

CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-4-1

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. Arrange the following compounds in the increasing order of their property indicated: (Any two)

(i) Acetaldehyde, Benzaldehyde, Acetophenone, Acetone (Reactivity towards HCN)

(ii) $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ (Acidic strength)

(iii) $\text{CH}_3\text{CH}_2\text{OH}$, CH_3CHO , CH_3COOH (Boiling point)

[2 marks]

Solution:

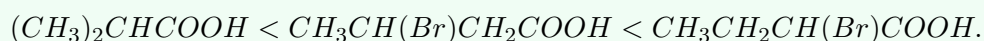
Concept:

- HCN addition involves nucleophilic attack on the carbonyl carbon. Electron donation and steric hindrance reduce its reactivity.
- Electron-withdrawing substituents stabilise carboxylate ions and increase acidity; their inductive effect weakens with distance.
- Intermolecular hydrogen bonding raises boiling point; carboxylic acids also form hydrogen-bonded dimers.

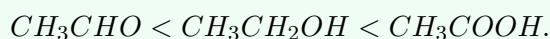
Step 1: (i) Reactivity towards HCN A phenyl group conjugated with the carbonyl reduces its electrophilicity through resonance. Acetophenone also contains a methyl group that donates electron density and hinders attack, making it least reactive. Benzaldehyde is less reactive than the aliphatic carbonyl compounds in this comparison. Acetone contains two electron-donating methyl groups, whereas acetaldehyde has one methyl group and a small hydrogen atom, making acetaldehyde most reactive. Hence,



Step 2: (ii) Acidic strength Bromine withdraws electron density through its $-I$ effect and stabilises the negatively charged carboxylate ion. The effect is stronger for Br on the carbon adjacent to COOH than for Br one carbon farther away. The unsubstituted alkyl acid lacks this electron-withdrawing group. Therefore,



Step 3: (iii) Boiling point Ethanal exhibits dipole–dipole attractions but has no O–H bond and cannot hydrogen bond to itself. Ethanol forms intermolecular hydrogen bonds and therefore boils higher. Ethanoic acid forms strongly associated dimers through two hydrogen bonds and has the highest boiling point. Consequently,



Step 4: Conclusion The increasing orders are (i) acetophenone, benzaldehyde, acetone, acetaldehyde; (ii) $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$; (iii) CH_3CHO , $\text{CH}_3\text{CH}_2\text{OH}$, CH_3COOH . Any two comparisons answer the question.

Quick Tip to Solve: Locate Br relative to COOH for acidity, and compare hydrogen bonding and dimer formation for boiling point.

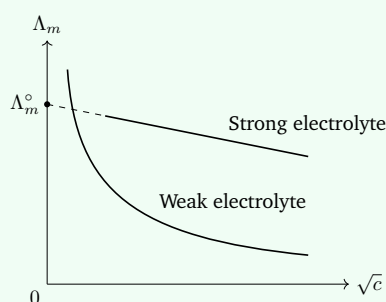
2. In a plot of Λ_m against the square root of concentration ($c^{1/2}$) for strong and weak electrolyte, the value of limiting molar conductivity of a weak electrolyte cannot be obtained graphically. Suggest a way to obtain this value. Also state the related law, if any. [2 marks]

Solution:

Concept:

- At infinite dilution, ions migrate independently and each ion contributes a definite amount to the limiting molar conductivity of an electrolyte.
- Kohlrausch's law gives $\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$, where ν_+ and ν_- count the cations and anions per formula unit and λ° denotes their limiting ionic molar conductivities.

Step 1: Use strong-electrolyte measurements Weak electrolytes ionise increasingly on dilution, so their conductivity plots are curved and cannot be reliably extrapolated to zero concentration. Extrapolate the approximately linear plots of suitable strong electrolytes to obtain their limiting values, then combine these values to supply the required ions.



Schematic conductivity plots: only the strong-electrolyte straight portion is extrapolated.

Step 2: Combine the values using Kohlrausch's law For example, to obtain the value for ethanoic acid, use HCl, sodium ethanoate and NaCl:

$$\begin{aligned}\Lambda_m^\circ(\text{HCl}) &= \lambda^\circ(\text{H}^+) + \lambda^\circ(\text{Cl}^-), \\ \Lambda_m^\circ(\text{CH}_3\text{COONa}) &= \lambda^\circ(\text{CH}_3\text{COO}^-) + \lambda^\circ(\text{Na}^+), \\ \Lambda_m^\circ(\text{NaCl}) &= \lambda^\circ(\text{Na}^+) + \lambda^\circ(\text{Cl}^-).\end{aligned}$$

Add the first two equations and subtract the third: the sodium and chloride contributions cancel, leaving the contributions of hydrogen and ethanoate ions.

Step 3: Conclusion Kohlrausch's law of independent migration of ions states that each ion contributes independently to molar conductivity at infinite dilution, irrespective of its counter-ion. Hence,

$$\begin{aligned}\Lambda_m^\circ(\text{CH}_3\text{COOH}) &= \Lambda_m^\circ(\text{HCl}) \\ &\quad + \Lambda_m^\circ(\text{CH}_3\text{COONa}) - \Lambda_m^\circ(\text{NaCl}).\end{aligned}$$

Quick Tip to Solve: Add strong electrolytes supplying the desired two ions, then subtract a salt to cancel the unwanted ions.

3. 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]

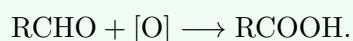
Solution:

Concept:

- Friedel-Crafts alkylation and acylation are electrophilic aromatic substitution reactions; a strongly deactivated benzene ring does not react readily.
- Oxidation of an aldehyde converts its $-\text{CHO}$ group into $-\text{COOH}$, whereas oxidation of a ketone requires cleavage of a carbon-carbon bond.

Step 1: (i) Effect of the carboxyl group in benzoic acid The $-\text{COOH}$ group withdraws electron density from the benzene ring through both its negative inductive effect and its negative resonance effect. This strongly deactivates the ring towards electrophilic substitution. Hence the ring cannot readily attack the electrophile generated in a Friedel-Crafts reaction. In addition, the carboxyl group interacts with the Lewis-acid catalyst AlCl_3 , further hindering the reaction. Thus benzoic acid does not undergo Friedel-Crafts alkylation or acylation under the usual conditions.

Step 2: (ii) Compare the changes required for oxidation An aldehyde has a hydrogen atom attached directly to the carbonyl carbon. It is readily oxidised to the corresponding carboxylic acid without breaking the carbon skeleton:



A ketone, RCOR' , has no hydrogen attached to its carbonyl carbon. Its oxidation therefore involves breaking a carbon-carbon bond adjacent to the carbonyl group and requires stronger oxidising agents and more vigorous conditions. This makes ketones much less readily oxidised than aldehydes.

Step 3: Conclusion (i) The strongly electron-withdrawing $-\text{COOH}$ group deactivates the ring in benzoic acid. (ii) Aldehydes oxidise without carbon-carbon bond cleavage, whereas ketones require such cleavage.

Quick Tip to Solve: For oxidation questions, first check whether the carbonyl carbon carries a hydrogen: aldehydes do, ketones do not.

Section B (24 marks)

4(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]

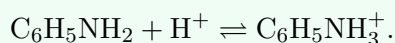
Solution:

Concept:

- Hydrogen bonding between an amine and water favours dissolution, while a large nonpolar hydrocarbon group reduces aqueous solubility.
- A free amino group donates its lone pair to an aromatic ring by resonance. Protonation removes this lone pair from conjugation and changes the directing effect.
- A nucleophile donates an available electron pair to an electron-deficient centre to form a covalent bond.

Step 1: (i) Compare the hydrophilic and hydrophobic parts Ethylamine, $\text{C}_2\text{H}_5\text{NH}_2$, forms intermolecular hydrogen bonds with water through its amino group. Nitrogen can accept a hydrogen bond using its lone pair, and the N – H bonds can donate hydrogen bonds. Its ethyl group is small, so hydration of the amino group is sufficient for appreciable solubility in water. Aniline, $\text{C}_6\text{H}_5\text{NH}_2$, can also hydrogen-bond with water, but it contains a much larger hydrophobic phenyl group. The nonpolar ring opposes hydration, so aniline is very sparingly soluble and is described as insoluble in this comparison.

Step 2: (ii) Account for the meta product in nitration In neutral aniline, the nitrogen lone pair is delocalised into the benzene ring. This increases electron density particularly at the ortho and para positions, so $-\text{NH}_2$ is an ortho- and para-directing group. However, the strongly acidic nitrating mixture protonates aniline:



The resulting anilinium ion has no available nitrogen lone pair for donation to the ring. Its positively charged $-\text{NH}_3^+$ group withdraws electron density, deactivates the ring and is meta-directing. Nitration of this protonated species therefore produces a substantial amount of m-nitroaniline after work-up, even though the free amino group is ortho- and para-directing.

Step 3: (iii) Identify the electron pair responsible for attack The nitrogen atom in an amine possesses a lone pair of electrons. It can donate this pair to an electrophile, such as the electron-deficient carbon atom of an alkyl halide, forming a new nitrogen-carbon bond. This electron-pair-donating ability makes amines nucleophiles. The same lone pair also explains their basicity, but nucleophilic behaviour specifically refers to attack on an electrophilic centre.

Step 4: Conclusion (i) Ethylamine is hydrated effectively; aniline's larger hydrophobic phenyl group limits its solubility. (ii) Acidic nitration forms meta-directing anilinium ions. (iii) Amines act as nucleophiles by donating the nitrogen lone pair.

Quick Tip to Solve: Before applying an amino group's directing effect, check the medium: strong acid converts $-\text{NH}_2$ into meta-directing $-\text{NH}_3^+$.

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

(i) Nitrobenzene to Aniline

(ii) Ethanamide to Methanamine

(iii) Ethanenitrile to Ethanamine

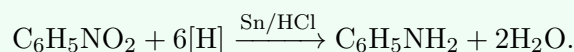
[3 marks]

Solution:

Concept:

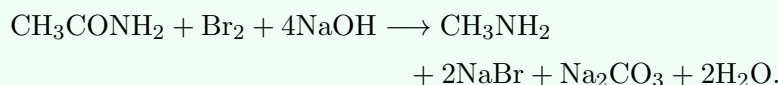
- Reduction of a nitro group converts $-\text{NO}_2$ into $-\text{NH}_2$ without changing the carbon skeleton.
- Hofmann bromamide degradation converts an amide RCONH_2 into RNH_2 , losing the carbonyl carbon. Reduction of a nitrile retains its nitrile carbon as $-\text{CH}_2\text{NH}_2$.

Step 1: (i) Reduce nitrobenzene to aniline Heat nitrobenzene with tin and hydrochloric acid, then treat the reaction mixture with sodium hydroxide to liberate the free amine from its salt. The overall reduction is



In the acidic medium the aniline is protonated; the alkaline work-up releases aniline. The benzene ring and its six carbon atoms remain intact.

Step 2: (ii) Degrade ethanamide to methanamine Warm ethanamide with bromine and aqueous sodium hydroxide. Hofmann bromamide degradation gives the primary amine containing one fewer carbon atom:



Thus the two-carbon amide yields one-carbon methanamine; the carbonyl carbon is removed into carbonate.

Step 3: (iii) Reduce ethanenitrile to ethanamine Reduce ethanenitrile using lithium aluminium hydride in dry ether, followed by hydrolysis. The net change is



The nitrile carbon becomes the methylene carbon bonded to nitrogen, so both carbon atoms are retained. This differs from amide degradation, which removes one carbon atom.

Step 4: Conclusion Use Sn/HCl , followed by NaOH , for nitrobenzene; Br_2/NaOH for ethanamide; and LiAlH_4 in dry ether followed by hydrolysis for ethanenitrile.

Quick Tip to Solve: Count carbon atoms first: amide-to-amine with one carbon less needs Hofmann degradation, whereas nitrile reduction retains both carbons.

- 5(a).** (i) Write the electronic configuration of d^5 on the basis of crystal field splitting theory if $\Delta_o < P$.
 (ii) $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic whereas $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic. Give reason to support this statement. [Atomic no.: Fe = 26]
 (iii) Write the number of ions produced from the complex $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ in solution. [3 marks]

Solution:

Concept:

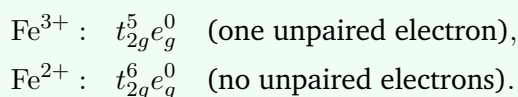
- In an octahedral field, the three t_{2g} orbitals lie below the two e_g orbitals. Electrons avoid pairing when the splitting energy Δ_o is smaller than the pairing energy P .
- Unpaired electrons cause paramagnetism; a configuration with all electrons paired is diamagnetic. Counterions outside the coordination sphere dissociate in water, while the complex ion remains intact.

Step 1: (i) Fill the high-spin d orbitals Since $\Delta_o < P$, promoting an electron into an e_g orbital costs less energy than pairing it in a t_{2g} orbital. By Hund's rule, five electrons occupy the five orbitals singly before pairing. Therefore the octahedral d^5 configuration is



with five unpaired electrons. This is a high-spin configuration; a paired t_{2g}^5 arrangement would correspond to the opposite energy ordering.

Step 2: (ii) Compare the two cyanide complexes Each cyanide ligand has charge -1 . For $[\text{Fe}(\text{CN})_6]^{3-}$, the iron oxidation state is $+3$, giving $\text{Fe}^{3+} : 3d^5$. For $[\text{Fe}(\text{CN})_6]^{4-}$, iron is $+2$, giving $\text{Fe}^{2+} : 3d^6$. Cyanide is a strong-field ligand and causes pairing, so the configurations are



Thus the ferricyanide complex is weakly paramagnetic, whereas the ferrocyanide complex is diamagnetic. Part (i) uses a weak-field condition; here cyanide instead produces a low-spin arrangement.

Step 3: (iii) Count the ions released into solution The two chlorides outside the square brackets are counterions. The six ammonia ligands remain bound within the complex cation. Dissociation is



One complex cation and two chloride anions give a total of three ions per formula unit; neutral coordinated ammonia molecules are not separately counted as ions.

Step 4: Conclusion (i) $t_{2g}^3 e_g^2$; (ii) the cyanide complexes have respectively one and zero unpaired electrons; (iii) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ produces 3 ions in solution.

Quick Tip to Solve: Find the metal oxidation state before counting d electrons, and count only the intact complex ion plus counterions outside the brackets.

- 5(b). (i) Calculate the spin only magnetic moment of the complex $[\text{CoF}_6]^{3-}$. (Atomic no. of Co = 27)
 (ii) Write the IUPAC name of the given complex: $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$
 (iii) Which out of the two complexes is more stable and why? $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ [3 marks]

Solution:**Concept:**

- For a transition-metal ion, remove the outer $4s$ electrons before the $3d$ electrons. A weak-field ligand gives a high-spin octahedral complex when the splitting energy is smaller than the pairing energy.
- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)} \text{ BM}$, where n is the number of unpaired electrons and BM denotes Bohr magnetons.
- Name coordinated ligands alphabetically before the metal and its oxidation state. Chelating ligands bind through more than one donor atom and generally give greater complex stability than comparable monodentate ligands.

Step 1: (i) Find the cobalt oxidation state and unpaired electrons Each fluoro ligand has charge -1 . If cobalt has oxidation state x , then $x - 6 = -3$, so $x = +3$. Neutral cobalt is $[\text{Ar}]3d^74s^2$, hence Co^{3+} is $3d^6$. Fluoride is a weak-field ligand, so the octahedral complex is high spin with configuration $t_{2g}^4e_g^2$. The t_{2g} set has two unpaired electrons and the e_g set has two more. Thus $n = 4$, and

$$\mu = \sqrt{4(4+2)} = \sqrt{24} = 2\sqrt{6} \approx 4.90 \text{ BM.}$$

Step 2: (ii) Name the chromium complex salt The chloride outside the square brackets has charge -1 , so the complex cation has charge $+1$. The four aqua ligands are neutral and the two coordinated chlorido ligands contribute -2 . Therefore $x - 2 = +1$, giving chromium oxidation state $+3$. Aqua precedes chlorido alphabetically; the prefixes tetra and di do not determine alphabetical order. The cationic metal retains the name chromium, followed by its oxidation state, and the counterion is chloride.

Step 3: (iii) Compare stability using the chelate effect Water is monodentate: each water molecule attaches to iron through one oxygen donor. Oxalate, $\text{C}_2\text{O}_4^{2-}$, is bidentate: each ligand attaches through two oxygen donors and forms a chelate ring with iron. Three oxalate ligands therefore fill six coordination positions while forming three chelate rings. This chelation increases stability compared with the corresponding complex containing six separate monodentate aqua ligands; it is the chelate effect.

Step 4: Conclusion (i) $\mu \approx 4.90 \text{ BM}$. (ii) Tetraaquadichloridochromium(III) chloride. (iii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is more stable because oxalate forms chelate rings, whereas water is monodentate.

Quick Tip to Solve: First find the metal oxidation state, then its d-electron count; weak-field fluoride keeps this cobalt(III) d^6 complex high spin.

6. (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:

- Colour of many transition-metal ions arises from absorption of visible light in d–d transitions between split d orbitals. An ion with a d^0 configuration cannot undergo such a transition.
- A half-filled d^5 subshell has extra stability. Oxidation removes an electron, so resistance to oxidation depends on whether this stable configuration is destroyed or produced.
- Oxygen and fluorine are highly electronegative elements and stabilize metals in high positive oxidation states through strong metal–ligand bonding.

Step 1: (i) Compare the d-electron configurations Titanium has atomic number 22 and ground-state configuration $[\text{Ar}]3d^24s^2$. Removing four electrons gives $\text{Ti}^{4+} = [\text{Ar}]3d^0$. It has no d electron available for excitation between split d orbitals, so it is colourless. Chromium has configuration $[\text{Ar}]3d^54s^1$, hence Cr^{3+} is $3d^3$; vanadium is $[\text{Ar}]3d^34s^2$, hence V^{3+} is $3d^2$. These latter ions have partially occupied d orbitals and can exhibit d–d transitions, explaining their colour.

Step 2: (ii) Compare oxidation of manganese(II) and iron(II) Mn^{2+} has the especially stable half-filled $3d^5$ configuration. Its oxidation to Mn^{3+} changes $3d^5$ to $3d^4$, destroying that stability; removal of the next electron is therefore relatively difficult. In contrast, Fe^{2+} is $3d^6$, and oxidation to Fe^{3+} produces the stable half-filled $3d^5$ configuration. Thus iron(II) is more readily oxidized, while manganese(II) is more resistant.

Step 3: (iii) Explain stabilization of the highest oxidation states A metal in a very high positive oxidation state requires ligands that strongly attract electron density and provide strong bonding. Oxygen and fluorine are highly electronegative and are particularly effective at stabilizing such states. Oxygen can also form multiple bonds with the metal, further stabilizing high oxidation states in oxides. Typical examples are manganese in Mn_2O_7 , where it is +7, and vanadium in VF_5 , where it is +5. These features explain the occurrence of the highest metal oxidation states in oxides or fluorides.

Step 4: Conclusion (i) Ti^{4+} is colourless because it is d^0 . (ii) Oxidation destroys the stable d^5 state of Mn^{2+} , but creates it for Fe^{3+} . (iii) Highly electronegative oxygen and fluorine stabilize high metal oxidation states through strong bonding; oxygen can also form multiple bonds.

Quick Tip to Solve: Write the d count on both sides of oxidation: Mn(II) loses d5 stability, whereas Fe(II) gains it on becoming Fe(III).

7. 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.

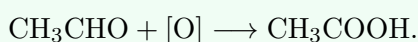
[3 marks]

Solution:

Concept:

- Aldehydes oxidise to carboxylic acids, retaining their carbon skeleton. The general reaction is $RCHO + [O] \rightarrow RCOOH$.
- The iodoform test gives yellow CHI_3 with a methyl carbonyl group; ethanal is the aldehyde that responds to this test.
- HCN adds across a carbonyl group to form a cyanohydrin. Hydrolysis converts its $-CN$ group into $-COOH$, retaining the hydroxyl group.

Step 1: Identify A and its oxidation product B The formula C_2H_4O , oxidation to an acid and a positive iodoform test identify A as ethanal, CH_3CHO . Its oxidation product B is ethanoic acid, CH_3COOH , with formula $C_2H_4O_2$:



An oxidising agent such as acidified potassium dichromate supplies the oxygen needed to convert the aldehyde group into the carboxyl group.

Step 2: Write the iodoform reaction With iodine and aqueous sodium hydroxide, ethanal gives the characteristic yellow precipitate of iodoform and sodium methanoate:

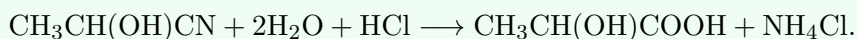


The methyl carbon becomes CHI_3 , while the aldehyde carbon becomes the methanoate ion; the equation conserves both carbon atoms.

Step 3: Identify C by HCN addition and hydrolysis Addition of HCN to ethanal produces its cyanohydrin C, 2-hydroxypropanenitrile:



The cyanide carbon adds one carbon to the original two-carbon skeleton. On heating with aqueous acid, the nitrile group hydrolyses to a carboxyl group:



This product is 2-hydroxypropanoic acid (lactic acid), exactly as stated, so it independently confirms the identity of A and C.

Step 4: Conclusion A is CH_3CHO (ethanal); B is CH_3COOH (ethanoic acid). C is $CH_3CH(OH)CN$, 2-hydroxypropanenitrile (ethanal cyanohydrin).

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

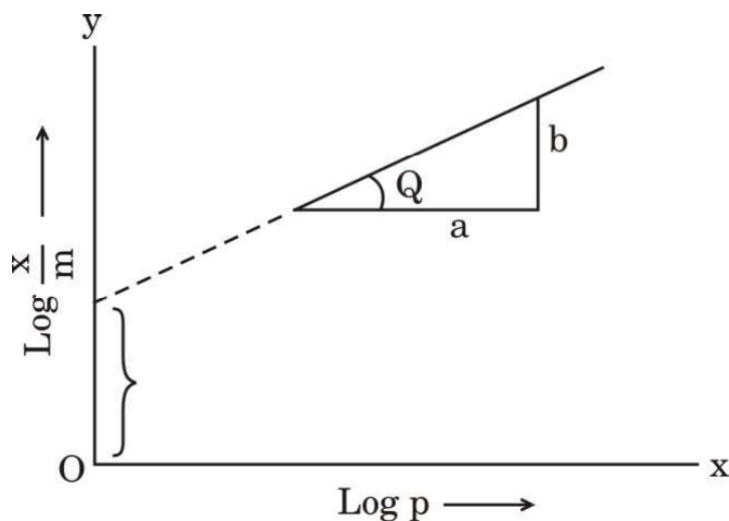
8. Observe the given figure and answer the following questions:

(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 relates the mass of gas adsorbed per unit mass of solid to gas pressure at constant temperature.
- Taking logarithms converts a power law into a straight line: $y = c + sx$, where s is the slope and c is the vertical intercept.

Step 1: (i) State the adsorption equation The Freundlich equation for adsorption of a gas on a solid is

$$\frac{x}{m} = kp^{1/n}.$$

Here x is the mass of gas adsorbed, m is the mass of adsorbent and p is the equilibrium gas pressure. The constants k and n depend on the gas, solid and temperature; normally $0 < 1/n < 1$.

Step 2: (ii) Obtain the slope of the plotted line Taking logarithms of the equation gives

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n} \log p.$$

The axes are $\log(x/m)$ versus $\log p$. The coefficient of $\log p$ is the slope. For the drawn triangle, vertical rise is b and horizontal run is a , giving

$$\text{slope} = \frac{b}{a} = \tan Q = \frac{1}{n}.$$

Step 3: (iii) Interpret the vertical intercept At the vertical axis, $\log p = 0$, so the equation gives $\log(x/m) = \log k$. Thus the bracketed intercept is $\log k$, not k . Take its antilogarithm to obtain the

Quick Tip to Solve: Match the graph to $y = c + sx$ after taking logarithms: the coefficient of $\log p$ gives the slope and the constant gives the intercept.

Freundlich constant k ; the slope likewise gives $1/n$, not n .

Step 4: Conclusion (i) $x/m = kp^{1/n}$; (ii) slope = $1/n = b/a = \tan Q$; (iii) the vertical intercept is $\log k$.

Quick Tip to Solve: Match the graph to $y = c + sx$ after taking logarithms: the coefficient of $\log p$ gives the slope and the constant gives the intercept.

9(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.

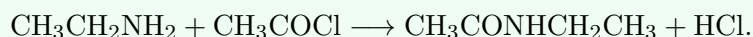
[3 marks]

Solution:

Concept:

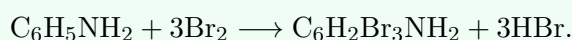
- Primary amines undergo acylation with acid chlorides to form substituted amides; the nitrogen acquires the acyl group, $\text{CH}_3\text{CO}-$.
- The $-\text{NH}_2$ group strongly activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- The carbylamine test converts a primary amine into an isocyanide on heating with chloroform and alcoholic potassium hydroxide.

Step 1: (i) Acylation of ethanamine Ethanamine reacts with acetyl chloride to produce *N*-ethylethanamide. An amino hydrogen is replaced by the acetyl group:



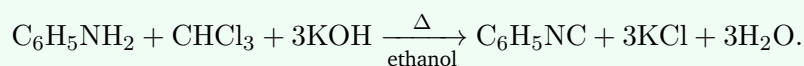
The carbon skeleton of ethanamine stays attached to nitrogen. The product is an amide, since nitrogen is now directly bonded to the carbonyl carbon; it is not a tertiary amine. In practice, a base or excess amine removes the hydrogen chloride formed.

Step 2: (ii) Bromination of aniline With bromine water at room temperature, substitution takes place at both ortho positions and at the para position:



The product is 2,4,6-tribromoaniline, obtained as a white precipitate. The strong activation by $-\text{NH}_2$ allows three substitutions without a Lewis-acid catalyst; stopping at monobromoaniline would therefore not describe the stated conditions.

Step 3: (iii) Carbylamine reaction of aniline On heating aniline with chloroform and ethanolic potassium hydroxide, phenyl isocyanide is formed:



Phenyl isocyanide has the characteristic offensive odour of carbylamines. Its connectivity is

Quick Tip to Solve: In the carbylamine equation, write the product as RNC and balance chloroform with three KOH , three KCl and three water molecules.

$\text{C}_6\text{H}_5-\text{N}\equiv\text{C}$, not that of benzonitrile, $\text{C}_6\text{H}_5-\text{C}\equiv\text{N}$. The coefficients account for all three chlorine atoms of chloroform.

Step 4: Conclusion The products are (i) *N*-ethylethanamide, (ii) 2,4,6-tribromoaniline (white precipitate), and (iii) phenyl isocyanide, with the balanced equations given above.

Quick Tip to Solve: In the carbylamine equation, write the product as RNC and balance chloroform with three KOH, three KCl and three water molecules.

OR

9(b). (i) Write the IUPAC name for the following organic compound: $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$

(ii) Write the equations for the following:

(I) Gabriel phthalimide synthesis

(II) Hoffmann bromamide degradation

[3 marks]

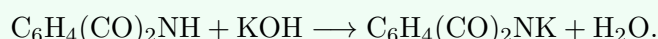
Solution:

Concept:

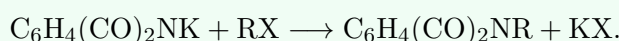
- Name an amine using an alkane chain attached to nitrogen as the parent; other groups on nitrogen receive the locant *N*.
- Gabriel synthesis alkylates potassium phthalimide and then hydrolyses the product to release a primary aliphatic amine.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , eliminating the carbonyl carbon and shortening the carbon chain by one.

Step 1: (i) Name the tertiary amine In $(\text{CH}_3\text{CH}_2)_2\text{NCH}_3$, nitrogen is bonded to two ethyl groups and one methyl group. Choose one ethyl group as the ethanamine parent. The other ethyl and the methyl group are substituents on nitrogen. Listing these substituents alphabetically gives *N*-ethyl-*N*-methylethanamine. The compound is tertiary because all three nitrogen substituents are carbon groups and there is no nitrogen-bound hydrogen.

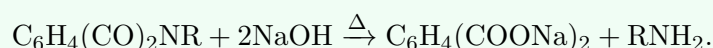
Step 2: (ii) (I) Gabriel phthalimide synthesis First prepare potassium phthalimide by removing the acidic imide hydrogen:



It reacts with an alkyl halide $\text{R}-\text{X}$, where R is an alkyl group and X a halogen:



Alkaline hydrolysis of the *N*-alkylphthalimide releases the primary amine:

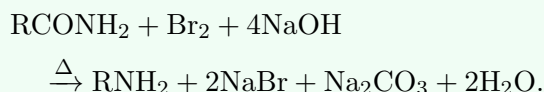


The carbonyl groups in the condensed formula belong to the five-membered imide ring fused to benzene. This method gives primary aliphatic amines; aryl halides do not undergo the required

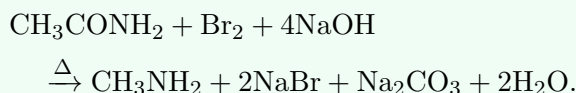
Quick Tip to Solve: Count carbon atoms before and after Hofmann degradation: remove only the carbonyl carbon, keeping the whole R group attached to nitrogen.

nucleophilic substitution under these conditions.

Step 3: (ii)(II) Hofmann bromamide degradation Heat a primary amide with bromine and aqueous sodium hydroxide:



For example, ethanamide gives methanamine:



The carbonyl carbon enters carbonate, while the group R migrates to nitrogen. Thus an amide with two carbon atoms gives an amine with one carbon atom.

Step 4: Conclusion (i) The IUPAC name is *N*-ethyl-*N*-methylethanamine. (ii) Gabriel synthesis yields a primary aliphatic amine from an alkyl halide, whereas Hofmann degradation yields a primary amine with one fewer carbon atom than the starting amide.

Quick Tip to Solve: Count carbon atoms before and after Hofmann degradation: remove only the carbonyl carbon, keeping the whole R group attached to nitrogen.

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



Given: $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.75 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.45 \text{ V}$ ($\log 10 = 1$)

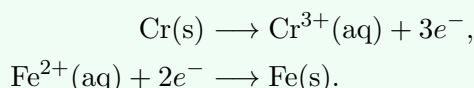
[3 marks]

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 K, this becomes $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log Q$. Pure solid metals have unit activity and are omitted from Q .

Step 1: Identify the electrodes and balance electron transfer The reduction potential of Fe^{2+}/Fe is greater than that of Cr^{3+}/Cr , so iron is the cathode and chromium is the anode. Their half-reactions are



Multiply the first reaction by two and the second by three. The balanced cell reaction is $2\text{Cr(s)} + 3\text{Fe}^{2+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{Fe(s)}$, so $n = 6$. Electrode potentials are intensive quantities and are not multiplied by these coefficients.

Step 2: Calculate the standard potential and reaction quotient Using both supplied values as reduction

Quick Tip to Solve: Balance the two half-reactions first: use six electrons and concentration powers two and three, without multiplying electrode potentials.

potentials,

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = (-0.45) - (-0.75) = 0.30 \text{ V}.$$

The stoichiometric coefficients become concentration powers:

$$Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} = \frac{(0.1)^2}{(0.01)^3} = 10^4, \quad \log Q = 4.$$

Step 3: Substitute into the Nernst equation At the specified temperature,

$$E_{\text{cell}} = 0.30 - \frac{0.0591}{6}(4) = 0.30 - 0.0394 \text{ V}.$$

The positive correction being subtracted reflects $Q > 1$: these concentrations reduce the emf below its standard value. The balanced reaction, rather than either individual half-reaction, determines the electron count used here.

Step 4: Conclusion The required Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$ at 298 K, and the emf is $\boxed{0.2606 \text{ V} \approx 0.261 \text{ V}}$.

Quick Tip to Solve: Balance the two half-reactions first: use six electrons and concentration powers two and three, without multiplying electrode potentials.

11(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 $E_{\text{M}^{2+}/\text{M}}^{\circ}$ 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 neutral atom need not itself have an incomplete d-subshell.
- Standard electrode potentials reflect the overall energy changes of metal atomisation, ionisation and ion hydration. Extra stability of an aqueous ion can make its reduction to the metal less favourable.
- Alloys are metallic mixtures. Similar atomic sizes allow atoms of one transition metal to replace atoms of another in the metallic crystal lattice.

Step 1: Explain why silver qualifies as a transition element The ground-state electronic configuration of silver is $[\text{Kr}] 4d^{10}5s^1$, so its neutral atom does indeed have a completely filled d-subshell. However, silver can exhibit the +2 oxidation state. The Ag^{2+} ion has configuration $[\text{Kr}] 4d^9$, which contains an incompletely filled d-subshell. It therefore satisfies the definition of a transition element. Merely examining the neutral atom, or the $4d^{10}$ configuration of Ag^+ , would miss the qualifying oxidation state.

Step 2: Explain the unusually negative potentials of manganese and zinc On forming Mn^{2+} , man-

Quick Tip to Solve: For transition-element classification, check the ion configurations too; for Mn and Zn electrode potentials, identify the stable divalent d configurations.

ganese acquires the especially stable half-filled $3d^5$ configuration. Zinc forms Zn^{2+} , with the especially stable completely filled $3d^{10}$ configuration. Formation of these stable divalent ions is favoured, while their reduction back to the respective metals is comparatively less favourable. Thus the standard reduction potentials $E_{Mn^{2+}/Mn}^\circ$ and $E_{Zn^{2+}/Zn}^\circ$ are more negative than would be expected from a smooth trend across the series. This explanation concerns the relative stability of the ions within the overall energy balance for electrode-potential values.

Step 3: Explain alloy formation Transition metals have similar atomic radii and compatible metallic crystal structures. Consequently, atoms of one metal can substitute for atoms of another in its lattice without greatly disturbing the structure, while metallic bonding is retained. This permits ready formation of solid solutions and hence alloys. The similarity in size is the key structural reason; alloy formation does not require the metals to have identical electronic configurations or identical oxidation states.

Step 4: Conclusion (i) Silver is a transition element because Ag^{2+} has an incomplete $4d^9$ subshell. (ii) Stable $3d^5$ and $3d^{10}$ configurations of Mn^{2+} and Zn^{2+} account for their unusually negative reduction potentials. (iii) Similar atomic sizes enable transition metals to replace one another in metallic lattices and form alloys.

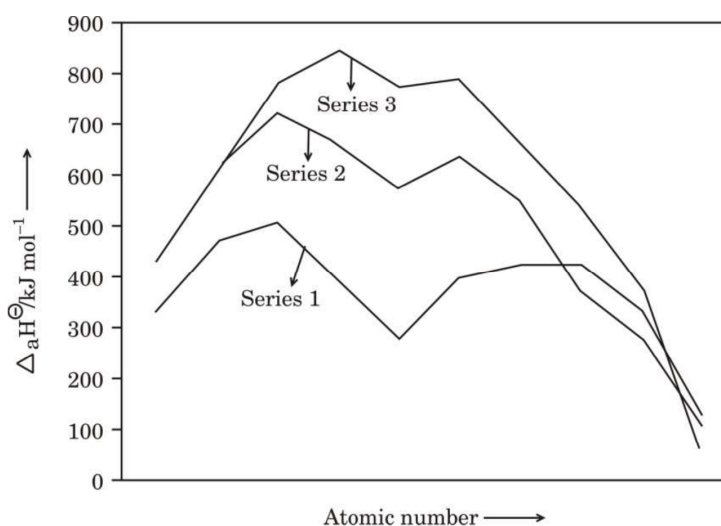
Quick Tip to Solve: For transition-element classification, check the ion configurations too; for Mn and Zn electrode potentials, identify the stable divalent d configurations.

OR

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

- Which element in 3d series has lowest enthalpy of atomisation?
- Why do metals of the second and third series have greater enthalpies of atomisation?
- Why are enthalpies of atomisation of transition metals quite high?

[3 marks]



Solution:

Concept:

- Enthalpy of atomisation, $\Delta_a H$, is the enthalpy required to form one mole of gaseous atoms from the element in its standard state. Stronger metallic bonding requires more energy for atomisation.
- Metallic bonding in transition elements involves valence s and d electrons. The availability of unpaired d electrons favours strong interatomic bonding.

Step 1: Identify the lowest value in the first series The first series in the figure represents the $3d$ series, from Sc to Zn. Its lowest point occurs at the right-hand end, corresponding to zinc. Thus Zn has the lowest enthalpy of atomisation in this series. Zinc has the configuration $[\text{Ar}]3d^{10}4s^2$; its filled $3d$ subshell has no unpaired electrons and contributes little to the strong bonding characteristic of the middle transition elements.

Step 2: Compare the second and third transition series The $4d$ and $5d$ orbitals are more spatially extended than the $3d$ orbitals. Their more effective interatomic overlap produces stronger metal-metal bonding. Consequently, separating the solid into gaseous atoms requires more energy, so corresponding metals in the second and third series generally have greater enthalpies of atomisation.

Step 3: Explain the high values for transition metals Transition metals generally possess several unpaired d electrons, together with valence s electrons, available for metallic bonding. The participation of these electrons creates strong cohesive forces between metal atoms. A large energy input is therefore needed to overcome these forces during atomisation; this accounts for their generally high enthalpies of atomisation. Filled-subshell zinc is the low-value exception illustrated by the graph.

Step 4: Conclusion (i) Zinc (Zn). (ii) More extensive $4d$ and $5d$ orbital overlap gives stronger metallic bonding. (iii) Participation of several unpaired d electrons in bonding gives transition metals high cohesive energies.

Quick Tip to Solve: Read the lowest point of series 1 as Zn; compare orbital overlap when explaining differences between the three series.

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: $\text{Rate} = k[A]^{1/2}[B]^{3/2}$ [1 mark]

Solution:

Concept:

- For a rate law $r = k[A]^x[B]^y$, the overall reaction order is $n = x + y$. The individual orders are the powers of the concentrations in the experimentally obtained rate law.
- Fractional individual orders are allowed; they are added algebraically just like integer orders.

Step 1: Read the concentration powers The given expression is $r = k[A]^{1/2}[B]^{3/2}$. Therefore the order with respect to A is $1/2$, and that with respect to B is $3/2$. Neither the number of reactants nor an assumed stoichiometric coefficient determines the required sum.

Step 2: Add the individual orders Using the definition of overall order,

$$n = \frac{1}{2} + \frac{3}{2} = \frac{4}{2} = 2.$$

The fractional dependence on each reactant thus combines to give an integer overall order.

Step 3: Conclusion The overall order is 2; the reaction is second order.

Quick Tip to Solve: Add the concentration exponents, including fractional ones; do not count the number of reactants.

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

Solution:

Concept:

- Increasing temperature generally increases the rate constant and hence the reaction rate at fixed reactant concentrations.

Quick Tip to Solve: Explain temperature effects through the fraction above activation energy, rather than collision frequency alone.

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

Step 1: Explain the molecular effect At a higher temperature molecules have greater kinetic energy. A larger fraction of collisions involve molecules with energy equal to or greater than the activation energy. More collisions can therefore lead to products in a given time.

Step 2: Relate this to the rate constant For a positive activation energy, increasing T makes $-E_a/(RT)$ less negative and increases k . Thus the rate normally rises with temperature. For many reactions near ordinary temperatures, a rise of about 10 K roughly doubles the rate, although this is an approximate empirical rule rather than a universal factor.

Step 3: Conclusion The rate of a reaction generally increases when temperature increases, because more molecules can overcome the activation-energy barrier.

Quick Tip to Solve: Explain temperature effects through the fraction above activation energy, rather than collision frequency alone.

12(iii). What is meant by rate of a reaction?

[1 mark]

Solution:

Concept:

- The rate of a reaction measures the change in concentration of a reactant or a product per unit time.
- Reactant concentration decreases during reaction, while product concentration increases; the conventional reaction rate is positive.

Step 1: Express rate using a concentration change For a reactant A with unit stoichiometric coefficient, its average rate of disappearance over an interval is

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

The negative sign converts the decrease in reactant concentration into a positive rate.

Step 2: State the equivalent product description and units For a product P with unit coefficient, $r_{\text{av}} = \Delta[P]/\Delta t$. Concentration measured in mol L^{-1} and time in seconds gives rate in $\text{mol L}^{-1} \text{s}^{-1}$. For non-unit coefficients, divide the disappearance or formation rate by the relevant stoichiometric coefficient to obtain a common reaction rate.

Step 3: Conclusion Rate of reaction is the decrease in reactant concentration or increase in product concentration per unit time.

Quick Tip to Solve: Use a minus sign for reactant disappearance and a plus sign for product formation to report a positive rate.

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, $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial amount and x is the amount reacted in time t .
- The half-life is $t_{1/2} = 0.693/k$. At 30% completion, 70% of the initial reactant remains; the logarithm must use the amount remaining.

Step 1: Obtain the rate constant from the half-life The time for 50% completion is the half-life, so $t_{1/2} = 77.78$ min. Thus

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

Keeping time in minutes ensures that the rate constant and the required time have consistent units.

Step 2: Use the fraction remaining for 30% completion Take the initial amount as 100 units. After 30% completion, 30 units have reacted and 70 units remain. Hence

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{100}{70} \\ &= \frac{2.303}{8.910 \times 10^{-3}} \log \frac{10}{7} \\ &= \frac{2.303}{8.910 \times 10^{-3}} (1 - 0.8450) \\ &\approx 40.06 \text{ min.} \end{aligned}$$

This is less than the half-life, as expected, because only 30% rather than 50% of the reactant is consumed.

Step 3: Conclusion The time required for 30% completion is approximately 40.1 min (about 40.05 min with unrounded constants).

Quick Tip to Solve: For a specified percentage completion, subtract it from 100 before forming the logarithmic ratio; 30% completion means 70% remains.

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:

- The integrated first order rate law is $t = \frac{2.303}{k} \log \frac{a}{a-x}$, where a is the initial amount and $a-x$ is the amount remaining.
- For the same reactant in a fixed reaction volume, the concentration ratio equals the mass ratio.

Quick Tip to Solve: Use the remaining 3 g in the denominator, and retain seconds because the supplied rate constant has units of inverse seconds.

Thus the initial and remaining masses may be used directly in the logarithm.

Step 1: Identify the initial and remaining reactant amounts The given rate constant is $k = 1 \times 10^{-3} \text{ s}^{-1}$. Initially the reactant has mass $a = 5 \text{ g}$, and its remaining mass is $a - x = 3 \text{ g}$. The consumed mass is 2 g , but the denominator in the integrated rate law is the remaining mass, not the consumed mass. Therefore the required ratio is $5/3$.

Step 2: Substitute in the first order rate law Using common logarithms and the supplied values,

$$\begin{aligned} t &= \frac{2.303}{1 \times 10^{-3}} \log \frac{5}{3} \\ &= 2303(\log 5 - \log 3) \\ &= 2303(0.6990 - 0.4771) \\ &= 2303(0.2219) \\ &= 511.0357 \text{ s.} \end{aligned}$$

The logarithm contains a dimensionless mass ratio. Since k is expressed in inverse seconds, the computed time is in seconds. As a check, the fraction remaining is $3/5 = 0.60$, so the time is less than the half-life $0.693/k = 693 \text{ s}$.

Step 3: Conclusion The time for the reactant mass to decrease from 5 g to 3 g is 511 s, approximately 8.52 min .

Quick Tip to Solve: Use the remaining 3 g in the denominator, and retain seconds because the supplied rate constant has units of inverse seconds.