalpies reflect strong metallic bonding, with zinc illustrating the low-value filled-subshell case.

Step 4: Conclusion (i) Zinc has the lowest enthalpy of atomisation in the $3d$ series. (ii) More effective $4d/5d$ orbital overlap strengthens bonding in the second and third series. (iii) Participation of available d and s electrons produces strong metallic bonds in transition metals.

Quick Tip to Solve: Follow the entire Series 1 curve: the manganese dip is not its minimum; the zinc endpoint is lower.

5(a). (i) Write the electronic configuration of d^4 on the basis of crystal field splitting theory, if $\Delta_o < P$.
(ii) $[Ni(CN)_4]^{2-}$ with square-planar structure is diamagnetic and $[NiCl_4]^{2-}$ with tetrahedral geometry is paramagnetic. Give reason to support the statement. [Atomic number: Ni = 28]
(iii) Write the number of ions produced in the solution from the following complex: $[PtCl_2(NH_3)_4]Cl_2$

[3 marks]

Solution:

Concept:

- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. When the splitting energy Δ_o is smaller than the electron-pairing energy P, electrons occupy higher orbitals before pairing.
- A complex with all electrons paired is diamagnetic; unpaired electrons make it paramagnetic. Only counter-ions outside the coordination sphere dissociate as separate ions in solution.

Step 1: (i) Distribute the four electrons Since $\Delta_o < P$, placing the fourth electron in an e_g orbital costs less energy than pairing it in a t_{2g} orbital. The first three electrons singly occupy the three t_{2g} orbitals and the fourth singly occupies one e_g orbital. Thus the high-spin configuration is $t_{2g}^3 e_g^1$, with four unpaired electrons.

Step 2: (ii) Compare the two nickel complexes In both complexes, each ligand has charge -1, so nickel is in the $+2$ oxidation state. Since $\mathrm{Ni} = [\mathrm{Ar}]3d^8 4s^2$, the metal ion is $\mathrm{Ni}^{2+} = [\mathrm{Ar}]3d^8$. Cyanide is a strong-field ligand. It causes pairing of the $3d$ electrons, leaving one $3d$ orbital available for dsp^2 hybridisation. The square-planar $[\mathrm{Ni(CN)_4}]^{2-}$ has all eight d electrons paired and is diamagnetic. Chloride is a weak-field ligand and does not cause this pairing. The tetrahedral $[\mathrm{NiCl_4}]^{2-}$ uses sp^3 hybridisation and retains two unpaired $3d$ electrons, making it paramagnetic.

Step 3: (iii) Count the ions released on dissolution The two chloride ions outside the square brackets are counter-ions; the two chlorido ligands inside remain bound to platinum. Hence the dissociation is

$$[\mathrm{PtCl_2(NH_3)_4}]\mathrm{Cl_2} \longrightarrow [\mathrm{PtCl_2(NH_3)_4}]^{2+} + 2\mathrm{Cl}^-.$$

One formula unit therefore produces one complex cation and two chloride anions, giving three ions in all.

Step 4: Conclusion (i) $t_{2g}^3 e_g^1$ (high spin). (ii) The cyanide complex has no unpaired electrons and is diamagnetic, whereas the chloride complex has two unpaired electrons and is paramagnetic. (iii) Three ions are produced per formula unit.

Quick Tip to Solve: For the platinum salt, count the bracketed complex as one ion and count only the two outside chlorides separately.

OR

5(b). (i) Calculate the spin only magnetic moment of the complex $[FeF_6]^{3-}$. (Atomic number of Fe = 26)

(ii) Write the IUPAC name of the given complex: $[Co(NH_3)_5Cl]Cl_2$

(iii) Why is the complex $[Co(en)_3]^{3+}$ more stable than $[CoF_6]^{3-}$? [3 marks]

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}$ BM, where n is the number of unpaired electrons and BM denotes Bohr magneton.
- In coordination nomenclature, ligands are named alphabetically before the metal; the metal oxidation state is written as a Roman numeral.
- A bidentate ligand binds through two donor atoms and forms a chelate ring. Such ring formation increases complex stability through the chelate effect.

Step 1: (i) Determine the iron oxidation state and unpaired electrons Let the oxidation state of iron in $[FeF_6]^{3-}$ be x. Each fluorido ligand has charge -1, so

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

Iron has atomic number 26 and configuration $[Ar]\,3d^6 4s^2$. Removing two $4s$ electrons and one $3d$ electron gives Fe^{3+} the configuration $[Ar]\,3d^5$. Fluoride is a weak-field ligand, so the octahedral complex is high spin with configuration $t_{2g}^3 e_g^2$. Thus all five d electrons are unpaired.

$$\mu = \sqrt{5(5+2)} = \sqrt{35} \approx 5.92\,\text{BM}.$$

Step 2: (ii) Name the cobalt complex In $[Co(NH_3)_5Cl]Cl_2$, the two chloride counterions show that the coordination entity has charge $+2$. Ammonia is neutral and the coordinated chloride has charge -1, giving $x - 1 = +2$, hence cobalt is in oxidation state $+3$. The five ammonia ligands give pentaammine, followed alphabetically by chlorido. The name is **pentaamminechloridocobalt(III) chloride**.

Step 3: (iii) Apply the chelate effect Ethane-1,2-diamine, abbreviated en, is bidentate: both nitrogen donor atoms coordinate to the same cobalt ion. Three en ligands therefore form three five-membered chelate rings in $[Co(en)_3]^{3+}$. In contrast, the six fluorido ligands in $[CoF_6]^{3-}$ are monodentate and form no chelate rings. The chelate effect provides extra stability to the en complex.

Step 4: Conclusion (i) The spin-only magnetic moment is 5.92 BM. (ii) The name is pentaamminechloridocobalt(III) chloride. (iii) The en complex is more stable because bidentate en forms chelate rings, whereas fluoride does not.

Quick Tip to Solve: Find the metal charge before counting its d electrons or naming it; for stability, check whether a ligand binds at two sites to form a ring.

6(a). Write equations involved in the following reactions:

(i) Ethanamine reacts with acetyl chloride.

(ii) Aniline reacts with bromine water at room temperature.

(iii) Aniline reacts with chloroform and ethanolic potassium hydroxide. [3 marks]

Solution:

Concept:

- Acylation replaces a hydrogen attached to the amine nitrogen by an acyl group, producing an amide from a primary amine and an acid chloride.
- The amino group strongly activates the benzene ring toward electrophilic substitution and directs incoming groups to its ortho and para positions.
- Primary amines undergo the carbylamine reaction with chloroform and alcoholic potassium hydroxide on heating, giving isocyanides.

Step 1: (i) Write the acylation of ethanamine The nitrogen atom of ethanamine attacks the carbonyl carbon of acetyl chloride. Replacement of chloride, with loss of a hydrogen from nitrogen, produces the secondary amide N-ethylethanamide:

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

A base can absorb the hydrogen chloride formed; if excess ethanamine is used, it traps the acid as ethylammonium chloride. The acyl group attaches to nitrogen without changing the ethyl carbon chain.

Step 2: (ii) Write the bromination of aniline Aniline reacts readily with bromine water at room temperature. The strongly activating amino group causes bromination at both ortho positions and the para position, forming a white precipitate of 2,4,6-tribromoaniline:

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

Each bromine molecule replaces one ring hydrogen and produces one molecule of hydrogen bromide, so three equivalents of bromine are required. No Lewis-acid catalyst is needed.

Step 3: (iii) Write the carbylamine reaction of aniline Aniline is a primary aromatic amine. On heating with chloroform and ethanolic potassium hydroxide, it forms phenyl isocyanide, which has an offensive odour:

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{\Delta} C_6H_5NC + 3\,KCl + 3\,H_2O.$$

The potassium hydroxide is used in ethanol. The product contains the isocyanide linkage $-N{\equiv}C$, with the phenyl group bonded to nitrogen; it is not benzonitrile, C_6H_5CN. Three potassium chloride molecules account for the three chlorine atoms of chloroform.

Step 4: Conclusion The products are (i) N-ethylethanamide, $CH_3CONHCH_2CH_3$; (ii) 2,4,6-tribromoaniline, a white precipitate; and (iii) phenyl isocyanide, C_6H_5NC. The balanced equations are given above.

Quick Tip to Solve: Track the reaction site: acetyl chloride reacts at nitrogen, bromine water substitutes the ring at 2,4,6, and chloroform with alcoholic KOH gives an isocyanide, not a nitrile.

OR

6(b). (i) Write the IUPAC name for the following organic compound: $(CH_3CH_2)_2NCH_3$

(ii) Write the equations for the following:

(I) Gabriel phthalimide synthesis

(II) Hoffmann bromamide degradation [3 marks]

Solution:

Concept:

- Name an amine using the longest carbon chain attached to nitrogen as the parent alkanamine; indicate the other groups on nitrogen by the locant N.
- Gabriel phthalimide synthesis gives a primary aliphatic amine by alkylation of potassium phthalimide followed by hydrolysis. Here R is an alkyl group and X is a halogen.
- Hoffmann bromamide degradation converts a primary amide, $\mathrm{RCONH_2}$, into $\mathrm{RNH_2}$ using bromine and aqueous alkali; the product has one carbon atom fewer than the amide.

Step 1: (i) Select the parent chain and nitrogen substituents In $(CH_3CH_2)_2NCH_3$, nitrogen is bonded to two ethyl groups and one methyl group, so this is a tertiary amine. Choose one ethyl group for the parent name ethanamine. The remaining ethyl and methyl groups are attached directly to nitrogen and are listed alphabetically, each with an N locant. This gives N-ethyl-N-methylethanamine.

Step 2: (ii)(I) Write the Gabriel synthesis in successive stages Treat phthalimide with ethanolic potassium hydroxide to replace its acidic nitrogen-bound hydrogen by potassium:

$$\mathrm{C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O.}$$

Potassium phthalimide reacts with a suitable alkyl halide by nucleophilic substitution to form an N-alkylphthalimide:

$$\mathrm{C_6H_4(CO)_2NK + RX \longrightarrow C_6H_4(CO)_2NR + KX.}$$

Heating this product with aqueous sodium hydroxide hydrolyses the imide and releases the primary amine:

$$\mathrm{C_6H_4(CO)_2NR + 2\,NaOH \xrightarrow{\Delta} C_6H_4(COONa)_2 + RNH_2.}$$

The other product is disodium phthalate. Only one alkyl group remains on nitrogen, giving a primary amine.

Step 3: (ii)(II) Balance the Hoffmann bromamide equation On warming a primary amide with bromine and aqueous sodium hydroxide, the overall reaction is

$$\mathrm{RCONH_2 + Br_2 + 4\,NaOH \xrightarrow{\Delta} RNH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O.}$$

The carbonyl carbon of the amide appears in carbonate rather than in the amine. For example, ethanamide gives methanamine, with one fewer carbon atom.

Step 4: Conclusion The name is N-ethyl-N-methylethanamine. The equations above show Gabriel synthesis of primary amines and Hoffmann degradation with loss of one carbon atom.

Quick Tip to Solve: In amine naming, put an N before each nitrogen substituent. For Hoffmann degradation, count the carbons: the product amine always has one fewer than the starting amide.

7(a). Write reasons for the following:

(i) Ethylamine is soluble in water whereas aniline is insoluble.

(ii) Amino group is o- and p-directing in aromatic electrophilic substitution reactions, but aniline on nitration gives a substantial amount of m-nitroaniline.

(iii) Amines behave as nucleophiles. [3 marks]

Solution:

Concept:

- Water solubility depends on the balance between hydrogen bonding of the polar amino group with water and the water-repelling effect of the hydrocarbon group.
- The amino group of aniline donates its nitrogen lone pair to the benzene ring by resonance, but protonation converts it into the electron-withdrawing anilinium group.
- A nucleophile donates an available electron pair to an electron-deficient centre to form a covalent bond; the nitrogen atom of an amine has such a lone pair.

Step 1: (i) Compare hydrogen bonding and hydrocarbon size Ethylamine, $C_2H_5NH_2$, forms hydrogen bonds with water through its nitrogen lone pair and its nitrogen-bound hydrogen atoms. Its ethyl group is small, so favourable amine–water interactions are sufficient to make it soluble. Aniline, $C_6H_5NH_2$, also forms hydrogen bonds, but its much larger non-polar phenyl group has a strong hydrophobic effect. Consequently its interaction with water cannot compensate adequately for the large hydrophobic portion, and it is only sparingly soluble, described as insoluble in the question. The difference is not an absence of hydrogen bonding in aniline.

Step 2: (ii) Identify the species present during nitration In neutral aniline, the $-NH_2$ group increases electron density mainly at the ortho and para positions by resonance, so it directs electrophilic substitution to those positions. However, the strongly acidic nitrating mixture protonates a considerable proportion of aniline:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3{}^+.$$

The anilinium ion has no nitrogen lone pair available for donation to the ring. Its $-NH_3{}^+$ group withdraws electron density and is meta-directing: the intermediates for ortho and para attack are particularly destabilised by the positively charged substituent. Nitration of the protonated species therefore gives the meta product, explaining the substantial amount of m-nitroaniline along with the products from unprotonated aniline.

Step 3: (iii) Explain electron-pair donation by nitrogen The nitrogen atom in an amine has an unshared pair of electrons that it can donate to an electron-deficient centre. For example, during alkylation it attacks the electrophilic carbon atom of an alkyl halide. Donation of the lone pair forms a new carbon–nitrogen bond while the halide ion leaves. Since a nucleophile is an electron-pair donor, this available nitrogen lone pair explains why amines behave as nucleophiles.

Step 4: Conclusion Ethylamine is soluble because hydrogen bonding outweighs the effect of its small alkyl group, whereas aniline has a large hydrophobic phenyl group. Strong acid produces meta-directing anilinium ions during nitration. The available nitrogen lone pair makes amines nucleophiles.

Quick Tip to Solve: For aniline, check the medium before choosing the directing effect: $-NH_2$ directs ortho/para, whereas its protonated form $-NH_3{}^+$ directs meta.

OR

7(b). How will you carry out the following conversions:

(i) Nitrobenzene to Aniline

(ii) Ethanamide to Methanamine

(iii) Ethanenitrile to Ethanamine [3 marks]

Solution:

Concept:

- Reduction converts a nitro group, $-NO_2$, into a primary amino group, $-NH_2$, without changing the carbon skeleton.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into RNH_2, with one carbon atom fewer.
- Reduction of a nitrile converts $-C{\equiv}N$ into $-CH_2NH_2$; the nitrile carbon remains in the amine.

Step 1: (i) Reduce nitrobenzene to aniline Heat nitrobenzene with tin and concentrated hydrochloric acid, then add sodium hydroxide to liberate free aniline from its salt. The net reduction is

$$C_6H_5NO_2 + 6[H] \xrightarrow[\text{then NaOH}]{\text{Sn/HCl}} C_6H_5NH_2 + 2H_2O.$$

Here $[H]$ denotes reducing hydrogen. The benzene ring is retained while the nitro group is reduced.

Step 2: (ii) Convert ethanamide to methanamine Warm ethanamide with bromine and aqueous sodium hydroxide. Hofmann bromamide degradation gives

$$CH_3CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The carbonyl carbon is lost from the organic product, so the two-carbon amide produces the required one-carbon amine.

Step 3: (iii) Reduce ethanenitrile to ethanamine Hydrogenate ethanenitrile in the presence of a nickel catalyst:

$$CH_3C{\equiv}N + 2H_2 \xrightarrow{Ni} CH_3CH_2NH_2.$$

Both carbon atoms are retained. Unlike amide degradation, this reduction changes the nitrogen-containing functional group without shortening the carbon chain.

Step 4: Conclusion Use Sn/HCl, followed by $NaOH$, for aniline; $Br_2/NaOH$ with warming for methanamine; and H_2/Ni for ethanamine.

Quick Tip to Solve: Count carbons first: a one-carbon decrease suggests Hofmann degradation, whereas nitrile reduction preserves every carbon atom.

8. A compound 'A' (C_2H_4O) on oxidation gives 'B' ($C_2H_4O_2$). 'A' undergoes Iodoform reaction to give yellow precipitate and reacts with HCN to form the compound 'C'. 'C' on hydrolysis gives 2-hydroxypropanoic acid. Identify the compounds 'A', 'B' and 'C'. Write down equations for the reactions involved. [3 marks]

Solution:

Concept:

- Aldehydes oxidise to carboxylic acids with the same number of carbon atoms. Ethanal is the aldehyde that gives a positive iodoform test.
- Addition of hydrogen cyanide to a carbonyl group forms a cyanohydrin, introducing one extra carbon atom. Hydrolysis converts its nitrile group into a carboxyl group.

Step 1: Identify A and its oxidation product B The molecular formula C_2H_4O, oxidation to $C_2H_4O_2$, and positive iodoform test together identify A as ethanal, CH_3CHO. Its aldehyde group is oxidised to a carboxyl group, giving B as ethanoic acid:

$$\underbrace{CH_3CHO}_{A} + [O] \xrightarrow{\text{acidified } K_2Cr_2O_7} \underbrace{CH_3COOH}_{B}.$$

Here $[O]$ denotes oxygen supplied by the oxidising agent.

Step 2: Write the iodoform reaction Ethanal reacts with iodine in aqueous sodium hydroxide to form a yellow precipitate of iodoform, CHI_3. The other carbon atom forms sodium methanoate:

$$CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3 \downarrow + HCOONa + 3NaI + 3H_2O.$$

This test supports the identification of A as ethanal.

Step 3: Form C by addition of HCN Hydrogen cyanide adds across the carbonyl group of ethanal. A small amount of potassium cyanide supplies the cyanide ion needed to catalyse the addition:

$$CH_3CHO + HCN \xrightarrow{\text{trace KCN}} \underbrace{CH_3CH(OH)CN}_{C}.$$

Thus C is ethanal cyanohydrin, whose IUPAC name is 2-hydroxypropanenitrile. Its chain contains three carbon atoms because HCN adds one carbon atom.

Step 4: Confirm C by hydrolysis On heating with dilute aqueous acid, the nitrile group becomes a carboxyl group while the hydroxyl group is retained:

$$CH_3CH(OH)CN + 2H_2O + HCl \xrightarrow{\Delta} CH_3CH(OH)COOH + NH_4Cl.$$

The organic product is 2-hydroxypropanoic acid (lactic acid), exactly as stated in the question.

Step 5: Conclusion A = CH_3CHO (ethanal), B = CH_3COOH (ethanoic acid), and C = $CH_3CH(OH)CN$ (2-hydroxypropanenitrile).

Quick Tip to Solve: Work backwards from lactic acid: replace its COOH group by CN to obtain C, then remove the added HCN to recover ethanal.

9. (i) Which ion amongst the following is colourless and why? Ti^{4+}, Cr^{3+}, V^{3+} (Atomic number of Ti = 22, Cr = 24, V = 23)

(ii) Why is Mn^{2+} much more resistant than Fe^{2+} towards oxidation?

(iii) Highest oxidation state of a metal is shown in its oxide or fluoride only. Justify the statement.

[3 marks]

Solution:

Concept:

- The colour of many transition-metal ions arises from absorption of visible light during transitions between split d orbitals. An ion with a d^0 configuration cannot undergo a d–d transition.
- A half-filled $3d^5$ subshell has extra stability. Oxidation removes an electron, so compare the d-electron configurations before and after oxidation.
- Oxygen and fluorine are highly electronegative and form strong bonds with metals, stabilising their high positive oxidation states.

Step 1: (i) Compare the electronic configurations Remove the $4s$ electrons before the $3d$ electrons when forming these ions. Their configurations are

$$\begin{aligned} Ti^{4+} &: [Ar]\, 3d^0, \\ Cr^{3+} &: [Ar]\, 3d^3, \\ V^{3+} &: [Ar]\, 3d^2. \end{aligned}$$

Thus Ti^{4+} has no d electron available for a d–d transition and is colourless. The other two ions have partially filled d subshells and show colour because visible light can promote a d electron between split d-energy levels.

Step 2: (ii) Compare the effect of oxidation on stability The configurations relevant to oxidation to the trivalent state are

$$\begin{aligned} Mn^{2+} : 3d^5 &\longrightarrow Mn^{3+} : 3d^4, \\ Fe^{2+} : 3d^6 &\longrightarrow Fe^{3+} : 3d^5. \end{aligned}$$

Oxidation of Mn^{2+} destroys its stable half-filled d subshell and therefore requires more energy. Oxidation of Fe^{2+} produces the stable half-filled Fe^{3+} configuration. Consequently, Mn^{2+} is much more resistant to oxidation than Fe^{2+}.

Step 3: (iii) Explain the role of oxygen and fluorine Their high electronegativities and small sizes favour strong metal–oxygen and metal–fluorine bonds, which stabilise a metal in a high oxidation state. Oxygen can additionally form multiple bonds with the metal. For example, manganese attains $+7$ in Mn_2O_7, while vanadium attains $+5$ in VF_5. These strong bonding interactions account for the occurrence of the highest oxidation states in oxides or fluorides.

Step 4: Conclusion (i) Ti^{4+} is colourless because it is $3d^0$. (ii) Mn^{2+} resists oxidation because its $3d^5$ configuration is already half-filled, whereas oxidation of Fe^{2+} produces $3d^5$. (iii) Strong bonding to highly electronegative oxygen or fluorine stabilises the highest metal oxidation states.

Quick Tip to Solve: Write the d-electron count first: d^0 explains the colourless ion, while comparing $d^5 \to d^4$ with $d^6 \to d^5$ explains the oxidation trend.

10. Write the Nernst equation and calculate the emf of the following cell at 298 K:

Zn | Zn^{2+} (0.001 M) || H^+ (0.01 M) | H_2 (g) (1 bar) | Pt (s)

Given: $E^\circ_{Zn^{2+}/Zn}$ = -0.76 V, $E^\circ_{H^+/H_2}$ = 0.00 V [log 10 = 1] [3 marks]

Solution:

Concept:

- For a cell reaction transferring n electrons, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF}\ln Q$, where Q is the reaction quotient, R the gas constant and F the Faraday constant.
- At $298\,\text{K}$, using base-10 logarithms, $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n}\log Q$ in volts. Standard cell emf equals the cathode reduction potential minus the anode reduction potential.

Step 1: Write the balanced cell reaction Zinc at the left electrode is oxidised, while hydrogen ions at the right electrode are reduced on platinum:

$$\begin{aligned}\text{Anode:}\quad & \text{Zn}\,(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\,\text{e}^-,\\ \text{Cathode:}\quad & 2\,\text{H}^+(\text{aq}) + 2\,\text{e}^- \longrightarrow \text{H}_2(\text{g}).\end{aligned}$$

Adding the half-reactions gives

$$\text{Zn}\,(\text{s}) + 2\,\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g}).$$

Thus $n = 2$. Platinum is an inert electrode; pure zinc has unit activity.

Step 2: Find the standard emf and reaction quotient Both given electrode potentials are reduction potentials, hence

$$E^\circ_{\text{cell}} = 0.00 - (-0.76) = 0.76\,\text{V}.$$

Using concentration ratios for ionic activities, and squaring the hydrogen-ion activity:

$$Q = \frac{a(\text{Zn}^{2+})\,[p(\text{H}_2)/p^\circ]}{a(\text{H}^+)^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

Here the standard pressure is $p^\circ = 1\,\text{bar}$.

Step 3: Substitute in the Nernst equation At $298\,\text{K}$, with $n = 2$ and $\log 10 = 1$:

$$\begin{aligned}E_{\text{cell}} &= 0.76 - \frac{0.0591}{2}\log 10\\ &= 0.76 - 0.02955\\ &= 0.73045\,\text{V}.\end{aligned}$$

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

Step 4: Conclusion The cell emf at $298\,\text{K}$ is $\boxed{E_{\text{cell}} \approx 0.730\,\text{V}}$, calculated using $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log Q$ with $Q = 10$.

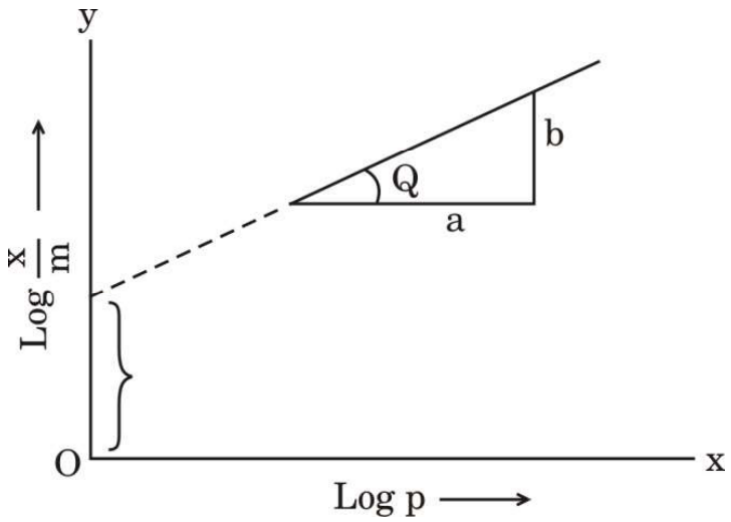
Quick Tip to Solve: Balance the cell reaction before forming Q: hydrogen ions must be squared, and the two transferred electrons put a 2 under 0.0591.

11. Observe the given figure and answer the following questions:

(i) Write the expression for adsorption of gases on solids in the form of an equation.

(ii) What is the slope of the graph?

(iii) What does the intercept of the line represent? [3 marks]



Solution:

Concept:

- The Freundlich adsorption isotherm describes the mass of gas adsorbed per unit mass of solid at constant temperature: $x/m = kp^{1/n}$. Here x is the mass of adsorbed gas, m is the mass of adsorbent and p is the equilibrium gas pressure.
- The constants k and n depend on the adsorbent, gas and temperature; ordinarily $0 < 1/n < 1$ in the pressure range where this empirical relation applies. Taking logarithms gives the straight-line form $Y = c + sX$, with slope s and vertical intercept c.

Step 1: Write the adsorption equation for part (i) The plotted quantities are $\log(x/m)$ on the vertical axis and $\log p$ on the horizontal axis. They correspond to the logarithmic form of the Freundlich isotherm:

$$\frac{x}{m} = kp^{1/n}, \qquad \log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p.$$

The amount adsorbed increases with pressure, while the fractional exponent accounts for its less than proportional increase over the applicable pressure range.

Step 2: Compare the coefficients to find the slope in part (ii) In a graph of Y against X, the coefficient of X is the slope. Thus the coefficient of $\log p$ is $1/n$. The right triangle drawn on the line also gives slope as vertical rise divided by horizontal run, namely b/a.

Step 3: Identify the vertical intercept in part (iii) At the vertical-axis intercept, $\log p = 0$; the pressure term in the straight-line equation therefore vanishes. The remaining ordinate is $\log k$. The intercept represents the logarithm of the Freundlich constant k, rather than k itself.

Step 4: Conclusion (i) $\boxed{x/m = kp^{1/n}}$, or $\log(x/m) = \log k + (1/n)\log p$. (ii) Slope $= \boxed{1/n = b/a}$. (iii) The vertical intercept is $\boxed{\log k}$.

Quick Tip to Solve: Match $\log(x/m) = \log k + (1/n)\log p$ to $Y = c + sX$: the coefficient gives the slope and the constant term gives the intercept.

Section C (5 marks)

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

The rate law for a chemical reaction relates the reaction rate with the concentrations or partial pressures of the reactants. For a general reaction aA + bB $\rightarrow$ C with no intermediate steps in its reaction mechanism, meaning that it is an elementary reaction, the rate law is given by r = k[A]^x[B]^y, where [A] and [B] express the concentrations of A and B in moles per litre. Exponents x and y vary for each reaction and are determined experimentally. The value of k varies with conditions that affect reaction rate, such as temperature, pressure, surface area, etc. The sum of these exponents is known as overall reaction order. A zero order reaction has a constant rate that is independent of the concentration of the reactants. A first order reaction depends on the concentration of only one reactant. A reaction is said to be second order when the overall order is two. Once we have determined the order of the reaction, we can go back and plug in one set of our initial values and solve for k.

Calculate the overall order of a reaction which has the following rate expression: Rate = k[A]$^{1/2}$ [B]$^{3/2}$ [1 mark]

Solution:

Concept:

- In an experimentally determined rate law, the exponent of each reactant concentration is the order with respect to that reactant.
- The overall order is the sum of these exponents. For $r = k[A]^x[B]^y$, it is $x + y$; the rate constant k is not included in this sum.

Step 1: Read the individual orders The given expression is $r = k[A]^{1/2}[B]^{3/2}$. Hence the order with respect to A is $1/2$, while the order with respect to B is $3/2$. Fractional individual orders are allowed.

Step 2: Add the concentration exponents Add the powers appearing in the rate expression:

$$\text{Overall order} = \frac{1}{2} + \frac{3}{2} = \frac{4}{2}.$$

Use these powers directly; reaction order is determined from the rate law, not by counting the reactants.

Step 3: Conclusion The overall order is $\boxed{2}$; this is a second-order reaction.

Quick Tip to Solve: Add $1/2$ and $3/2$ using their common denominator; do not multiply the exponents or include k.

12(ii). What is the effect of temperature on rate of reaction? [1 mark]

Solution:

Concept:

- For most chemical reactions, raising the temperature increases the rate constant and therefore increases the reaction rate at the same reactant concentrations.

Quick Tip to Solve: Explain heating through the increased fraction of molecules above the activation energy; increased collision frequency alone is not the main explanation.

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where A is the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.

Step 1: Explain the effect of heating Increasing temperature raises molecular kinetic energy. A larger fraction of reacting molecules then possesses energy equal to or greater than the activation energy, so a larger fraction of collisions can produce reaction.

Step 2: Relate temperature to the rate constant For positive activation energy, increasing T makes $-E_a/(RT)$ less negative and increases k. With concentrations held fixed in the rate law, this makes the reaction faster. For many reactions near ordinary temperatures, a rise of $10\,\text{K}$ increases the rate by about two to three times; this is an approximate trend, not an exact universal factor.

Step 3: Conclusion The reaction rate generally increases with an increase in temperature, because more molecules have sufficient energy for effective collisions.

Quick Tip to Solve: Explain heating through the increased fraction of molecules above the activation energy; increased collision frequency alone is not the main explanation.

12(iii). What is meant by rate of a reaction? [1 mark]

Solution:

Concept:

- Reaction rate measures how quickly a reaction proceeds: the decrease in reactant concentration or increase in product concentration per unit time.
- Concentration changes are measured over a time interval for the average rate; a derivative gives the instantaneous rate. A common unit is mol $\text{L}^{-1}\,\text{s}^{-1}$.

Step 1: Express the rate using concentration change For a simple reaction $A \rightarrow B$ with unit stoichiometric coefficients, over a time interval Δt, the average rate is

$$r_{\text{av}} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}.$$

The square brackets represent concentration.

Step 2: Explain the sign convention A reactant is consumed, so its concentration change is negative; the minus sign makes its disappearance rate positive. A product is formed, so its concentration increases and its rate expression needs no minus sign. For a general reaction, divide each concentration-change expression by the corresponding stoichiometric coefficient to obtain the same reaction rate.

Step 3: Conclusion Rate of reaction is the change in concentration of a reactant or product per unit time, expressed positively as reactant disappearance or product formation.

Quick Tip to Solve: State both concentration change and time in the definition, and use a minus sign when calculating the rate from a reactant's decrease.

12(iv)(a). A first order reaction takes 77.78 minutes for 50% completion. Calculate the time required for 30% completion of this reaction. (log 10 = 1, log 7 = 0.8450) [2 marks]

Solution:

Concept:

- For a first order reaction, the half-life is $t_{1/2} = 0.693/k$, where k is the rate constant. A reaction reaching 50% completion has undergone one half-life.
- The integrated rate law is $t = (2.303/k)\log([A]_0/[A]_t)$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations, and $\log$ denotes the base-ten logarithm.

Step 1: Calculate the rate constant from the half-life The given time for 50% completion is $t_{1/2} = 77.78\,\text{min}$. Therefore,

$$k = \frac{0.693}{77.78} = 8.910 \times 10^{-3}\,\text{min}^{-1}.$$

Keeping the time in minutes gives the rate constant in inverse minutes.

Step 2: Use the fraction of reactant remaining At 30% completion, 70% of the initial reactant remains; hence $[A]_t = 0.70[A]_0$. The logarithmic ratio is

$$\log\frac{[A]_0}{[A]_t} = \log\frac{10}{7} = \log 10 - \log 7 = 1 - 0.8450 = 0.1550.$$

Substituting this ratio in the first order rate law gives

$$t = \frac{2.303 \times 77.78}{0.693} \times 0.1550 = 40.0646\,\text{min}.$$

Step 3: Conclusion The time required for 30% completion is approximately $\boxed{40.06\,\text{min}}$, which is less than the time for 50% completion, as expected.

Quick Tip to Solve: For 30% completion, put the remaining fraction 0.70 in the denominator of the logarithm; using 0.30 would calculate the time for 70% completion.

OR

12(iv)(b). A first order reaction has a rate constant 1×10^{-3} per sec. How long will 5 g of this reactant take to reduce to 3 g? (log 3 = 0.4771; log 5 = 0.6990) [2 marks]

Solution:

Concept:

- For a first order reaction, the integrated rate law is $t = (2.303/k)\log([A]_0/[A]_t)$, where k is the rate constant and $[A]_0$, $[A]_t$ are initial and remaining concentrations.
- For the same reactant at constant volume, concentration is proportional to its mass, so $[A]_0/[A]_t = m_0/m_t$. The logarithm uses the mass remaining, not the mass that has reacted.

Step 1: Identify the mass ratio and time unit The initial mass is $m_0 = 5\,\text{g}$ and the remaining mass is $m_t = 3\,\text{g}$. Thus the concentration ratio is $5/3$. Since the rate constant is $k = 1 \times 10^{-3}\,\text{s}^{-1}$, the

Quick Tip to Solve: Use the ratio initial mass/remaining mass, $5/3$, and retain seconds while substituting a rate constant given in s^{-1}.

calculated time will be in seconds. Although $2\,\text{g}$ has reacted, that value is not the remaining mass in the rate equation.

Step 2: Substitute in the first order rate equation Using the supplied logarithms,

$$\log \frac{5}{3} = \log 5 - \log 3 = 0.6990 - 0.4771 = 0.2219.$$

Therefore,

$$t = \frac{2.303}{1 \times 10^{-3}} \times 0.2219 = 511.0357\,\text{s}.$$

The logarithmic ratio is positive because the remaining mass is less than the initial mass, giving a physically positive elapsed time.

Step 3: Conclusion The reactant takes approximately $\boxed{511\,\text{s}}$, or $8.52\,\text{min}$, to decrease from $5\,\text{g}$ to $3\,\text{g}$.

Quick Tip to Solve: Use the ratio initial mass/remaining mass, $5/3$, and retain seconds while substituting a rate constant given in s^{-1}.