CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-4-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

(ii) This question paper is divided into **three** Sections – **A, B** and **C**.

(iii) **Section A** – Questions no. **1 to 3** are very short answer type questions, carrying **2 marks** each.

(iv) **Section B** – Questions no. **4 to 11** are short answer type questions, carrying **3 marks** each.

(v) **Section C** – Question no. **12** is case based question, carrying **5** marks.

(vi) Use of log tables and calculators is **not** allowed.

Section A (6 marks)

1. 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 and require a sufficiently electron-rich aromatic ring.
- Oxidation of an aldehyde converts its formyl group, $-\mathrm{CHO}$, into $-\mathrm{COOH}$; oxidation of a ketone generally requires cleavage of a carbon-carbon bond.

Step 1: (i) Explain the effect of the carboxyl group In benzoic acid, the $-\mathrm{COOH}$ group withdraws electron density from the benzene ring through both its electron-withdrawing inductive effect and resonance effect. The ring is therefore strongly deactivated towards attack by the electrophile used in a Friedel-Crafts reaction. In addition, the carboxyl group interacts with the Lewis acid catalyst, $\mathrm{AlCl_3}$. Consequently, benzoic acid does not undergo the usual Friedel-Crafts alkylation or acylation reaction.

Step 2: (ii) Compare the bond changes needed for oxidation An aldehyde has a hydrogen attached directly to its carbonyl carbon. It can therefore be oxidised to the corresponding carboxylic acid without breaking a carbon-carbon bond:

$$\mathrm{RCHO} + [\mathrm{O}] \longrightarrow \mathrm{RCOOH}.$$

A ketone has two carbon groups attached to the carbonyl carbon and no such hydrogen. Its oxidation requires stronger conditions and carbon-carbon bond cleavage. Thus aldehydes are readily oxidised even by mild oxidising agents, whereas ketones resist mild oxidation.

Step 3: Conclusion (i) The strongly electron-withdrawing $-\mathrm{COOH}$ group deactivates the benzene ring towards Friedel-Crafts substitution. (ii) Aldehydes oxidise without carbon-carbon bond cleavage, whereas oxidation of ketones requires such cleavage and is therefore more difficult.

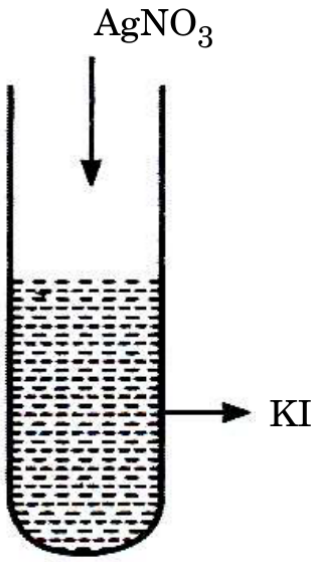
Quick Tip to Solve: For oxidation comparisons, check whether the carbonyl carbon bears a hydrogen: an aldehyde does, but a ketone does not.

2. Observe the given figure and answer the following questions: (Any two)

(i) What is the charge on AgI colloidal particles?

(ii) What is the reason for the origin of the charge on AgI?

(iii) If KI is added to $AgNO_3$, what will be the charge on AgI colloidal particles? [2 marks]



Solution:

Concept:

- Colloidal particles acquire charge by preferential adsorption of ions from the dispersion medium. An ion common to the colloidal material is preferentially adsorbed.
- Silver iodide is formed by $Ag^+ + I^- \longrightarrow AgI$. The ion supplied by the reagent in excess determines the sign of the charge on the sol.

Step 1: (i) Identify the charge for the arrangement shown The figure shows silver nitrate solution being added to potassium iodide solution. During preparation, KI is in excess, so iodide ions remain available in the dispersion medium. The freshly formed AgI particles preferentially adsorb I^- ions. Their surface therefore acquires a negative charge.

Step 2: (ii) Explain the origin of the charge The charge arises from preferential adsorption of iodide ions, I^-, supplied by the excess potassium iodide. These are common ions of the silver iodide precipitate. The particle together with its adsorbed iodide layer is negatively charged; counterions in the surrounding medium maintain overall electrical neutrality of the dispersion.

Step 3: (iii) Reverse the order of addition If potassium iodide is added to silver nitrate solution, $AgNO_3$ is in excess during preparation. The AgI particles now preferentially adsorb the common Ag^+ ions from the medium. This produces a positively charged silver iodide sol. Thus the order of addition changes which ion is in excess and consequently changes the sign of the particle charge.

Step 4: Conclusion (i) Negative charge. (ii) Preferential adsorption of I^- ions from excess KI. (iii) Positive charge, due to adsorption of Ag^+ ions from excess $AgNO_3$. Any two of these parts may be answered as requested.

Quick Tip to Solve: Read the arrow in the preparation figure: the reagent already in the vessel is in excess and supplies the adsorbed common ion.

3. (i) $(CH_3)_3C$ - CHO does not undergo aldol condensation. Why?

(ii) Distinguish between Acetophenone and Benzophenone with the help of a chemical test. [2 marks]

Solution:

Concept:

- Aldol condensation requires at least one hydrogen on the carbon adjacent to the carbonyl group, called an α-hydrogen, for formation of an enolate intermediate.
- Methyl ketones containing $-COCH_3$ give the iodoform test: iodine in aqueous alkali produces a yellow precipitate of CHI_3.

Step 1: (i) Examine the carbon adjacent to the aldehyde group In $(CH_3)_3C - CHO$, the α-carbon is the central carbon bonded to three methyl groups and to the aldehyde carbon. It carries no hydrogen. The hydrogens on the three methyl groups are not α-hydrogens because those carbons are not directly adjacent to the carbonyl carbon. Hence the compound cannot form the required enolate and does not undergo aldol condensation.

Step 2: (ii) Perform the iodoform test Warm separate samples with iodine and aqueous sodium hydroxide. Acetophenone, $C_6H_5COCH_3$, contains the methyl ketone group and gives a yellow precipitate of iodoform:

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

Benzophenone, $C_6H_5COC_6H_5$, has phenyl groups on both sides of its carbonyl group and lacks $-COCH_3$. It gives no yellow iodoform precipitate under the same conditions. The different observations distinguish the two ketones.

Step 3: Conclusion (i) $(CH_3)_3C - CHO$ does not undergo aldol condensation because it has no α-hydrogen. (ii) Acetophenone gives a yellow CHI_3 precipitate with $I_2/NaOH$, whereas benzophenone does not.

Quick Tip to Solve: Locate the carbon directly next to the carbonyl before counting alpha hydrogens; for the iodoform test look specifically for the COCH3 group.

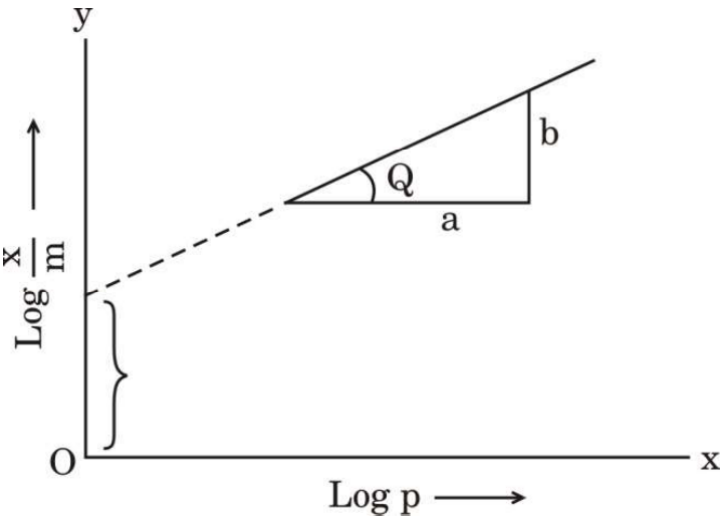
Section B (24 marks)

4. 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:

- At fixed temperature, the Freundlich adsorption isotherm is $x/m = kp^{1/n}$, where x is the mass of adsorbed gas, m is the mass of solid adsorbent, p is gas pressure, and k, n are constants for the chosen gas, solid and temperature.
- In a straight-line equation $y = c + sX$, s is the slope and c the vertical intercept. Here the axes represent $y = \log(x/m)$ and $X = \log p$.

Step 1: Write the adsorption equation for part (i) The required Freundlich equation and its logarithmic form are

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

Taking logarithms turns the pressure power law into the straight line shown. Both axes must use the same logarithm base.

Step 2: Determine the slope for part (ii) Comparing the logarithmic equation with $y = c + sX$, the coefficient of $\log p$ is $1/n$. From the triangle shown, the rise is b and the horizontal run is a, so

$$\text{slope} = \frac{\Delta \log(x/m)}{\Delta \log p} = \frac{1}{n} = \frac{b}{a} = \tan Q.$$

Thus the triangle and the adsorption equation give the same slope.

Step 3: Interpret the intercept for part (iii) At the vertical-axis intercept, $\log p = 0$. Substituting this into the line equation gives $\log(x/m) = \log k$. Hence the indicated intercept represents $\log k$, rather than k itself. Taking its antilogarithm gives the adsorption constant k.

Quick Tip to Solve: On this logarithmic adsorption graph, read the coefficient of $\log p$ as the slope and the constant term as the intercept; take an antilogarithm only to recover k.

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: On this logarithmic adsorption graph, read the coefficient of $\log p$ as the slope and the constant term as the intercept; take an antilogarithm only to recover k.

5(a). (i) Write the electronic configuration of d^4 on the basis of crystal field splitting theory, if $\Delta_o > P$.
(ii) $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex. (Atomic number: Co = 27, Ni = 28)
(iii) Write the number of ions produced from the complex $[Pt(NH_3)_6]Cl_4$ in solution. [3 marks]

Solution:

Concept:

- In an octahedral crystal field, the three t_{2g} orbitals lie below the two e_g orbitals. The splitting energy is Δ_o, while P is the energy needed to pair two electrons in one orbital. If $\Delta_o > P$, electrons pair in t_{2g} before occupying e_g.
- An inner orbital octahedral complex uses two $(n-1)d$, one ns and three np orbitals: d^2sp^3 hybridisation. An outer orbital complex uses two nd orbitals along with ns and np: sp^3d^2 hybridisation.
- On dissolution, ions outside the square brackets dissociate from the complex ion. Neutral ligands such as NH_3 remain coordinated and are not counted as separate ions.

Step 1: Fill the orbitals for part (i) Since $\Delta_o > P$, pairing in a lower-energy t_{2g} orbital costs less energy than promotion to an e_g orbital. The first three electrons singly occupy the three t_{2g} orbitals; the fourth pairs in one of these orbitals. The configuration is therefore

$$d^4 : \qquad t_{2g}^4 e_g^0.$$

The three t_{2g} orbital occupancies are $(2, 1, 1)$, so this low-spin configuration has two unpaired electrons.

Step 2: Explain the cobalt complex in part (ii) Neutral cobalt has configuration $[Ar]3d^7 4s^2$. Removing two $4s$ electrons and one $3d$ electron gives Co^{3+} as $[Ar]3d^6$. In $[Co(NH_3)_6]^{3+}$, the ligand field produces pairing of these six electrons in three $3d$ orbitals. This leaves two vacant $3d$ orbitals available for hybridisation with the $4s$ and three $4p$ orbitals. Thus d^2sp^3 hybridisation uses inner $3d$ orbitals, accounting for the inner orbital complex.

Step 3: Explain the nickel complex in part (ii) Neutral nickel is $[Ar]3d^8 4s^2$, so Ni^{2+} is $[Ar]3d^8$. Eight electrons cannot fit in only three $3d$ orbitals, whose total capacity is six. Thus two vacant $3d$ orbitals cannot be made available for octahedral d^2sp^3 hybridisation. The complex instead uses the $4s$, three $4p$, and two outer $4d$ orbitals, giving sp^3d^2 hybridisation. Hence $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Step 4: Count the dissolved ions for part (iii) The four chloride ions lie outside the coordination sphere, whereas all six neutral ammonia ligands remain attached to platinum. Dissociation of one formula unit is

$$[Pt(NH_3)_6]Cl_4 \longrightarrow [Pt(NH_3)_6]^{4+} + 4\,Cl^-.$$

Quick Tip to Solve: For octahedral inner orbital hybridisation, check whether two inner d orbitals can be vacant; for ion counting, count the bracketed complex once and then add only its outside counterions.

It produces one complex cation and four chloride anions. The total is therefore $1 + 4 = 5$ ions; the six coordinated ammonia molecules do not add to this ion count.

Step 5: Conclusion (i) $t_{2g}^4 e_g^0$; (ii) $[Co(NH_3)_6]^{3+}$ uses inner $3d$ orbitals with d^2sp^3 hybridisation, while $[Ni(NH_3)_6]^{2+}$ uses outer $4d$ orbitals with sp^3d^2 hybridisation; (iii) $[Pt(NH_3)_6]Cl_4$ gives five ions in solution.

Quick Tip to Solve: For octahedral inner orbital hybridisation, check whether two inner d orbitals can be vacant; for ion counting, count the bracketed complex once and then add only its outside counterions.

OR

5(b). (i) Calculate the spin only magnetic moment of the complex $[Fe(H_2O)_6]^{2+}$. (Atomic number of Fe = 26)

(ii) Which out of the following two complexes is more stable and why? $[CoF_6]^{3-}$, $[Co(C_2O_4)_3]^{3-}$

(iii) Write the IUPAC name of the given complex: $[Pt(NH_3)_2Cl_2]$. [3 marks]

Solution:

Concept:

- For a complex with n unpaired electrons, the spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\text{BM}$, where BM denotes the Bohr magneton.
- A weak-field ligand gives a high-spin arrangement in an octahedral complex; chelating ligands attach through multiple donor atoms and enhance complex stability.
- Name ligands alphabetically before the metal, and indicate the metal oxidation state by a Roman numeral. Neutral ammine and anionic chlorido are the ligand names here.

Step 1: (i) Find the unpaired electrons and magnetic moment Iron has atomic number 26, so its ground-state configuration is $[Ar]3d^64s^2$. Formation of Fe^{2+} removes the two $4s$ electrons, giving $3d^6$. Water is a weak-field ligand, so the octahedral complex is high spin with arrangement $t_{2g}^4 e_g^2$. There is one pair and four unpaired electrons. Hence

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

Step 2: (ii) Compare the ligand denticities Both complexes contain cobalt in oxidation state $+3$. Fluoride is monodentate, whereas each oxalate ion, $C_2O_4{}^{2-}$, is bidentate and binds through two oxygen donor atoms. Three oxalate ligands form three chelate rings around the metal. Thus $[Co(C_2O_4)_3]^{3-}$ is more stable than $[CoF_6]^{3-}$ because of the chelate effect.

Step 3: (iii) Name the platinum complex In the neutral complex $[Pt(NH_3)_2Cl_2]$, both ammine ligands are neutral and each chlorido ligand has charge -1. If the platinum oxidation state is x, charge balance gives $x + 2(0) + 2(-1) = 0$, hence $x = +2$. Alphabetical order places ammine before chlorido; multiplicative prefixes do not affect this order. The neutral complex retains the metal name platinum. Since the formula does not specify geometry, no cis or trans descriptor is assigned.

Step 4: Conclusion (i) $\mu \approx 4.90\,\text{BM}$. (ii) $[Co(C_2O_4)_3]^{3-}$ is more stable due to the chelate effect. (iii) The IUPAC name is **diamminedichloridoplatinum(II)**.

Quick Tip to Solve: Remove the iron 4s electrons first, then count unpaired electrons in the high-spin d6 arrangement; determine platinum's charge from the two chlorido ligands.

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:

- A primary amine undergoes acylation with an acid chloride to form an N-substituted amide. The amine nitrogen attacks the electrophilic carbonyl carbon.
- The amino group strongly activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- Primary amines react with chloroform and alcoholic potassium hydroxide on heating to form isocyanides in the carbylamine reaction.

Step 1: (i) Acylation of ethanamine Ethanamine, $CH_3CH_2NH_2$, reacts with acetyl chloride, CH_3COCl, to form N-ethylethanamide. The acetyl group replaces one hydrogen attached to nitrogen:

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

The carbonyl carbon of acetyl chloride becomes bonded to nitrogen. The ethyl group remains attached to nitrogen, so the product is an amide and not an ester. A base or excess amine can remove the HCl formed.

Step 2: (ii) Bromination of aniline Aniline reacts readily with bromine water at room temperature without a Lewis-acid catalyst. The strongly activating amino group permits substitution at both ortho positions and the para position:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr.$$

The product is **2,4,6-tribromoaniline**, obtained as a white precipitate. Three ring hydrogens are replaced, so three molecules of bromine are consumed and three molecules of hydrogen bromide are formed. Under these conditions, the reaction does not stop at monobromination.

Step 3: (iii) Carbylamine reaction of aniline Aniline is a primary amine and gives the carbylamine reaction with chloroform and ethanolic potassium hydroxide on heating:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{ethanol}]{\Delta} C_6H_5NC + 3KCl + 3H_2O.$$

Phenyl isocyanide, C_6H_5NC, has an offensive odour. The phenyl group is bonded to nitrogen in the isocyanide; it is not the nitrile C_6H_5CN. The three chlorine atoms of chloroform account for the three molecules of KCl, and the equation is balanced for all atoms.

Step 4: Conclusion The products are (i) **N-ethylethanamide**, (ii) **2,4,6-tribromoaniline** (white precipitate), and (iii) **phenyl isocyanide** on heating with chloroform and ethanolic KOH, according to the balanced equations above.

Quick Tip to Solve: Keep the ethyl group on nitrogen during acylation; use three Br2 for bromine water and write NC, not CN, for the carbylamine product.

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:

- In naming an amine, choose an alkyl group attached to nitrogen as the parent alkanamine; other groups attached to nitrogen are named with the locant N.
- Gabriel synthesis produces primary aliphatic amines through alkylation of potassium phthalimide followed by hydrolysis.
- Hofmann bromamide degradation converts a primary amide into a primary amine having one carbon atom fewer, using bromine and aqueous alkali.

Step 1: (i) Name the tertiary amine The nitrogen in $(CH_3CH_2)_2NCH_3$ is bonded to two ethyl groups and one methyl group. Choose one ethyl group as the parent, giving ethanamine. The remaining ethyl and methyl groups are substituents on nitrogen and are listed alphabetically. Thus its IUPAC name is $\boxed{N\text{-ethyl-}N\text{-methylethanamine}}$. The N-locants distinguish these substituents from substituents on the carbon chain.

Step 2: (ii)(I) Write Gabriel phthalimide synthesis Phthalimide first reacts with potassium hydroxide to form potassium phthalimide. Reaction with a primary alkyl halide RX, where R is an alkyl group and X a halogen, gives an N-alkylphthalimide. Alkaline hydrolysis then liberates the primary amine:

$$C_6H_4(CO)_2NH + KOH \longrightarrow C_6H_4(CO)_2NK + H_2O,$$
$$C_6H_4(CO)_2NK + RX \longrightarrow C_6H_4(CO)_2NR + KX,$$
$$C_6H_4(CO)_2NR + 2KOH \xrightarrow{\Delta} C_6H_4(COOK)_2 + RNH_2.$$

The final products are potassium phthalate and the primary amine. The nitrogen of phthalimide becomes the nitrogen of the amine; the alkyl group remains intact.

Step 3: (ii)(II) Write Hofmann bromamide degradation Heat a primary amide with bromine and aqueous sodium hydroxide. The balanced general equation is

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

Here R is the group attached to the carbonyl carbon. The carbonyl carbon is removed from the organic product and appears in carbonate, so the resulting primary amine has one carbon atom fewer than the starting amide.

Step 4: Conclusion The compound is N-ethyl-N-methylethanamine. Gabriel synthesis gives RNH_2 by alkylating and hydrolysing phthalimide, while Hofmann degradation gives RNH_2 from $RCONH_2$ with loss of the carbonyl carbon.

Quick Tip to Solve: In amine names use N for groups on nitrogen; in Hofmann degradation remove the amide carbonyl carbon when counting the product's carbons.

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 with water and the size of the nonpolar hydrocarbon portion of a molecule.
- The amino group donates its nitrogen lone pair to a benzene ring, but protonation converts it to an electron-withdrawing anilinium group.
- A nucleophile is an electron-pair donor that attacks an electron-deficient centre to form a covalent bond.

Step 1: (i) Compare solubility in water Ethylamine, $C_2H_5NH_2$, forms intermolecular hydrogen bonds with water: its nitrogen lone pair can accept a hydrogen bond and its $N-H$ bonds can donate hydrogen bonds. Its ethyl group is small, so these favourable interactions make it soluble in water. Aniline, $C_6H_5NH_2$, also has an amino group capable of hydrogen bonding, but its large nonpolar phenyl group opposes hydration. This hydrophobic portion dominates, making aniline practically insoluble (only sparingly soluble) in water. The difference is therefore not an absence of hydrogen bonding in aniline.

Step 2: (ii) Explain the meta product on nitration In free aniline, the nitrogen lone pair is delocalised into the ring by resonance, increasing electron density especially at the ortho and para positions. Thus $-NH_2$ normally directs electrophilic substitution to these positions. However, the strongly acidic nitrating mixture protonates a substantial proportion of aniline:

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

In the anilinium ion, nitrogen has no available lone pair to donate to the ring. The positively charged $-NH_3^+$ group withdraws electron density and is meta-directing. Nitration of this protonated species, followed by deprotonation, therefore gives a substantial amount of m-nitroaniline, alongside products associated with free aniline.

Step 3: (iii) Explain nucleophilic behaviour Amines contain a lone pair of electrons on nitrogen. They can donate this pair to an electron-deficient centre, creating a new covalent bond; hence they behave as nucleophiles. For example, in alkylation an amine attacks the partially positive carbon bonded to the halogen in an alkyl halide. Although the lone pair in aniline is partly delocalised into its ring and is less readily available than in an aliphatic amine, its nitrogen can still participate in nucleophilic reactions.

Step 4: Conclusion Ethylamine is water-soluble because hydrogen bonding outweighs its small nonpolar group; aniline's larger phenyl group limits solubility. Acidic nitration forms meta-directing anilinium ions, giving substantial m-nitroaniline. Amines are nucleophiles because nitrogen donates its lone pair.

Quick Tip to Solve: For aniline in an acidic reaction, check whether $-NH_2$ has become $-NH_3^+$ before deciding the directing effect.

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 of a nitro group converts $-NO_2$ into $-NH_2$ without changing the carbon skeleton. Tin and hydrochloric acid reduce nitrobenzene; alkali then liberates the free amine from its salt.
- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into RNH_2, with one fewer carbon atom, using bromine and aqueous alkali.
- Reduction of a nitrile RCN converts its nitrile carbon into a $-CH_2NH_2$ group. Unlike the Hofmann reaction, this reduction retains the total number of carbon atoms.

Step 1: (i) Reduce nitrobenzene to aniline Heat nitrobenzene with tin and hydrochloric acid. The nitro group is reduced, and aniline is initially present as anilinium chloride in the acidic medium. Add aqueous sodium hydroxide to obtain free aniline. The reduction and liberation can be represented as:

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

$$C_6H_5NH_3Cl + NaOH \longrightarrow C_6H_5NH_2 + NaCl + H_2O.$$

Here $[H]$ denotes reducing hydrogen equivalents, and the second equation explicitly shows the necessary alkaline work-up.

Step 2: (ii) Degrade ethanamide to methanamine Treat ethanamide with bromine and aqueous sodium hydroxide and warm. Hofmann bromamide degradation removes the carbonyl carbon, so the two-carbon amide gives the one-carbon primary amine:

$$CH_3CONH_2 + Br_2 + 4NaOH \longrightarrow CH_3NH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

Methanamine is CH_3NH_2. Ordinary reduction of ethanamide would retain both carbons and would therefore not give this target.

Step 3: (iii) Reduce ethanenitrile to ethanamine Reduce ethanenitrile with lithium aluminium hydride in dry ether, followed by aqueous work-up:

$$CH_3CN + 4[H] \xrightarrow{\text{LiAlH}_4/\text{ether}} CH_3CH_2NH_2.$$

Both carbon atoms are retained: the nitrile carbon becomes the carbon of the $-CH_2NH_2$ group. The product is ethanamine, a primary amine.

Step 4: Conclusion Use Sn/HCl, followed by $NaOH$, for nitrobenzene to aniline; $Br_2/NaOH$ for ethanamide to methanamine; and LiAlH_4 in dry ether followed by aqueous work-up for ethanenitrile to ethanamine.

Quick Tip to Solve: Count carbons first: Hofmann degradation removes the amide carbonyl carbon, whereas nitro and nitrile reductions preserve the carbon skeleton.

8. Arrange the following compounds in the increasing order of their property indicated:

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

(ii) $(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$ **(Acidic strength)**

(iii) CH_3CH_2OH, CH_3CHO, CH_3COOH **(Boiling point)** [3 marks]

Solution:

Concept:

- HCN adds to a carbonyl compound by nucleophilic attack of CN^- on its electrophilic carbonyl carbon. Electron donation and steric crowding reduce this reactivity; aldehydes are generally more reactive than ketones.
- Carboxylic acid strength increases when an electron-withdrawing substituent stabilises the carboxylate ion through its negative inductive effect. This effect becomes weaker as the substituent moves farther from $-COOH$.
- Boiling point depends on intermolecular attractions. Hydrogen bonding raises the boiling points of alcohols and carboxylic acids, and carboxylic acids associate strongly as hydrogen-bonded dimers.

Step 1: (i) Compare reactivity towards HCN An aldehyde has only one carbon group and one hydrogen attached to its carbonyl carbon, whereas a ketone has two carbon groups. Thus aldehydes offer less steric hindrance and less electron donation to the carbonyl carbon. Phenyl conjugation reduces carbonyl electrophilicity, placing acetophenone below acetone and benzaldehyde below acetaldehyde. The increasing order is:

$$\text{Acetophenone} < \text{Acetone} < \text{Benzaldehyde} < \text{Acetaldehyde}.$$

Step 2: (ii) Compare acidic strength In $(CH_3)_2CHCOOH$, the alkyl groups have an electron-releasing inductive effect, which opposes stabilisation of the carboxylate ion. Bromine has an electron-withdrawing inductive effect and increases acidity. In $CH_3CH(Br)CH_2COOH$, bromine is on the beta carbon; in $CH_3CH_2CH(Br)COOH$, it is on the alpha carbon, nearer the carboxyl group. Its effect is therefore stronger in the latter compound. The increasing order is:

$$(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH.$$

Step 3: (iii) Compare boiling points Ethanal, CH_3CHO, has dipole-dipole attractions but lacks an $O-H$ group, so its molecules cannot form hydrogen bonds with one another. Ethanol, CH_3CH_2OH, has intermolecular hydrogen bonding and boils at a higher temperature. Ethanoic acid, CH_3COOH, forms strongly associated dimers with two hydrogen bonds, giving the highest boiling point. Hence:

$$CH_3CHO < CH_3CH_2OH < CH_3COOH.$$

Step 4: Conclusion Increasing orders: (i) acetophenone < acetone < benzaldehyde < acetaldehyde; (ii) $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$; (iii) $CH_3CHO < CH_3CH_2OH < CH_3COOH$.

Quick Tip to Solve: For these orders, check aldehyde versus ketone, then phenyl conjugation; locate Br relative to COOH; and compare no hydrogen bonding, alcohol bonding and acid dimers.

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:

- A transition-metal ion commonly shows colour through absorption of visible light in a d-d transition. Such a transition needs an occupied d orbital and another d orbital of higher energy available to receive the electron.
- A half-filled d^5 subshell has extra stability. Oxidation removes electrons, 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 In forming transition-metal cations, the $4s$ electrons are removed before the $3d$ electrons. The configurations of the given ions are

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

The d^0 ion has no d electron available for a d-d transition. The other two ions have partially filled d orbitals and can show colour through such transitions.

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

$$\mathrm{Mn}^{2+} : [\mathrm{Ar}]\, 3d^5, \quad \mathrm{Mn}^{3+} : [\mathrm{Ar}]\, 3d^4,$$
$$\mathrm{Fe}^{2+} : [\mathrm{Ar}]\, 3d^6, \quad \mathrm{Fe}^{3+} : [\mathrm{Ar}]\, 3d^5.$$

Oxidising Mn^{2+} destroys its stable half-filled $3d^5$ configuration. In contrast, oxidation of Fe^{2+} produces the stable half-filled configuration of Fe^{3+}. Thus the electronic-configuration change favours oxidation of the iron ion more than that of the manganese ion.

Step 3: (iii) Explain the role of oxygen and fluorine The highest oxidation state corresponds to extensive involvement of the metal's valence electrons in bonding. Oxygen and fluorine, being highly electronegative, attract electron density strongly and make strong metal–oxygen or metal–fluorine bonds. These bonds stabilise the metal in its highest oxidation state. For example, manganese has oxidation state $+7$ in $\mathrm{Mn_2O_7}$, while vanadium has oxidation state $+5$ in $\mathrm{VF_5}$. Oxygen can additionally stabilise high oxidation states through multiple bonding to a metal.

Step 4: Conclusion (i) Ti^{4+} is colourless because it is $3d^0$ and cannot undergo a d-d transition. (ii) Mn^{2+} resists oxidation because its stable $3d^5$ configuration would be lost, whereas oxidation of Fe^{2+} gives stable $3d^5$. (iii) Strong bonds with highly electronegative oxygen or fluorine stabilise the highest oxidation states of metals.

Quick Tip to Solve: Remove $4s$ electrons first when finding an ion's d count; then look for d^0 to explain absence of d-d colour and d^5 to compare oxidation stability.

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

Zn | Zn^{2+} (0.1 M) || Cd^{2+} (0.01) | Cd

Given: $E^{\circ}_{Zn^{2+}/Zn}$ = -0.76 V, $E^{\circ}_{Cd^{2+}/Cd}$ = -0.40 V (log 10 = 1) [3 marks]

Solution:

Concept:

- The cell emf is $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$, using reduction potentials for both electrodes. The left-hand electrode in the given cell is the anode and the right-hand electrode is the cathode.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred per balanced reaction and Q is its reaction quotient. Potentials are in volts and the logarithm is to base ten.
- Pure solids have unit activity and do not appear in Q. For these dilute solutions, use the numerical molar concentrations to represent the ionic activities relative to the standard concentration.

Step 1: Write the electrode reactions and reaction quotient Zinc undergoes oxidation at the anode: $\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-}$. Cadmium ions undergo reduction at the cathode: $\mathrm{Cd^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cd(s)}$. Adding gives the balanced cell reaction

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

Two electrons are transferred, so $n = 2$. Only the aqueous ions enter the quotient:

$$Q = \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cd^{2+}}]} = \frac{0.1}{0.01} = 10.$$

Step 2: Calculate the standard cell emf Both given values are reduction potentials, so subtract the zinc value from the cadmium value:

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\mathrm{Cd^{2+}/Cd}} - E^{\circ}_{\mathrm{Zn^{2+}/Zn}} \\ &= (-0.40) - (-0.76) = 0.36\,\mathrm{V}. \end{aligned}$$

Step 3: Apply the Nernst equation to the cell For this cell at 298 K, substitute $n = 2$ and the concentration ratio into the required equation:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2}\log\frac{[\mathrm{Zn^{2+}}]}{[\mathrm{Cd^{2+}}]}.$$

Using $\log 10 = 1$,

$$\begin{aligned} E_{\text{cell}} &= 0.36 - \frac{0.0591}{2}\log 10 \\ &= 0.36 - 0.02955 = 0.33045\,\mathrm{V}. \end{aligned}$$

Since $Q > 1$, the nonstandard concentrations lower the emf below its standard value, consistent with the negative correction.

Step 4: Conclusion The Nernst equation for the given cell uses $n = 2$ and $Q = [\mathrm{Zn^{2+}}]/[\mathrm{Cd^{2+}}] = 10$. At 298 K, its emf is $\boxed{E_{\text{cell}} \approx 0.330\,\mathrm{V}}$.

Quick Tip to Solve: Write the balanced reaction before forming Q: the zinc ion is the product, so put $[\mathrm{Zn^{2+}}]$ in the numerator and use $n = 2$.

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 $E^{\circ}_{M^{2+}/M}$ 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 $M^{2+}(aq) + 2e^- \rightarrow M(s)$. Extra stability of the divalent ion can make its reduction less favourable.
- An alloy is a metallic mixture or solid solution; similar atomic sizes allow one metal atom to replace another in a crystal lattice.

Step 1: (i) Apply the transition-element definition to silver The ground-state electronic configuration of silver is $Ag : [Kr]4d^{10}5s^1$, so its neutral atom has a filled d-subshell. However, silver also exhibits the $+2$ oxidation state. Removing the $5s$ electron and one $4d$ electron gives $Ag^{2+} : [Kr]4d^9$, which has an incompletely filled d-subshell. The definition considers accessible oxidation states as well as the neutral atom; a filled d-subshell in the atom alone therefore does not exclude silver.

Step 2: (ii) Explain the unusually negative reduction potentials Manganese forms $Mn^{2+} : [Ar]3d^5$, with an especially stable half-filled d-subshell. Zinc forms $Zn^{2+} : [Ar]3d^{10}$, with an especially stable completely filled d-subshell. These stable divalent configurations favour the ions relative to the trend expected across the series. Consequently, reduction of these ions to the metals is relatively unfavourable, accounting for their more negative $E^{\circ}_{M^{2+}/M}$ values. The relevant configurations here are those of the divalent ions, not just those of the neutral atoms.

Step 3: (iii) Relate alloy formation to atomic sizes Transition metals have comparable atomic radii and often similar crystal structures. An atom of one transition metal can therefore substitute for an atom of another in the metallic lattice with relatively little distortion. Their compatible metallic bonding stabilises the resulting solid solution, so mixtures of transition metals readily form alloys.

Step 4: Conclusion (i) Silver qualifies because Ag^{2+} has the incomplete $4d^9$ configuration. (ii) The stable $3d^5$ and $3d^{10}$ configurations of Mn^{2+} and Zn^{2+}, respectively, account for their unusually negative reduction potentials. (iii) Similar atomic sizes permit substitution in metallic lattices and hence alloy formation.

Quick Tip to Solve: For transition-element questions, check an ionic d-configuration too; for these potentials, write Mn(II) as d5 and Zn(II) as d10 before explaining their stability.

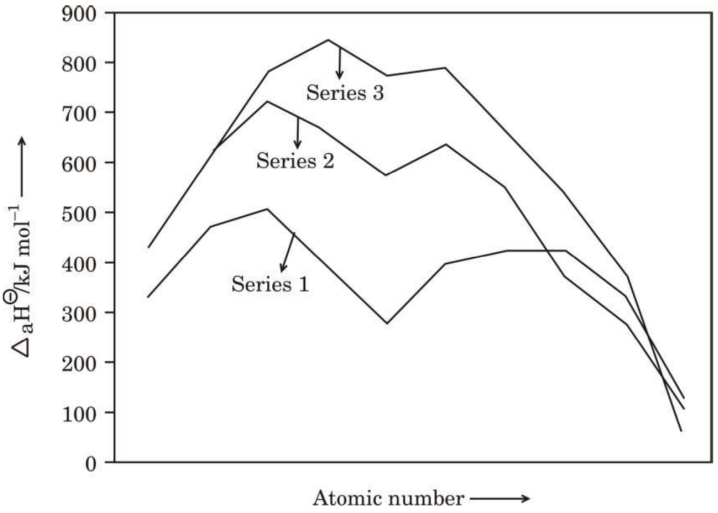
OR

11(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 enthalpy change for producing one mole of separate gaseous atoms from an element in its standard state. For a metal, $\mathrm{M(s)} \rightarrow \mathrm{M(g)}$ requires breaking metallic bonds.
- Stronger metal-metal bonding gives a greater enthalpy of atomisation; both s- and d-electrons can contribute to metallic bonding in transition metals.
- Unpaired d-electrons and effective overlap of metal orbitals strengthen interatomic bonding.

Step 1: (i) Identify the lowest point in the first series The curve marked Series 1 represents the 3d series. Its lowest value occurs at the right-hand end, corresponding to zinc, the last element of that series. Zinc has the configuration $[Ar]3d^{10}4s^2$; its filled $3d$ subshell has no unpaired d-electrons. The resulting metal-metal bonding is relatively weak compared with the bonding in most other members of the series, so comparatively little energy is needed to separate zinc atoms.

Step 2: (ii) Compare the second and third series with the first The curves marked Series 2 and Series 3 lie generally above Series 1. Metals of the 4d and 5d series form stronger metal-metal bonds than corresponding metals of the 3d series. Their more spatially extended d-orbitals allow effective overlap and stronger interatomic bonding. Greater participation of d-electrons in bonding, associated with the available unpaired electrons, makes their enthalpies of atomisation generally higher. Thus more energy is required to separate these metals into gaseous atoms.

Step 3: (iii) Explain the generally high values for transition metals Transition metals generally possess several unpaired d-electrons in addition to their outer s-electrons. The involvement of both sets of electrons leads to strong interatomic metallic bonding. Atomisation must overcome these cohesive forces to produce isolated gaseous atoms, so its enthalpy is quite high. This explanation is a general

Quick Tip to Solve: Read the lowest endpoint of the Series 1 curve as zinc, and explain each higher atomisation enthalpy by the extra energy needed to break stronger metal-metal bonds.

trend: the filled d-subshell of zinc accounts for its unusually low value rather than contradicting the trend.

Step 4: Conclusion (i) Zinc has the lowest enthalpy of atomisation in the 3d series. (ii) The second and third series generally have stronger metal-metal bonding and hence greater enthalpies of atomisation. (iii) Strong bonding involving s-electrons and unpaired d-electrons gives transition metals generally high enthalpies of atomisation.

Quick Tip to Solve: Read the lowest endpoint of the Series 1 curve as zinc, and explain each higher atomisation enthalpy by the extra energy needed to break stronger metal-metal bonds.

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:

- For $r = k[A]^x[B]^y$, the order with respect to A is x, the order with respect to B is y, and the overall order is $x + y$.
- Reaction order is read from the experimentally determined rate law; fractional individual orders are allowed.

Step 1: Identify the individual orders In the given expression $r = k[A]^{1/2}[B]^{3/2}$, the concentration exponents are $1/2$ for A and $3/2$ for B. The rate constant k does not contribute to the sum of concentration powers.

Step 2: Add the concentration exponents The overall order is the sum of the orders with respect to all reactants appearing in the rate expression:

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

Use the powers in this rate law directly; coefficients of a separate chemical equation are not needed

Quick Tip to Solve: Add the two fractional concentration powers first: one-half plus three-halves equals two, even though neither individual order is an integer.

for this calculation.

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

Quick Tip to Solve: Add the two fractional concentration powers first: one-half plus three-halves equals two, even though neither individual order is an integer.

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

Solution:

Concept:

- Temperature changes the rate constant and hence the reaction rate at fixed reactant concentrations.
- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, R is the gas constant and T is absolute temperature.

Step 1: Consider the energy of reacting molecules On increasing temperature, the average kinetic energy of the molecules increases. A larger fraction of molecules then has energy equal to or greater than the activation energy needed for reaction.

Step 2: Connect effective collisions with the rate More collisions are effective in forming products. For the usual case of positive activation energy, the Arrhenius equation shows that k increases with T, so the reaction proceeds faster at the same concentrations. For many reactions near room temperature, a $10\,\text{K}$ rise approximately doubles the rate; this is an approximate trend, not a universal exact factor.

Step 3: Conclusion The rate of a reaction generally increases with increase in temperature and decreases on cooling.

Quick Tip to Solve: Explain the temperature effect through the increased fraction of molecules above activation energy, not merely faster motion.

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

Solution:

Concept:

- Reaction rate measures how quickly reactants are consumed or products are formed.
- Concentration change divided by the corresponding time interval gives the average rate; its usual unit is $\text{mol}\,\text{L}^{-1}\,\text{s}^{-1}$.

Step 1: Track the concentration change As a reaction proceeds, reactant concentration decreases and product concentration increases. The rate describes this change per unit time, rather than the total amount converted without specifying a time interval.

Step 2: Express a positive rate For a simple reaction $A \rightarrow B$ with unit stoichiometric coefficients, over a time interval Δt,

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

Quick Tip to Solve: Use a minus sign for reactant disappearance and a plus sign for product appearance so the reported rate is positive.

The minus sign compensates for the decreasing reactant concentration. For general stoichiometry, divide each concentration-change rate by its corresponding stoichiometric coefficient to obtain the common reaction rate.

Step 3: Conclusion The rate of a reaction is the change in concentration of a reactant or product per unit time.

Quick Tip to Solve: Use a minus sign for reactant disappearance and a plus sign for product appearance so the reported rate is positive.

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:

- The integrated first-order rate equation is $k = \frac{2.303}{t} \log \frac{a}{a-x}$, where a is the initial amount and x is the amount reacted in time t.
- For a first-order reaction, $t_{1/2} = 0.693/k$. The time for a specified percentage conversion is independent of the initial amount.

Step 1: Obtain the rate constant from half-completion At 50% completion, half of the initial reactant remains, so the stated time is the half-life:

$$t_{1/2} = 77.78\,\text{min}, \qquad k = \frac{0.693}{77.78} = 8.910 \times 10^{-3}\,\text{min}^{-1}.$$

The time unit is kept in minutes throughout, so the rate constant must be expressed per minute.

Step 2: Substitute the unreacted fraction at the required conversion At 30% completion, 70% remains: $a - x = 0.70a$. Thus the logarithm uses the initial amount divided by the remaining amount, not the reacted amount. Using the supplied base-ten logarithms,

$$\begin{aligned} \log \frac{a}{a-x} &= \log \frac{10}{7} \\ &= \log 10 - \log 7 = 1 - 0.8450 = 0.1550, \\ t &= \frac{2.303}{8.910 \times 10^{-3}}(0.1550) \\ &\approx 40.06\,\text{min}. \end{aligned}$$

This is shorter than the half-life, as expected because only 30%, rather than 50%, has reacted.

Step 3: Conclusion The time required for 30% completion is approximately $\boxed{40.06\,\text{min}}$.

Quick Tip to Solve: Convert percentage reacted to percentage remaining before using the first-order logarithm: here use 70, not 30.

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, $t = \frac{2.303}{k} \log \frac{a}{a-x}$, where a is the initial amount and $a - x$ is the amount remaining after time t.
- At constant volume, the concentration ratio equals the ratio of masses of the same reactant. A first-order rate constant has units of inverse time.

Step 1: Identify the initial and remaining amounts The initial reactant mass is $a = 5\,\text{g}$, and the final mass remaining is $a - x = 3\,\text{g}$. Although $2\,\text{g}$ has reacted, it is the remaining mass $3\,\text{g}$ that belongs in the denominator of the integrated rate equation. The rate constant is $k = 1 \times 10^{-3}\,\text{s}^{-1}$, so the calculated time will be in seconds.

Step 2: Evaluate the logarithm and calculate the time Substitute the mass ratio and use the supplied logarithms:

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

Since the reactant decreases from $5\,\text{g}$ to $3\,\text{g}$, the initial-to-final ratio exceeds one and its logarithm is positive, giving a positive elapsed time.

Step 3: Conclusion The required time is $\boxed{511\,\text{s}}$, approximately $8.52\,\text{min}$.

Quick Tip to Solve: In the first-order expression, divide the initial mass by the mass still present; the mass consumed is not the denominator.