CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-4-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) This question paper is divided into **five** sections – **Section A, B, C, D** and **E**.

(iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – questions number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – questions number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – questions number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is not allowed.

Section A (16 marks)

*Questions no. **1** to **16** are Multiple Choice type Questions, carrying **1** mark each.*

1. In an electrochemical cell, the following reaction takes place:

$2Cu^{+}(aq) + Zn(s) \rightarrow 2Cu(s) + Zn^{2+}(aq)$

$E^{\circ}_{cell} = 1.28$ V

As the reaction progresses, what will happen to the overall voltage of the cell? [1 mark]

(A) Voltage will remain constant.

(B) It will decrease as $[Zn^{2+}]$ increases.

(C) It will increase as $[Cu^{+}]$ increases.

(D) It will increase as $[Zn^{2+}]$ increases.

Correct Answer: (B) It will decrease as $[Zn^{2+}]$ increases.

Solution:

Concept:

- The Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/nF)\ln Q$, where Q is the reaction quotient and n is the number of electrons transferred.
- Pure solids have unit activity. For dilute solutions, ionic activities are represented by their concentrations relative to the standard concentration.

Step 1: Write the reaction quotient Zinc loses two electrons, while two Cu^{+} ions each gain one electron. Thus $n = 2$. The solids Zn and Cu do not appear in the concentration quotient:

$$Q = \frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{+}]^{2}}.$$

Step 2: Follow the changes as the reaction proceeds The forward reaction produces Zn^{2+} and consumes Cu^{+}, so the numerator increases while the denominator decreases. Consequently Q increases and the quantity subtracted from E°_{cell} increases. The voltage therefore cannot remain constant as in (A). Option (D) reverses the effect of increasing $[\mathrm{Zn}^{2+}]$; (C) refers to increasing $[\mathrm{Cu}^{+}]$, whereas this reactant concentration actually falls during the stated reaction.

Step 3: Conclusion The cell voltage decreases as $[\mathrm{Zn}^{2+}]$ increases. Hence, the correct option is (B).

Quick Tip to Solve: Put product-ion concentrations above reactant-ion concentrations in Q; an increase in Q lowers the cell potential.

2. Out of Fe^{3+}, Sc^{3+}, Cr^{3+} and Co^{3+} ions, the one which is colourless in aqueous solution is:
[Atomic number: Fe = 26, Sc = 21, Cr = 24, Co = 27] [1 mark]

(A) Sc^{3+}

(B) Fe^{3+}

(C) Cr^{3+}

(D) Co^{3+}

Correct Answer: (A) Sc^{3+}

Solution:

Concept:

- Aqueous transition-metal ions commonly show colour because visible light can promote electrons between split d orbitals.
- A d^0 ion has no d electron available for a d-d transition. When forming these ions, remove $4s$ electrons before $3d$ electrons.

Step 1: Determine the configuration of the scandium ion Scandium, with atomic number 21, has configuration $[Ar]3d^1 4s^2$. Removing three electrons gives Sc^{3+} : $[Ar]3d^0$. There is therefore no d electron that can absorb visible light through a d-d transition in this aqueous ion.

Step 2: Compare the other ions The corresponding configurations are Fe^{3+} : $3d^5$, Cr^{3+} : $3d^3$ and Co^{3+} : $3d^6$, with the $[Ar]$ core understood. Each has a partially occupied d subshell and gives coloured aqueous species. Thus the empty d subshell distinguishes scandium from the ions in (B), (C) and (D).

Step 3: Conclusion Sc^{3+} is colourless in aqueous solution. Hence, the correct option is (A).

Quick Tip to Solve: For Sc^{3+}, remove both $4s$ electrons and the single $3d$ electron: the resulting d^0 configuration identifies the colourless ion.

3. Hoffmann Bromamide degradation reaction is given by: [1 mark]

(A) $ArNO_2$

(B) $ArNH_2$

(C) $ArCONH_2$

(D) $ArCH_2NH_2$

Correct Answer: (C) $ArCONH_2$

Solution:

Concept:

- Hoffmann bromamide degradation converts a primary amide, $RCONH_2$, into a primary amine, RNH_2, using bromine and aqueous alkali.
- The product amine contains one carbon atom fewer than the starting amide because the carbonyl carbon is removed.

Step 1: Identify the required functional group The starting compound must contain the primary amide group $-CONH_2$. Of the printed choices, only $ArCONH_2$ has this group; here Ar represents an

Quick Tip to Solve: Look for $-CONH_2$ in the reactant; Hoffmann degradation removes its carbonyl carbon and leaves $-NH_2$.

aryl group. Its balanced reaction with bromine and sodium hydroxide is

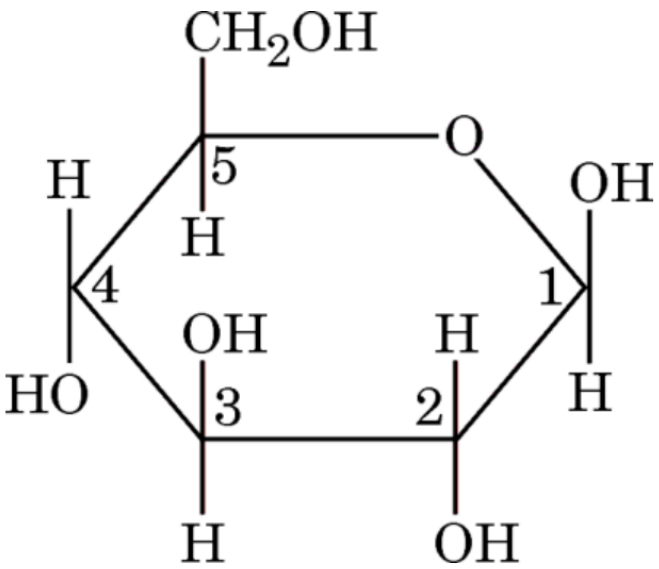
$$\mathrm{ArCONH_2 + Br_2 + 4\,NaOH \longrightarrow ArNH_2 + 2\,NaBr + Na_2CO_3 + 2\,H_2O.}$$

Step 2: Eliminate compounds with other functional groups $\mathrm{ArNO_2}$ is a nitro compound and does not contain an amide group. $\mathrm{ArNH_2}$ and $\mathrm{ArCH_2NH_2}$ are already amines and have no carbonyl group for this degradation. In particular, $\mathrm{ArNH_2}$ is the product from the aromatic amide, so it must not be confused with the required starting compound.

Step 3: Conclusion Hoffmann bromamide degradation is given by $\mathrm{ArCONH_2}$. Hence, the correct option is (C).

Quick Tip to Solve: Look for $-\mathrm{CONH_2}$ in the reactant; Hoffmann degradation removes its carbonyl carbon and leaves $-\mathrm{NH_2}$.

4. In the Haworth structure of the following carbohydrate, various carbon atoms have been numbered. The anomeric carbon is numbered as: [1 mark]



(A) 1

(B) 2

(C) 3

(D) 5

Correct Answer: (A) 1

Solution:

Concept:

- The anomeric carbon is the carbonyl carbon of an open-chain sugar that becomes a new stereogenic centre on ring formation.
- In a cyclic hemiacetal, the anomeric carbon is bonded to two oxygen atoms: the ring oxygen and

Quick Tip to Solve: In a Haworth ring, find the carbon attached both to the ring oxygen and to an $-\mathrm{OH}$ oxygen; that is the anomeric carbon.

the oxygen of a hydroxyl group.

Step 1: Locate the carbon bonded to two oxygens In the printed Haworth structure, the right-hand carbon labelled 1 is directly bonded to the ring oxygen and also carries an $-OH$ group. These two carbon-oxygen bonds identify the hemiacetal centre formed from the aldehyde carbon of the open-chain aldose.

Step 2: Check the other numbered positions Carbons 2 and 3 carry hydroxyl groups but are not directly attached to the ring oxygen. Carbon 5 is attached to the ring oxygen, but its other substituents include $-CH_2OH$ and hydrogen; it does not carry the anomeric hydroxyl group. Therefore being next to the ring oxygen alone is insufficient: the carbon must be attached to both oxygens.

Step 3: Conclusion The anomeric carbon is numbered 1. Hence, the correct option is (A).

Quick Tip to Solve: In a Haworth ring, find the carbon attached both to the ring oxygen and to an $-OH$ oxygen; that is the anomeric carbon.

5. The value of Henry's constant K_H is: [1 mark]

(A) greater for gases with higher solubility

(B) greater for gases with lower solubility

(C) constant for all gases

(D) not related to the solubility of gases

Correct Answer: (B) greater for gases with lower solubility

Solution:

Concept:

- Henry's law in the convention used here is $p = K_H x$, where p is the gas partial pressure above the solution and x is its mole fraction in the liquid.
- Compare gas solubilities at the same temperature and pressure in the same solvent. A larger dissolved mole fraction means greater solubility.

Step 1: Express solubility in terms of the constant Rearranging Henry's law gives

$$x = \frac{p}{K_H}.$$

At fixed partial pressure, the dissolved mole fraction varies inversely with K_H. For example, doubling K_H while holding p constant halves x, so less gas dissolves.

Step 2: Compare the statements Option (A) reverses this inverse relationship: higher solubility corresponds to a smaller, not larger, K_H. Option (C) is incorrect because the constant depends on the gas, solvent and temperature. Option (D) is incorrect because the equation explicitly connects K_H to the dissolved mole fraction and hence to solubility.

Step 3: Conclusion Henry's constant is greater for gases with lower solubility under the same comparison conditions. Hence, the correct option is (B).

Quick Tip to Solve: First write $p = K_H x$; at fixed p, a larger denominator in $x = p/K_H$ means lower gas solubility.

6. Out of the following statements, the incorrect statement is: [1 mark]

(A) La is actually an element of transition series.

(B) Zr and Hf have almost identical atomic radii because of lanthanoid contraction.

(C) Ionic radius decreases from La^{3+} to Lu^{3+} ion.

(D) Lanthanoids are radioactive in nature.

Correct Answer: (D) Lanthanoids are radioactive in nature.

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in size along the series, caused by increasing nuclear charge and the poor shielding of $4f$ electrons.
- Radioactivity is not a general property of all lanthanoids. Promethium has no stable isotope, whereas the other lanthanoids have naturally occurring stable isotopes.

Step 1: Check the electronic and size statements Lanthanum has the ground-state configuration $[Xe]5d^16s^2$; its partially occupied d subshell makes statement (A) correct. Lanthanoid contraction offsets the expected size increase from Zr to Hf, explaining their nearly identical atomic radii in (B). The same contraction causes the overall decrease in ionic radius from La^{3+} to Lu^{3+}, so (C) is also correct.

Step 2: Examine the claim about radioactivity The statement that lanthanoids are radioactive as a class is too broad. Promethium is the lanthanoid for which all isotopes are radioactive; most members are not exclusively radioactive elements. The general statement that all members are radioactive applies to the actinoid series instead, which is the source of the tempting confusion here.

Step 3: Conclusion The incorrect statement is "Lanthanoids are radioactive in nature." Hence, the correct option is (D).

Quick Tip to Solve: Separate the series: all actinoids are radioactive, while promethium is the lanthanoid with no stable isotope.

7. Out of 2-Bromobutane, 1-Bromobutane, 2-Bromopropane and 1-Bromopropane, the molecule which is chiral in nature is: [1 mark]

(A) 2-Bromobutane

(B) 1-Bromobutane

(C) 2-Bromopropane

(D) 1-Bromopropane

Correct Answer: (A) 2-Bromobutane

Solution:

Concept:

- For these simple haloalkanes, a tetrahedral carbon attached to four different groups is a stereogenic centre and produces a chiral molecule.

Quick Tip to Solve: At carbon 2 of 2-bromobutane, list Br, H, methyl and ethyl; the unequal alkyl groups are the decisive feature.

- Identical groups on the candidate carbon prevent it from being a stereogenic centre. Compare whole attached groups, not just their first atoms.

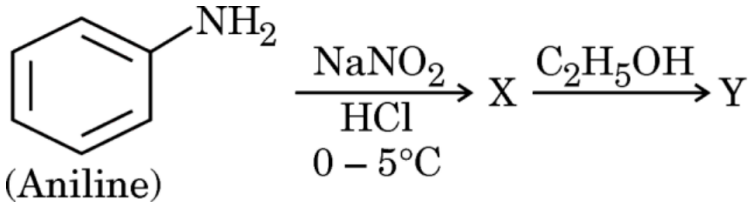
Step 1: Inspect the substituted carbon of 2-bromobutane The structure is $CH_3-CH(Br)-CH_2-CH_3$. Its second carbon is bonded to bromine, hydrogen, a methyl group $-CH_3$ and an ethyl group $-CH_2CH_3$. All four groups differ, so this carbon is stereogenic and its mirror-image arrangements are not superimposable.

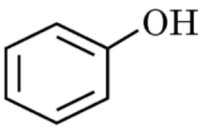
Step 2: Test the remaining candidates In 1-bromobutane and 1-bromopropane, the bromine-bearing terminal carbon is $-CH_2Br$, with two identical hydrogen atoms; neither molecule has another stereogenic carbon. In 2-bromopropane, $CH_3-CH(Br)-CH_3$, the central carbon is bonded to two identical methyl groups. Thus none of (B), (C) or (D) satisfies the four-different-groups test.

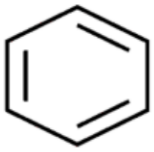
Step 3: Conclusion 2-Bromobutane is chiral. Hence, the correct option is (A).

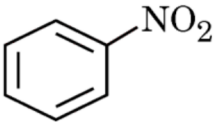
Quick Tip to Solve: At carbon 2 of 2-bromobutane, list Br, H, methyl and ethyl; the unequal alkyl groups are the decisive feature.

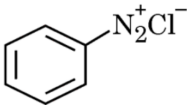
8. In the given reaction sequence, the structure of Y would be: [1 mark]

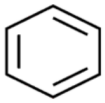


(A) Phenol 

(B) Benzene 

(C) Nitrobenzene 

(D) Benzenediazonium chloride 

Correct Answer: (B) Benzene 

Solution:

Concept:

- Aniline reacts with nitrous acid generated from $NaNO_2$ and HCl at 0–5 °C to give a diazonium salt.
- Ethanol reduces an aromatic diazonium group to hydrogen; nitrogen gas is liberated and ethanol is oxidised to ethanal.

Step 1: Identify the intermediate Diazotisation converts the amino group into a diazonium group, so

Quick Tip to Solve: For a diazonium salt, ethanol replaces the diazonium group by H; warm water replaces it by OH.

X is benzenediazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2Cl + NaCl + 2\,H_2O.$$

The low temperature keeps this intermediate stable during its preparation.

Step 2: Apply the reaction with ethanol Ethanol replaces the diazonium group by hydrogen:

$$C_6H_5N_2Cl + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Phenol requires hydrolysis with warm water. Nitrobenzene is not formed by this reduction, while benzenediazonium chloride is X, the intermediate consumed in the second step.

Step 3: Conclusion Y is benzene, C_6H_6. Hence, the correct option is (B).

Quick Tip to Solve: For a diazonium salt, ethanol replaces the diazonium group by H; warm water replaces it by OH.

9. The product of the oxidation of I^- with MnO_4^- in alkaline medium is: [1 mark]

(A) IO_4^-

(B) I_2

(C) IO^-

(D) IO_3^-

Correct Answer: (D) IO_3^-

Solution:

Concept:

- Permanganate is an oxidising agent whose reduction product depends on the medium.
- In alkaline medium, iodide is oxidised to iodate, IO_3^-, while permanganate is reduced to manganese dioxide.

Step 1: Track the oxidation of iodine Iodine has oxidation state -1 in I^- and $+5$ in IO_3^-. It therefore loses six electrons per iodine atom. The balanced reaction is

$$2\,MnO_4^- + I^- + H_2O \longrightarrow 2\,MnO_2 + IO_3^- + 2\,OH^-.$$

Step 2: Compare the printed alternatives Iodate is the characteristic product for this oxidation in alkaline medium. Iodine, I_2, is obtained when iodide is oxidised by acidified permanganate. Hypoiodite, IO^-, and periodate, IO_4^-, are not the products of the stated reaction; their iodine oxidation states are $+1$ and $+7$, respectively.

Step 3: Conclusion The oxidation product is iodate, IO_3^-. Hence, the correct option is (D).

Quick Tip to Solve: Check the medium first: alkaline permanganate oxidises iodide to iodate, whereas acidified permanganate gives iodine.

10. Polyhalogen compounds have wide application in industries and agriculture. DDT is also a very important polyhalogen compound. It is a: [1 mark]

(A) greenhouse gas

(B) fertilizer

(C) biodegradable insecticide

(D) non-biodegradable insecticide

Correct Answer: (D) non-biodegradable insecticide

Solution:

Concept:

- DDT is dichlorodiphenyltrichloroethane, a chlorinated organic compound used as an insecticide.
- Non-biodegradable compounds resist breakdown by biological processes and persist in the environment.

Step 1: Identify the use of DDT DDT kills insects and has been used to control insect pests and disease vectors. It is therefore an insecticide, rather than a fertilizer that supplies essential nutrients to plants. Its relevant classification here is not that of a greenhouse gas.

Step 2: Check its persistence DDT is resistant to microbial degradation and can accumulate in fatty tissues. Its persistence and increase in concentration along food chains distinguish it from biodegradable insecticides. Thus, the word biodegradable in option (C) makes that option incorrect even though the insecticide classification is right.

Step 3: Conclusion DDT is a non-biodegradable insecticide. Hence, the correct option is (D).

Quick Tip to Solve: Link DDT with persistence and biomagnification; these properties identify it as a non-biodegradable insecticide.

11. What amount of electric charge is required for the reduction of 1 mole of MnO_4^- into Mn^{2+}? [1 mark]

(A) 1F

(B) 5F

(C) 4F

(D) 6F

Correct Answer: (B) 5F

Solution:

Concept:

- One faraday, F, is the charge carried by one mole of electrons, approximately $96485\,\mathrm{C\,mol^{-1}}$.
- The required charge is $Q = n_e F$, where n_e is the amount of electrons transferred in moles.

Step 1: Determine the change in oxidation state Let the oxidation state of manganese in MnO_4^- be x. Then $x + 4(-2) = -1$, giving $x = +7$. Reduction to Mn^{2+} lowers it to $+2$, so each manganese atom gains five electrons.

Quick Tip to Solve: For one mole, subtract the final metal oxidation state from the initial one; the decrease gives the required number of faradays.

Step 2: Convert electron transfer to charge The reduction half-reaction is

$$\mathrm{MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + 4\,H_2O}.$$

Thus, one mole of permanganate consumes five moles of electrons, and $Q = 5F$. The alternatives $1F$, $4F$ and $6F$ do not match the five-unit oxidation-state decrease; the charge is not found from the ionic charge alone.

Step 3: Conclusion The electric charge required is $5F$, approximately 4.82×10^5 C. Hence, the correct option is (B).

Quick Tip to Solve: For one mole, subtract the final metal oxidation state from the initial one; the decrease gives the required number of faradays.

12. Alkenes are formed by heating alcohols with conc. H_2SO_4. The first step in the reaction is:

[1 mark]

(A) formation of carbocation

(B) formation of ester

(C) protonation of alcohol molecule

(D) elimination of water

Correct Answer: (C) protonation of alcohol molecule

Solution:

Concept:

- Concentrated sulphuric acid catalyses dehydration of an alcohol to an alkene by making the hydroxyl group a better leaving group.
- Protonation at oxygen converts $\mathrm{R{-}OH}$ to the oxonium ion $\mathrm{R{-}OH_2^+}$, which can lose neutral water.

Step 1: Activate the hydroxyl group The oxygen atom of the alcohol uses a lone pair to accept a proton from the acid:

$$\mathrm{R{-}OH + H^+ \rightleftharpoons R{-}OH_2^+}.$$

This occurs first because an unprotonated hydroxyl group would have to leave as $\mathrm{OH^-}$, a poor leaving group under acidic conditions.

Step 2: Place the later events in sequence After protonation, water can depart in the acid-catalysed dehydration pathway, and removal of a proton from an adjacent carbon gives the alkene. Carbocation formation, where applicable, follows activation of the alcohol; it is not the first event. Ester formation is not the initial step of the stated dehydration mechanism, and elimination of water likewise follows protonation.

Step 3: Conclusion The first step is protonation of the alcohol molecule. Hence, the correct option is (C).

Quick Tip to Solve: In acid-catalysed dehydration, first convert the poor leaving group OH into the better leaving group water by protonation.

13. Assertion (A): Electrolysis of aqueous NaCl gives H_2 at cathode and Cl_2 at anode.
Reason (R): Chlorine has higher oxidation potential than H_2O. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (C) Assertion (A) is true, but Reason (R) is false.

Solution:

Concept:

- Aqueous sodium chloride yields hydrogen at the cathode by reduction of water and chlorine at the anode by oxidation of chloride under the usual brine-electrolysis conditions.
- Actual electrolysis products depend on both electrode potentials and overpotential, the extra potential needed to drive an electrode reaction at an appreciable rate.

Step 1: Evaluate the assertion Water is reduced preferentially to sodium ions at the cathode, while chloride ions are oxidised at the anode:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-,$$
$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^-.$$

Thus, the stated hydrogen and chlorine products make the assertion true in the standard electrolysis of aqueous sodium chloride.

Step 2: Evaluate the reason The reason is false. The standard reduction potentials are about $+1.36\,V$ for Cl_2/Cl^- and $+1.23\,V$ for O_2/H_2O. Their reverse oxidation potentials show that chloride oxidation is not favoured over water oxidation merely by the standard potential comparison.

Step 3: Test the proposed explanation Oxygen evolution requires a significant overpotential. This kinetic effect allows chlorine evolution to occur preferentially in brine; the claimed higher oxidation potential in the reason does not explain the anode product. Options (A) and (B) incorrectly treat the reason as true, while (D) incorrectly rejects the assertion.

Step 4: Conclusion The assertion is true, but the reason is false. Hence, the correct option is (C).

Quick Tip to Solve: For aqueous sodium chloride, remember oxygen overpotential at the anode: standard potential values alone do not predict the observed chlorine product.

14. Assertion (A): Cuprous salts are diamagnetic.

Reason (R): Cuprous ion has completely filled 3d-orbitals. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept:

- Diamagnetism occurs when all electrons are paired; unpaired electrons give a paramagnetic contribution.
- Cuprous denotes copper(I), Cu^{+}. Electrons are removed from the $4s$ orbital before the $3d$ orbitals when a copper atom forms this ion.

Step 1: Evaluate the assertion A neutral copper atom has the configuration $[Ar]\,3d^{10}4s^{1}$. Loss of its $4s$ electron gives the cuprous ion the configuration $[Ar]\,3d^{10}$. There are no unpaired electrons, so cuprous salts are diamagnetic and the assertion is true.

Step 2: Evaluate the reason The five $3d$ orbitals of Cu^{+} contain ten electrons, with two electrons of opposite spin in each orbital. Its $3d$ subshell is completely filled, so the reason is also true.

Step 3: Connect the reason to the assertion The filled $3d$ subshell directly accounts for the absence of unpaired electrons and therefore explains the diamagnetism. Thus, the two statements are not merely independently true; they are causally linked. Options (B), (C) and (D) fail because they deny either this link or the truth of one statement.

Step 4: Conclusion Both statements are true, and the reason correctly explains the assertion. Hence, the correct option is (A).

Quick Tip to Solve: For copper ions, remove the $4s$ electron first: cuprous is $3d^{10}$ and diamagnetic, whereas cupric is $3d^{9}$ and paramagnetic.

15. Assertion (A): n-Butyl chloride has higher boiling point than n-Butyl bromide.
Reason (R): C–Cl bond is more polar than C–Br bond. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- The boiling point of a haloalkane depends on the net intermolecular attractions, including London dispersion forces and dipole interactions.
- For the same alkyl group, a larger, more polarisable halogen generally raises the boiling point. Bond polarity alone does not determine the order.

Step 1: Evaluate the assertion Bromine is larger and more polarisable than chlorine. Thus n-butyl bromide has stronger dispersion attractions than n-butyl chloride and a higher boiling point. The assertion reverses the actual order and is false.

Step 2: Evaluate the reason Chlorine is more electronegative than bromine, so the electronegativity difference in a carbon–chlorine bond is greater than in a carbon–bromine bond. Therefore the reason, stating that the carbon–chlorine bond is more polar, is true.

Step 3: Match the truth values The greater bond polarity of the chloride does not outweigh the stronger dispersion forces in the bromide. Options (A), (B) and (C) all require a true assertion, so none applies to this pair of statements.

Step 4: Conclusion The assertion is false, but the reason is true. Hence, the correct option is (D).

Quick Tip to Solve: For haloalkanes with the same alkyl group, compare halogen size and polarisability before using bond polarity to predict boiling points.

16. Assertion (A): Acetanilide is less basic than aniline.

Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen. [1 mark]

(A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(B) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(C) Assertion (A) is true, but Reason (R) is false.

(D) Assertion (A) is false, but Reason (R) is true.

Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:

Concept:

- The basicity of a nitrogen compound depends on the availability of its lone pair to accept a proton.
- Acetylation converts aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$; an amide nitrogen lone pair is delocalised towards the carbonyl group.

Step 1: Evaluate the assertion In aniline the nitrogen lone pair is delocalised into the benzene ring. In acetanilide it is strongly involved in resonance with the adjacent carbonyl group, making it even less available for proton acceptance. Therefore acetanilide is less basic than aniline, and the assertion is true.

Step 2: Evaluate the reason The acetyl group withdraws electron density through its carbonyl group. Resonance donation of the nitrogen lone pair towards the carbonyl oxygen gives nitrogen partial positive character. Thus acetylation decreases electron density on nitrogen, and the reason is true.

Step 3: Test the explanatory connection This reduced availability of electron density at nitrogen directly explains the decrease in basicity. Option (B) incorrectly denies this connection, while (C) and (D) incorrectly declare one of the statements false.

Step 4: Conclusion Both statements are true, and the reason correctly explains the assertion. Hence, the correct option is (A).

Quick Tip to Solve: Identify the new amide linkage after acetylation: a nitrogen lone pair adjacent to a carbonyl group is much less available for basic behaviour.

Section B (10 marks)

17(a). Reactant 'A' underwent a decomposition reaction. The concentration of 'A' was measured periodically and recorded in the table given below:

Time/Hours	[A]/M
0	0.40
1	0.20
2	0.10
3	0.05

Based on the above data, predict the order of the reaction and write the expression for the rate law. [2 marks]

Solution:

Concept:

- The half-life $t_{1/2}$ is the time required for a reactant concentration to fall to half its value at the start of that interval.
- For a first-order reaction, $t_{1/2} = \ln 2/k$, independent of the starting concentration, and the differential rate law is $-d[A]/dt = k[A]$, where k is the rate constant.

Step 1: Compare successive concentration intervals From 0 to 1 hour, the concentration falls from 0.40 to $0.20\,\text{M}$. It again halves to $0.10\,\text{M}$ after the next hour and to $0.05\,\text{M}$ after one more hour. Each halving therefore requires exactly 1 hour, even though the concentration at the start of each interval changes.

Step 2: Identify the order and write its rate law This concentration-independent half-life is characteristic of first-order kinetics. Equal time intervals give equal fractional decreases rather than equal absolute decreases, so a zero-order law is not appropriate. The first-order integrated equation also gives a constant value of k for each interval:

$$k = \frac{1}{1\,\text{h}} \ln \frac{0.40}{0.20} = 0.693\,\text{h}^{-1}.$$

The same ratio of 2 occurs for the other consecutive readings.

Step 3: Conclusion The reaction is first order, and its rate law is $\text{Rate} = -\dfrac{d[A]}{dt} = k[A]$.

Quick Tip to Solve: Look for repeated halving in equal time intervals: a constant half-life immediately identifies a first-order reaction.

OR

17(b). The reaction between $H_2(g)$ and $I_2(g)$ was carried out in a sealed isothermal container. The rate law for the reaction was found to be:

Rate = $k[H_2][I_2]$

If 1 mole of $H_2(g)$ was added to the reaction chamber and the temperature was kept constant, then predict the change in rate of the reaction and the rate constant. [2 marks]

Solution:

Concept:

- In the experimentally determined law $r = k[H_2][I_2]$, the rate r is directly proportional to the concentration of each reactant when the other concentration is fixed.
- For a given reaction, the rate constant k depends on temperature and the catalytic conditions; changing the reactant concentration alone does not change it.

Step 1: Apply the change in hydrogen concentration Adding hydrogen to the reaction chamber raises its concentration. For chamber volume V, the immediate concentration increase is $\Delta[H_2] = (1\,\text{mol})/V$, while the iodine concentration is initially unchanged. Therefore

$$r_{\text{old}} = k[H_2]_{\text{old}}[I_2],$$
$$r_{\text{new}} = k\big([H_2]_{\text{old}} + \Delta[H_2]\big)[I_2].$$

Thus the reaction rate increases immediately. Its numerical factor cannot be calculated because the original hydrogen amount is not specified; adding one mole does not necessarily double the rate.

Step 2: Examine the rate constant The container is maintained at constant temperature, and no catalyst change is specified. Consequently the added hydrogen changes the concentration factor in the rate law but leaves k unchanged. The rate constant must not be confused with the reaction rate itself.

Step 3: Conclusion Adding 1 mole of H_2 increases the reaction rate, while the rate constant remains unchanged at the same temperature.

Quick Tip to Solve: In $r = k[H_2][I_2]$, change only the hydrogen concentration factor after adding hydrogen; constant temperature keeps k fixed.

18. $PtCl_4 \cdot 2KCl$ doesn't give precipitate of AgCl with $AgNO_3$ solution. Write the structural formula and IUPAC name of the complex. [2 marks]

Solution:

Concept:

- Aqueous silver nitrate gives an immediate AgCl precipitate with free ionisable chloride ions; chloride ligands within the coordination sphere do not behave as free chloride counterions.
- A coordination formula places the metal and its directly bonded ligands inside square brackets, with counterions outside. Ligand charges determine the metal oxidation state.

Step 1: Place the chloride ions in the coordination sphere The composition $PtCl_4 \cdot 2\,KCl$ contains one

Quick Tip to Solve: No silver chloride precipitate means no chloride outside the brackets; put all six chlorido ligands around platinum before calculating its oxidation state.

platinum atom, six chlorine atoms and two potassium atoms. Since no AgCl precipitate is obtained, there are no free chloride counterions. All six chloride ions must therefore be coordinated to platinum, leaving the two potassium ions outside the coordination sphere. The coordination formula is $K_2[PtCl_6]$, containing the octahedral anion $[PtCl_6]^{2-}$.

Step 2: Determine the oxidation state and name the complex Let the oxidation state of platinum be x. Each chlorido ligand has charge -1, and the two potassium ions require a complex-ion charge of -2. Hence

$$x + 6(-1) = -2 \quad \Rightarrow \quad x = +4.$$

Six chlorido ligands give the prefix hexachlorido. Because the complex ion is anionic, the metal is named platinate, followed by its oxidation state (IV). Name the potassium cation first.

Step 3: Conclusion Structural (coordination) formula: $K_2[PtCl_6]$. IUPAC name: **potassium hexachloridoplatinate(IV)**.

Quick Tip to Solve: No silver chloride precipitate means no chloride outside the brackets; put all six chlorido ligands around platinum before calculating its oxidation state.

19. Define fuel cell. Give two advantages of fuel cell over ordinary cell. [2 marks]

Solution:

Concept:

- A galvanic cell converts the chemical energy of a spontaneous redox reaction into electrical energy.
- In a fuel cell, the fuel and oxidant are fed continuously to the electrodes, while reaction products are removed.

Step 1: Define a fuel cell A fuel cell is a galvanic cell that converts the energy of combustion of a continuously supplied fuel directly into electrical energy. For example, a hydrogen–oxygen fuel cell uses H_2 as the fuel and O_2 as the oxidant, with the overall reaction

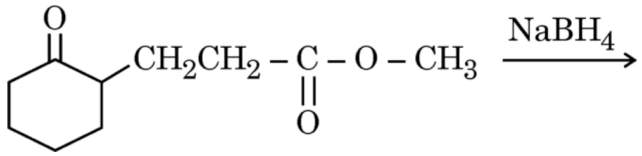
$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O\,(l).$$

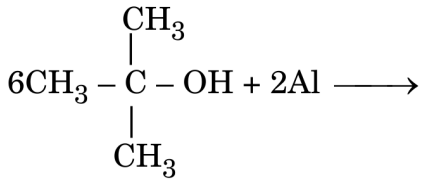
Step 2: State two advantages First, a fuel cell operates continuously as long as fuel and oxidant are supplied. Unlike an ordinary primary cell, its useful operation is not limited by a fixed initial quantity of reactants inside the cell. Second, the hydrogen–oxygen fuel cell is environmentally clean: its reaction product is water, so operation does not release the polluting products associated with many conventional energy sources or spent ordinary cells.

Step 3: Conclusion A fuel cell directly generates electricity from continuously supplied fuel and oxidant. Continuous operation and clean operation (water formation in the hydrogen–oxygen cell) are two advantages.

Quick Tip to Solve: Define the cell using continuous reactant supply, then use the hydrogen–oxygen cell to give a clear clean-product advantage.

20. Write the structures of the main products of the following reactions: [2 marks]

(a) 

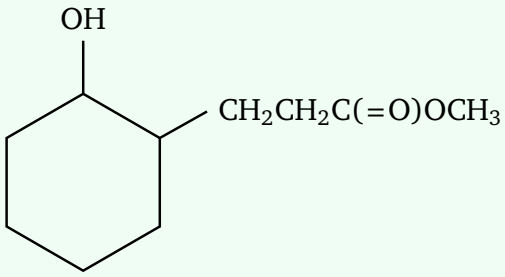
(b) 

Solution:

Concept:

- $NaBH_4$ selectively reduces aldehydes and ketones to alcohols; an ester group is not reduced under the usual conditions.
- Alcohols react with aluminium to form aluminium alkoxides and liberate hydrogen: $6\,ROH + 2\,Al \longrightarrow 2\,Al(OR)_3 + 3\,H_2$.

Step 1: Reduce the ketone in part (a) The starting compound contains a ketone carbonyl within the six-membered ring and a side-chain ester, $-CH_2CH_2COOCH_3$. Sodium borohydride reduces only the ring C=O group to CH–OH; the ester and the carbon skeleton remain unchanged. The product is methyl 3-(2-hydroxycyclohexyl)propanoate, whose connectivity is drawn below. No stereochemical configuration is specified in the question.



Product (a): ring carbonyl reduced; side-chain ester retained

Step 2: Replace the alcoholic hydrogen in part (b) The alcohol is tert-butyl alcohol, $(CH_3)_3COH$. Aluminium replaces the hydrogen attached to oxygen, forming aluminium tert-butoxide. Since aluminium is trivalent, three alkoxide groups bind to each aluminium atom:

$$6\,(CH_3)_3COH + 2\,Al \longrightarrow 2\,Al[OC(CH_3)_3]_3 + 3\,H_2\uparrow.$$

The carbon–oxygen bonds of the tert-butoxy groups remain intact. Six alcoholic hydrogen atoms combine to form three hydrogen molecules.

Step 3: Conclusion (a) The ring ketone becomes a secondary alcohol, giving methyl 3-(2-hydroxycyclohexyl)propanoate, with its ester unchanged. (b) The products are $2\,Al[OC(CH_3)_3]_3$ and $3\,H_2$.

Quick Tip to Solve: With $NaBH_4$, circle the ketone carbonyl and leave the ester untouched; with Al, replace only the hydrogen of the alcohol's OH group.

21. What is meant by essential amino acids? Why are amino acids amphoteric in nature? [2 marks]

Solution:

Concept:

- Essential amino acids must be obtained from the diet because the human body cannot synthesise them in sufficient amounts.
- Amino acids possess an acidic carboxyl group, $-COOH$, and a basic amino group, $-NH_2$; they can therefore react with both bases and acids.

Step 1: Define essential amino acids Essential amino acids are amino acids that cannot be synthesised by the human body in the amounts required for normal growth and maintenance, and must therefore be supplied through food. Valine and leucine are examples. The term essential refers to dietary necessity, not to whether an amino acid is important in proteins.

Step 2: Explain the amphoteric behaviour In water, an amino acid exists largely as a zwitterion, $H_3N^+-CHR-COO^-$, containing both positive and negative charges. Its carboxylate group accepts a proton from an acid, whereas its ammonium group donates a proton to a base:

$$H_3N^+-CHR-COO^- + H^+ \longrightarrow H_3N^+-CHR-COOH.$$

$$H_3N^+-CHR-COO^- + OH^- \longrightarrow H_2N-CHR-COO^- + H_2O.$$

Here R denotes the side chain. Thus the same amino acid can act as a base towards an acid and as an acid towards a base.

Step 3: Conclusion Essential amino acids must be obtained from food. Amino acids are amphoteric because their acidic and basic groups allow them to react with both bases and acids.

Quick Tip to Solve: Draw the zwitterion first: add H^+ at COO^- for acid, and remove a proton from $NH_3{}^+$ for base.

Section C (21 marks)

22(a). Account for the following:

(i) Allyl chloride is hydrolysed more readily than n-propyl chloride.

(ii) Isocyanides are formed when alkyl halides are treated with silver cyanide.

(iii) Methyl chloride reacts faster with OH^- ion in S_N2 reaction than t-butyl chloride. [3 marks]

Solution:

Concept:

- Allylic substitution is favoured by delocalisation: the adjacent double bond stabilises an allylic carbocation and can also stabilise the substitution transition state.
- Cyanide is an ambident nucleophile: either carbon or nitrogen can form a bond to an alkyl group, producing a nitrile or an isocyanide respectively.
- An S_N2 reaction involves a single concerted backside attack. Steric crowding at the carbon bearing

Quick Tip to Solve: Match each comparison to one cause: allylic resonance for (i), the attacking end of cyanide for (ii), and backside-access steric hindrance for (iii).

the leaving group lowers its reaction rate.

Step 1: Explain the faster hydrolysis of allyl chloride (i) In allyl chloride, $CH_2{=}CH{-}CH_2Cl$, the carbon bearing chlorine is next to a double bond. Cleavage of the carbon–chlorine bond can produce an allylic carbocation whose positive charge is delocalised:

$$CH_2{=}CH{-}CH_2{}^{+} \longleftrightarrow CH_2{}^{+}{-}CH{=}CH_2.$$

This resonance stabilisation favours substitution; the adjacent π system also stabilises the transition state for direct nucleophilic substitution. In contrast, n-propyl chloride has no adjacent double bond and no comparable resonance stabilisation. Hence allyl chloride undergoes hydrolysis more readily.

Step 2: Identify the attacking atom in silver cyanide (ii) AgCN is predominantly covalent, with the carbon end linked to silver. The nitrogen end is available to attack the alkyl halide. Bond formation through nitrogen gives an alkyl isocyanide:

$$R{-}X + AgCN \longrightarrow R{-}NC + AgX.$$

Ionic cyanides such as KCN, in contrast, supply free cyanide ions which mainly attack through carbon to form $R{-}CN$.

Step 3: Compare steric hindrance in the two chlorides (iii) In methyl chloride, CH_3Cl, the carbon bonded to chlorine is surrounded only by small hydrogen atoms. The OH^- ion can approach from the side opposite chlorine with little obstruction. In tert-butyl chloride, $(CH_3)_3CCl$, three methyl groups shield the reaction centre and strongly hinder this backside attack and its crowded transition state. Therefore the methyl compound reacts much faster by the S_N2 mechanism; a tertiary substrate is essentially unreactive by this pathway.

Step 4: Conclusion (i) Allylic resonance stabilisation increases hydrolysis reactivity. (ii) Covalent AgCN reacts through nitrogen to form isocyanides. (iii) Methyl chloride has much less steric hindrance to OH^- backside attack than tert-butyl chloride.

Quick Tip to Solve: Match each comparison to one cause: allylic resonance for (i), the attacking end of cyanide for (ii), and backside-access steric hindrance for (iii).

OR

22(b). Complete the following reactions by writing the structural formulae of 'A' and 'B':

(i) $CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{\text{HBr}} A \xrightarrow{\text{aq. KOH}} B$

(ii) $CH_3CH_2CHClCH_3 \xrightarrow[\Delta]{\text{alc. KOH}} A \xrightarrow{HBr} B$

(iii) $A \xrightarrow{Mg} CH_3CH_2MgCl \xrightarrow[H^+]{H_2O} B$ **(Main product)** [3 marks]

Solution:

Concept:

- Peroxide causes anti-Markovnikov addition of HBr: bromine attaches to the less substituted carbon.

Quick Tip to Solve: Circle the conditions first: peroxide changes HBr addition, aqueous versus alcoholic alkali selects substitution versus elimination, and water converts a Grignard reagent to an alkane.

- Aqueous KOH substitutes halogen by hydroxyl; hot alcoholic alkali eliminates hydrogen halide, favouring the more substituted alkene.
- Magnesium forms a Grignard reagent in dry ether; water protonates its carbon bonded to magnesium to give an alkane.

Step 1: Identify the products in sequence (i) Peroxide directs bromine to the terminal carbon of propene, producing 1-bromopropane. Aqueous alkali then replaces bromine with OH without changing the carbon skeleton:

$$\mathrm{CH_3CH{=}CH_2} \xrightarrow[\text{Peroxide}]{\text{HBr}} \mathrm{CH_3CH_2CH_2Br}$$

$$\mathrm{CH_3CH_2CH_2Br + KOH\,(aq)} \longrightarrow \mathrm{CH_3CH_2CH_2OH + KBr}$$

Thus, $A = \mathrm{CH_3CH_2CH_2Br}$ and $B = \mathrm{CH_3CH_2CH_2OH}$ (propan-1-ol).

Step 2: Apply elimination and addition in sequence (ii) Alcoholic alkali and heat favour elimination to but-2-ene by Saytzeff's rule. Addition of HBr to this symmetrical alkene gives 2-bromobutane.

$$\mathrm{CH_3CH_2CHClCH_3} \xrightarrow[\Delta]{\text{alc.\ KOH}} \mathrm{CH_3CH{=}CHCH_3}$$

$$\mathrm{CH_3CH{=}CHCH_3 + HBr} \longrightarrow \mathrm{CH_3CH_2CHBrCH_3}$$

Thus, $A = \mathrm{CH_3CH{=}CHCH_3}$ and $B = \mathrm{CH_3CH_2CHBrCH_3}$.

Step 3: Reverse Grignard formation and hydrolyse in sequence (iii) The ethyl Grignard reagent comes from chloroethane. Magnesium inserts into its carbon–chlorine bond; acidic water then protonates the ethyl group:

$$\mathrm{CH_3CH_2Cl + Mg} \xrightarrow{\text{dry ether}} \mathrm{CH_3CH_2MgCl}$$

$$\mathrm{CH_3CH_2MgCl + H_2O} \longrightarrow \mathrm{CH_3CH_3 + Mg(OH)Cl}$$

Hence, $A = \mathrm{CH_3CH_2Cl}$; the main organic product B is ethane, $\mathrm{CH_3CH_3}$.

Step 4: Conclusion The structural formulae (A, B) are: (i) $(\mathrm{CH_3CH_2CH_2Br}, \mathrm{CH_3CH_2CH_2OH})$; (ii) $(\mathrm{CH_3CH{=}CHCH_3}, \mathrm{CH_3CH_2CHBrCH_3})$; (iii) $(\mathrm{CH_3CH_2Cl}, \mathrm{CH_3CH_3})$.

Quick Tip to Solve: Circle the conditions first: peroxide changes HBr addition, aqueous versus alcoholic alkali selects substitution versus elimination, and water converts a Grignard reagent to an alkane.

23. Calculate the cell voltage of the voltaic cell which is set up by joining following half-cells at 25°C: Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.1 M)

Given: $E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Al^{3+}/Al} = -1.66$ V [3 marks]

Solution:

Concept:

- In a voltaic cell, the half-cell with the higher reduction potential is the cathode. The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

Quick Tip to Solve: Balance electrons before using Nernst: here $n = 6$, while the ion exponents are 2 for aluminium and 3 for nickel. Never multiply standard electrode potentials.

- At $25^\circ\mathrm{C}$, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Identify and balance the electrode reactions Nickel has the more positive standard reduction potential, so Ni^{2+} is reduced at the cathode and aluminium is oxidised at the anode. Balance the electrons using the least common multiple of 2 and 3:

$$\begin{aligned} \text{Anode:} \quad & 2\,\mathrm{Al} \longrightarrow 2\,\mathrm{Al}^{3+} + 6\,\mathrm{e}^- \\ \text{Cathode:} \quad & 3\,\mathrm{Ni}^{2+} + 6\,\mathrm{e}^- \longrightarrow 3\,\mathrm{Ni} \\ \text{Overall:} \quad & 2\,\mathrm{Al} + 3\,\mathrm{Ni}^{2+} \longrightarrow 2\,\mathrm{Al}^{3+} + 3\,\mathrm{Ni}. \end{aligned}$$

Thus $n = 6$. Electrode potentials are intensive quantities and are not multiplied by the balancing coefficients.

Step 2: Calculate the standard potential and reaction quotient Subtract the anode reduction potential from the cathode reduction potential:

$$E^\circ_{\text{cell}} = (-0.25) - (-1.66) = 1.41\,\mathrm{V}.$$

Only the dissolved ions appear in the concentration quotient. Using the given molar concentrations as the numerical activities,

$$Q = \frac{[\mathrm{Al}^{3+}]^2}{[\mathrm{Ni}^{2+}]^3} = \frac{(0.001)^2}{(0.1)^3} = 10^{-3}.$$

Hence $\log Q = -3$.

Step 3: Substitute into the Nernst equation The concentration correction is positive because the reaction quotient is below unity:

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}(-3) \\ &= 1.41 + 0.02955 = 1.43955\,\mathrm{V}. \end{aligned}$$

The positive potential confirms that aluminium oxidation and nickel-ion reduction give the spontaneous cell reaction under the stated conditions.

Step 4: Conclusion The cell voltage at $25^\circ\mathrm{C}$ is $\boxed{E_{\text{cell}} \approx 1.44\,\mathrm{V}}$, with aluminium as the anode and nickel as the cathode.

Quick Tip to Solve: Balance electrons before using Nernst: here $n = 6$, while the ion exponents are 2 for aluminium and 3 for nickel. Never multiply standard electrode potentials.

24. Give explanation for each of the following observations:

(a) With the same d-orbital configuration (d^4), Mn^{3+} ion is an oxidising agent whereas Cr^{2+} ion is a reducing agent.

(b) Actinoid contraction is greater from element to element than that among lanthanoids.

(c) Transition metals form large number of interstitial compounds with H, B, C and N. [3 marks]

Solution:

Concept:

- Redox behaviour depends on the relative stability of the initial and final oxidation states. An oxidising agent accepts electrons; a reducing agent donates electrons.
- Poor shielding by f-electrons increases effective nuclear attraction across the inner transition series and causes a progressive decrease in atomic and ionic sizes.
- Interstitial compounds form when small atoms occupy vacant spaces in the crystal lattice of a metal without greatly changing the underlying metal framework.

Step 1: Compare the stable states reached by the two ions (a) Both Mn^{3+} and Cr^{2+} have the configuration $[Ar]3d^4$, but their favourable electron changes are different. Manganese(III) accepts an electron to form the especially stable half-filled $3d^5$ configuration:

$$Mn^{3+} + e^- \longrightarrow Mn^{2+} \qquad (d^4 \longrightarrow d^5).$$

It is therefore an oxidising agent. Chromium(II) instead loses an electron to give Cr^{3+}, which has a stable $3d^3$ configuration:

$$Cr^{2+} \longrightarrow Cr^{3+} + e^- \qquad (d^4 \longrightarrow d^3).$$

In an octahedral environment this is the favourably stabilised t_{2g}^3 arrangement. Thus Cr^{2+} acts as a reducing agent; the shared initial d^4 configuration alone does not determine the redox behaviour.

Step 2: Explain the greater actinoid contraction (b) As atomic number increases, the added f-electrons do not fully screen the increasing nuclear charge. Actinoid $5f$-electrons shield one another even less effectively than lanthanoid $4f$-electrons. The effective nuclear attraction therefore increases more strongly across the actinoids, drawing the electron cloud inward and producing the greater element-to-element contraction stated in the question.

Step 3: Relate interstitial compounds to atomic size (c) Transition metals have closely packed crystal lattices containing interstitial holes. Hydrogen, boron, carbon and nitrogen atoms are small enough to occupy these spaces between metal atoms. Their incorporation into the lattice produces many interstitial compounds, often with variable composition, while retaining the basic metal framework. The small size of these atoms relative to the metal atoms is the key structural reason.

Step 4: Conclusion (a) Mn^{3+} gains an electron to reach d^5, whereas Cr^{2+} loses one to reach d^3. (b) Poorer shielding by $5f$-electrons causes the greater actinoid contraction. (c) Small H, B, C and N atoms fit into interstitial holes in transition-metal lattices.

Quick Tip to Solve: For redox comparisons, write the configuration after gaining or losing one electron; for contraction compare shielding, and for interstitial compounds compare atomic sizes.

25. An aqueous solution of NaOH was made and its molar mass from the measurement of osmotic pressure at 27°C was found to be 25 g mol^{-1}. Calculate the percentage dissociation of NaOH in this solution.

[Atomic mass: Na = 23 u, O = 16 u, H = 1 u] [3 marks]

Solution:

Concept:

- Osmotic pressure is a colligative property: $\pi = inRT/V$, where i is the van't Hoff factor, n the initial moles of solute, R the gas constant and T the absolute temperature.
- Dissociation increases the number of solute particles and lowers the apparent molar mass: $i = M_{\text{normal}}/M_{\text{observed}}$. If each dissociated formula unit produces ν ions, $i = 1 + \alpha(\nu - 1)$, where α is the fraction dissociated.

Step 1: Calculate the normal molar mass Add the supplied atomic masses of sodium, oxygen and hydrogen for one formula unit of NaOH:

$$M_{\text{normal}} = 23 + 16 + 1 = 40\,\text{g mol}^{-1}.$$

The measured apparent value, $25\,\text{g mol}^{-1}$, is smaller because osmotic pressure counts ions as separate solute particles.

Step 2: Obtain the van't Hoff factor For a mass w of solute, compare the true expression with the expression used to obtain an apparent molar mass without allowing for dissociation:

$$\pi = i\frac{wRT}{M_{\text{normal}}V},$$
$$\pi = \frac{wRT}{M_{\text{observed}}V}.$$

Dividing these relations gives

$$i = \frac{M_{\text{normal}}}{M_{\text{observed}}} = \frac{40}{25} = 1.60.$$

Both molar masses refer to the same solution at 27°C, so temperature cancels from the ratio.

Step 3: Relate the particle count to dissociation The dissociation is $\text{NaOH} \longrightarrow \text{Na}^+ + \text{OH}^-$, producing two ions per dissociated formula unit. Starting with one mole, the amounts after dissociation are $1 - \alpha$ mole of undissociated solute and α mole of each ion. Hence,

$$i = (1 - \alpha) + \alpha + \alpha = 1 + \alpha, \qquad \alpha = 1.60 - 1 = 0.60.$$

Step 4: Conclusion The percentage dissociation of NaOH in the given solution is $\alpha \times 100 = \boxed{60\%}$.

Quick Tip to Solve: For a solute producing two ions, first divide normal molar mass by apparent molar mass, then subtract one and multiply by 100.

26. Arrange the following compounds as asked:

(a) in decreasing order of pK_b values

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $C_6H_5NHCH_3$, $C_6H_5NH_2$

(b) increasing order of boiling point

C_2H_5OH, $C_2H_5NH_2$, $(CH_3)_2NH$

(c) increasing order of solubility in water

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ [3 marks]

Solution:

Concept:

- Basicity depends on the availability of the nitrogen lone pair. Since $pK_b = -\log K_b$, a stronger base has a smaller pK_b.
- Hydrogen bonding affects boiling points and water solubility. The nonpolar hydrocarbon portion opposes hydration, whereas the amino group can form hydrogen bonds with water.

Step 1: Compare basicities for part (a) In aromatic amines the nitrogen lone pair is delocalised into the benzene ring, reducing its availability for accepting a proton. Thus both aromatic amines are weaker bases than the ethylamines. The electron-releasing methyl group makes $C_6H_5NHCH_3$ more basic than $C_6H_5NH_2$. Among the two aliphatic amines, the combined inductive and solvation effects make diethylamine stronger than ethylamine in aqueous solution. Reversing this basicity order gives the requested decreasing order of pK_b:

$$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH.$$

Step 2: Compare intermolecular attractions for part (b) Ethanol forms stronger intermolecular hydrogen bonds than the amines because oxygen is more electronegative than nitrogen. It therefore has the highest boiling point among these compounds of similar molar masses. Ethylamine has two nitrogen-bound hydrogens and associates more extensively through hydrogen bonding than the isomeric secondary amine, dimethylamine, which has only one. Thus the increasing boiling-point order is

$$(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH.$$

Step 3: Compare hydration and hydrocarbon size for part (c) All three amines can interact with water through hydrogen bonding, but the large hydrophobic phenyl group makes aniline least soluble. The hydrocarbon portion is larger in diethylamine than in ethylamine, so the latter interacts more favourably with water relative to its molecular size. The requested increasing order of solubility is

$$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2.$$

Step 4: Conclusion (a) Decreasing pK_b: $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$.
(b) Increasing boiling point: $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$.
(c) Increasing water solubility: $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$.

Quick Tip to Solve: Reverse the basic-strength order for decreasing pK_b; compare hydrogen bonding for boiling point and hydrophobic group size for water solubility.

27. An aromatic compound 'A' with molecular formula C_8H_8O gives positive 2,4-DNP test. It gives yellow precipitate of compound 'B' on treatment with sodium hypoiodite. Compound 'A' does not react with Tollen's or Fehling's reagent; on drastic oxidation with $KMnO_4$ it forms a carboxylic acid 'C'. Elucidate the structures of A, B and C. Also give their IUPAC names. [3 marks]

Solution:

Concept:

- A positive 2,4-dinitrophenylhydrazine (2,4-DNP) test indicates an aldehyde or ketone carbonyl group. Aldehydes ordinarily reduce Tollens' reagent, whereas simple ketones do not.
- Methyl ketones, containing $RCOCH_3$, give the iodoform test: alkaline iodine or sodium hypoiodite produces yellow CHI_3. Strong oxidation can cleave the carbon chain adjacent to a ketone carbonyl.

Step 1: Identify the carbonyl compound A The positive 2,4-DNP test establishes a carbonyl group. The negative Tollens' test excludes an ordinary aldehyde, so A is a ketone; its negative Fehling's test is also consistent with this. The yellow precipitate with sodium hypoiodite further identifies the $-COCH_3$ group. Combining this methyl ketone unit with an aromatic ring and the formula C_8H_8O gives

$$A = C_6H_5-C(=O)-CH_3.$$

This structure has eight carbons, eight hydrogens and one oxygen, exactly as required. Its IUPAC name is **1-phenylethan-1-one**; its common name is acetophenone.

Step 2: Identify the yellow precipitate B In the haloform reaction, the methyl group of the methyl ketone is converted into iodoform. The remaining acyl fragment becomes a carboxylate in alkaline solution. The balanced reaction with sodium hypoiodite is

$$C_6H_5COCH_3 + 3\,NaOI \longrightarrow C_6H_5COONa + CHI_3\downarrow + 2\,NaOH.$$

Thus B has the structure $H-C(I)_3$, or CHI_3. Its IUPAC name is **triiodomethane**, commonly called iodoform.

Step 3: Identify the acid C after oxidation Drastic oxidation of acetophenone with $KMnO_4$ cleaves the ketone side chain and produces the aromatic carboxylic acid, benzoic acid. The benzene ring remains attached to the carboxyl carbon:

$$C_6H_5COCH_3 \xrightarrow[\text{drastic oxidation}]{KMnO_4} C_6H_5-C(=O)-OH.$$

This is a transformation scheme showing the requested aromatic product. C is C_6H_5COOH, named **benzoic acid** (the retained IUPAC name), also called benzenecarboxylic acid.

Step 4: Conclusion A: $C_6H_5COCH_3$, 1-phenylethan-1-one.

B: CHI_3, triiodomethane.

C: C_6H_5COOH, benzoic acid (benzenecarboxylic acid).

Quick Tip to Solve: Combine a positive 2,4-DNP test, a negative Tollens' test and yellow iodoform to identify a methyl ketone before using the molecular formula to attach the aromatic ring.

28(a). Can sodium ethoxide and t-butyl chloride be used for the preparation of t-butyl ethyl ether? Give suitable explanation. Justify your answer by suggesting the appropriate starting material required for preparation of t-butyl ethyl ether. [2 marks]

Solution:

Concept:

- Williamson ether synthesis involves nucleophilic substitution, in which an alkoxide ion attacks an alkyl halide by the S_N2 mechanism.
- A primary alkyl halide favours substitution; a tertiary alkyl halide is sterically hindered and undergoes elimination with a strong base such as an alkoxide.

Step 1: Examine the proposed reactants In tert-butyl chloride, $(CH_3)_3CCl$, the carbon bonded to chlorine is tertiary. The surrounding methyl groups hinder the backside attack needed for S_N2 substitution. Sodium ethoxide, C_2H_5ONa, therefore acts mainly as a base and removes a beta hydrogen. Elimination produces 2-methylpropene instead of the desired ether:

$$(CH_3)_3CCl + NaOC_2H_5 \longrightarrow CH_2{=}C(CH_3)_2 + C_2H_5OH + NaCl.$$

Step 2: Place the halogen on the primary group Reverse the roles of the two alkyl groups. Use sodium tert-butoxide as the alkoxide and ethyl bromide as the primary alkyl halide. The ethyl carbon is accessible to nucleophilic attack, so displacement of bromide forms the ether:

$$(CH_3)_3CONa + CH_3CH_2Br \longrightarrow (CH_3)_3COCH_2CH_3 + NaBr.$$

This choice places the bulky tert-butyl group in the alkoxide, where it does not create a tertiary carbon bearing the leaving group.

Step 3: Conclusion No, sodium ethoxide and tert-butyl chloride are unsuitable because elimination predominates. Prepare tert-butyl ethyl ether using sodium tert-butoxide and ethyl bromide.

Quick Tip to Solve: For an unsymmetrical ether, attach the halogen to the less hindered alkyl group: use ethyl halide here, not tert-butyl halide.

28(b). Give the IUPAC name of above mentioned ether. [1 mark]

Solution:

Concept:

- In substitutive IUPAC nomenclature, an ether is named as an alkoxyalkane: the smaller alkyl group and oxygen form the alkoxy substituent.
- Select the carbon chain on the larger alkyl side as the parent and assign locants to all substituents on that chain.

Step 1: Identify the two groups attached to oxygen The ether has the condensed structure $CH_3CH_2OC(CH_3)_3$. The ethyl side together with oxygen gives the ethoxy group, $CH_3CH_2O^-$. The tert-butyl side supplies the parent carbon skeleton.

Quick Tip to Solve: Do not count across oxygen when finding the parent carbon chain; the tert-butyl side gives propane with two substituents at carbon 2.

Step 2: Number the parent chain The longest continuous carbon chain on the tert-butyl side has three carbons, so the parent is propane. Carbon 2 bears both the ethoxy group and a methyl group. List ethoxy before methyl alphabetically when writing the substituent names.

Step 3: Conclusion The IUPAC name of tert-butyl ethyl ether is **2-ethoxy-2-methylpropane**.

Quick Tip to Solve: Do not count across oxygen when finding the parent carbon chain; the tert-butyl side gives propane with two substituents at carbon 2.

Section D (8 marks)

The following questions are case-based questions. Read the case carefully and answer the questions that follow.

29. According to the generally accepted definition of the ideal solution there are equal interaction forces acting between molecules belonging to the same or different species. (This is equivalent to the statement that the activity of the components equals the concentration.) Strictly speaking, this condition is fulfilled only in exceptional cases for mixtures (optical isomers, isotopic mixtures of an element, hydrocarbon mixtures). It is still usual to talk about ideal solutions as limiting cases in reality since very dilute solutions behave ideally with respect to the solvent. This view is further supported by the fact that Raoult's law empirically found for describing the behaviour of the solvent in dilute solutions can be deduced thermodynamically via the assumption of ideal behaviour of the solvent.

Answer the following questions: [4 marks]

29(a). Give one example of miscible liquid pair which shows negative deviation from Raoult's law. What is the reason for such deviation? [2 marks]

Solution:

Concept:

- Raoult's law predicts $p_i = x_i p_i^0$, where p_i is the partial vapour pressure of component i, x_i its liquid-phase mole fraction and p_i^0 its pure vapour pressure at the same temperature.
- Negative deviation occurs when unlike intermolecular attractions are stronger than those in the pure liquids, reducing the tendency of molecules to escape into the vapour.

Step 1: Choose a miscible liquid pair Acetone, CH_3COCH_3, and chloroform, $CHCl_3$, form a miscible liquid mixture that shows negative deviation from Raoult's law. On mixing, the hydrogen atom of chloroform forms a hydrogen bond with the oxygen atom of acetone's carbonyl group.

Step 2: Relate the attraction to vapour pressure The acetone-chloroform attraction is stronger than the average attractions between molecules in the separate pure liquids. Consequently, the molecules are held more strongly in the liquid mixture and fewer escape into the vapour at a given temperature. The observed partial pressures, and hence the total vapour pressure, are lower than the ideal values predicted by Raoult's law:

$$p_{\text{total}} < x_{\text{acetone}} p^0_{\text{acetone}} + x_{\text{chloroform}} p^0_{\text{chloroform}}.$$

Quick Tip to Solve: Link stronger unlike attractions to reduced escape into vapour: this gives negative deviation, as in acetone mixed with chloroform.

Step 3: Conclusion Acetone and chloroform show negative deviation because hydrogen bonding between the unlike molecules strengthens their attraction and lowers the vapour pressure below the Raoult's-law prediction.

Quick Tip to Solve: Link stronger unlike attractions to reduced escape into vapour: this gives negative deviation, as in acetone mixed with chloroform.

29(b)(i). State Raoult's law for a solution containing volatile components. [1 mark]

Solution:

Concept:

- Raoult's law relates the partial vapour pressure of each volatile component to its mole fraction in the liquid solution at a fixed temperature.
- For component i, p_i denotes its partial vapour pressure, x_i its liquid-phase mole fraction, and p_i^0 its pure-liquid vapour pressure at the same temperature.

Step 1: State the proportionality The partial vapour pressure of each volatile component of an ideal solution is directly proportional to its mole fraction in the solution. Its proportionality constant is the vapour pressure of that component in the pure state:

$$p_i = x_i p_i^0.$$

Step 2: Apply the law to both components For two volatile liquids A and B, apply the relation separately: $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$. Their total vapour pressure is the sum of the two partial pressures, $p_{\text{total}} = x_A p_A^0 + x_B p_B^0$, with $x_A + x_B = 1$.

Step 3: Conclusion Raoult's law states that $\boxed{p_i = x_i p_i^0}$ for every volatile component of an ideal solution at a given temperature.

Quick Tip to Solve: Use the liquid-phase mole fraction and the pure-component vapour pressure at the same temperature for each component separately.

OR

29(b)(ii). Raoult's law is a special case of Henry's law. Comment. [1 mark]

Solution:

Concept:

- Henry's law has the form $p_i = K_{H,i} x_i$, where p_i is the partial pressure, x_i the dissolved component's mole fraction and $K_{H,i}$ its Henry's-law constant at a fixed temperature.
- Raoult's law is $p_i = p_i^0 x_i$, where p_i^0 is the vapour pressure of the pure liquid component at that temperature.

Step 1: Compare the pressure relations Both laws make the partial pressure directly proportional to

Quick Tip to Solve: Write both laws as pressure equals constant times mole fraction, then equate the two constants to identify the special case.

the component's mole fraction in the solution. They differ in the proportionality constant: Henry's law uses $K_{H,i}$, while Raoult's law uses p_i^0.

Step 2: Identify the special condition When the Henry's-law constant equals the vapour pressure of the pure component at the same temperature, substituting $K_{H,i} = p_i^0$ into Henry's equation gives

$$p_i = K_{H,i} x_i = p_i^0 x_i,$$

which is precisely the Raoult's-law relation.

Step 3: Conclusion Raoult's law is the special case of Henry's law for which $\boxed{K_{H,i} = p_i^0}$.

Quick Tip to Solve: Write both laws as pressure equals constant times mole fraction, then equate the two constants to identify the special case.

29(c). Write two characteristics of an ideal solution. [1 mark]

Solution:

Concept:

- An ideal solution has approximately equal strengths of like and unlike intermolecular attractions and obeys Raoult's law throughout the composition range.
- Its thermodynamic characteristics are described by the enthalpy change on mixing, ΔH_{mix}, and the volume change on mixing, ΔV_{mix}.

Step 1: State the heat effect of mixing The enthalpy of mixing is zero: $\Delta H_{\text{mix}} = 0$. Energy required to separate molecules of the pure liquids is balanced by the energy released when unlike molecules attract each other. Thus, mixing does not evolve or absorb heat.

Step 2: State the volume effect of mixing The volume change on mixing is zero: $\Delta V_{\text{mix}} = 0$. At the same temperature and pressure, the solution volume equals the sum of the volumes of its components before mixing; there is no contraction or expansion.

Step 3: Conclusion Two characteristics of an ideal solution are $\boxed{\Delta H_{\text{mix}} = 0}$ and $\boxed{\Delta V_{\text{mix}} = 0}$.

Quick Tip to Solve: For the two thermodynamic characteristics, remember zero heat effect and zero volume change on mixing; temperature and pressure must be the same.

30. Ribose and 2-deoxyribose have an important role in biology. Among the most important derivatives are those with phosphate groups attached at the 5 position. Mono-, di- and tri-phosphate forms are important, as well as 3-5 cyclic monophosphates. Purines and pyrimidines form an important class of compounds with ribose and deoxyribose. When these purine and pyrimidine derivatives are coupled to a ribose sugar, they are called nucleosides. Answer the following questions: [4 marks]

30(a). What products would be formed when DNA is hydrolysed? How is DNA different from RNA with reference to a structure? [2 marks]

Solution:

Concept:

- DNA is a polynucleotide. Each nucleotide contains a pentose sugar, a nitrogenous base and a phosphate group.
- Complete hydrolysis separates these constituents; DNA and RNA differ in their sugar, one pyrimidine base and usual strand arrangement.

Step 1: Identify the products of complete hydrolysis Hydrolysis of DNA first breaks its polymer chain into smaller units. On complete hydrolysis, it gives 2-deoxy-D-ribose, phosphoric acid (H_3PO_4) and the four nitrogenous bases adenine, guanine, cytosine and thymine. Thus, nucleotides are intermediate hydrolysis products, whereas sugar, phosphoric acid and bases are the final constituent products asked for here.

Step 2: Compare the structures of DNA and RNA DNA contains 2-deoxy-D-ribose, with H at the $2'$ carbon; RNA contains D-ribose, with an OH group at that carbon. DNA contains thymine, whereas RNA contains uracil; adenine, guanine and cytosine occur in both. DNA normally consists of two complementary polynucleotide strands wound into a double helix, held together by hydrogen bonds between paired bases. RNA is usually a single polynucleotide strand, although it can fold back on itself.

Step 3: Conclusion Complete DNA hydrolysis yields 2-deoxy-D-ribose, phosphoric acid and adenine, guanine, cytosine and thymine. DNA is normally double-stranded and contains deoxyribose and thymine; RNA is usually single-stranded and contains ribose and uracil.

Quick Tip to Solve: Recall DNA hydrolysis as sugar + phosphate + bases; compare DNA and RNA using sugar, base and strand structure.

30(b). Differentiate between nucleotide and nucleoside. [1 mark]

Solution:

Concept:

- A nucleoside consists of a nitrogenous base linked to a pentose sugar by an N-glycosidic linkage.
- A nucleotide is the phosphate ester of a nucleoside, so it additionally contains a phosphate group.

Step 1: Identify the components of a nucleoside The nitrogenous base is joined to ribose or deoxyribose. This base–sugar unit is a nucleoside; it contains no phosphate group. Adenosine, made from adenine and ribose, is an example.

Quick Tip to Solve: Check for phosphate: its presence distinguishes a nucleotide from the corresponding nucleoside.

Step 2: Add the distinguishing phosphate group When phosphoric acid forms an ester with a sugar hydroxyl group of the nucleoside, a nucleotide is obtained. Thus, a nucleotide has three components: base, sugar and phosphate. Adenosine monophosphate is an example of a nucleotide.

Step 3: Conclusion Nucleoside = nitrogenous base + pentose sugar; nucleotide = nitrogenous base + pentose sugar + phosphate group.

Quick Tip to Solve: Check for phosphate: its presence distinguishes a nucleotide from the corresponding nucleoside.

30(c)(i). Mention two important functions of nucleic acid. [1 mark]

Solution:

Concept:

- The sequence of bases in nucleic acids carries genetic information.
- DNA stores hereditary information, while RNA participates in expressing it through protein synthesis.

Step 1: State their role in heredity DNA stores the information that determines inherited characteristics. Replication copies this information before cell division, allowing it to pass from parent cells to daughter cells and from one generation to the next.

Step 2: State their role in protein synthesis Nucleic acids direct the synthesis of proteins. The information in DNA is transcribed into RNA; messenger RNA supplies the coding sequence, while transfer RNA and ribosomal RNA help assemble amino acids into proteins. The base sequence therefore determines the amino acid sequence.

Step 3: Conclusion Two important functions are storage and transmission of hereditary information, and direction of protein synthesis.

Quick Tip to Solve: Remember the two functions as heredity and protein synthesis; link DNA to information and RNA to its expression.

OR

30(c)(ii). Name the linkage which joins two nucleotides. Name the base that is found in nucleotide of RNA but not in DNA. [1 mark]

Solution:

Concept:

- Adjacent nucleotides in a nucleic acid chain are joined through phosphate ester bonds in the sugar–phosphate backbone.
- RNA contains the pyrimidine base uracil in place of the thymine found in DNA.

Step 1: Identify the bond between adjacent nucleotides A phosphate group connects the $3'$ hydroxyl

Quick Tip to Solve: Along a strand remember phosphodiester bonds; for the RNA-specific base replace DNA's thymine with uracil.

position of one pentose sugar to the $5'$ position of the next sugar. Since the phosphate forms two ester linkages, this connecting bond is called a $3', 5'$-phosphodiester linkage. Hydrogen bonds instead connect complementary bases across paired strands.

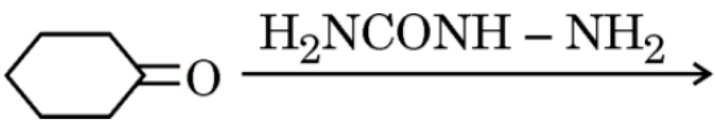
Step 2: Identify the base characteristic of RNA The usual bases of RNA are adenine, guanine, cytosine and uracil. DNA has adenine, guanine, cytosine and thymine. Comparing the two lists identifies uracil as the RNA base absent from the standard DNA nucleotide set.

Step 3: Conclusion The linkage is the $3', 5'$-phosphodiester linkage, and the base is uracil.

Quick Tip to Solve: Along a strand remember phosphodiester bonds; for the RNA-specific base replace DNA's thymine with uracil.

Section E (15 marks)

31(a)(i)(I). Complete the following reactions by writing the structure of the main products: [1 mark]



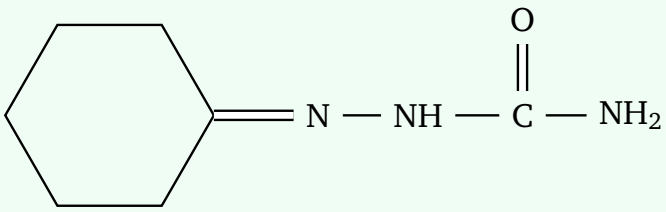
Solution:

Concept:

- Semicarbazide, $H_2N-NH-C(=O)-NH_2$, condenses with a carbonyl compound to form a semicarbazone with elimination of H_2O.
- The terminal hydrazino $-NH_2$ group attacks the carbonyl carbon; the $-CONH_2$ group is resonance-stabilised and does not form the new double bond.

Step 1: Identify the reacting group Cyclohexanone contains a ketone group within its six-membered ring. Semicarbazide reacts at this carbonyl group while the carbon skeleton and all five methylene groups remain unchanged.

Step 2: Form the semicarbazone linkage Condensation replaces the carbonyl $C=O$ group by $C=N-NH-C(=O)-NH_2$. The original carbonyl oxygen and two hydrogens from the attacking amino group are removed as H_2O. The structure below shows the main organic product.



Cyclohexanone semicarbazone

Step 3: Conclusion The main product is cyclohexanone semicarbazone, with an exocyclic $C=N-NH-C(=O)-NH_2$ group on the unchanged cyclohexane ring.

Quick Tip to Solve: Replace only the ketone oxygen by $N-NH-C(=O)-NH_2$; preserve the ring and the carbonyl group already present in semicarbazide.

31(a)(i)(II). Complete the following reactions by writing the structure of the main products:

$(CH_3)_2Cd + 2\ CH_3COCl \rightarrow$ [1 mark]

Solution:

Concept:

- Dialkylcadmium reagents react with acid chlorides to give ketones, replacing the chlorine of each acyl group by an alkyl group.
- Dimethylcadmium, $(CH_3)_2Cd$, supplies two methyl groups, so one mole reacts with two moles of an acid chloride.

Step 1: Identify the two groups on the ketone Acetyl chloride, CH_3COCl, already has a methyl group attached to its carbonyl carbon. Replacing Cl by the methyl group supplied by dimethylcadmium places a methyl group on each side of the carbonyl.

Step 2: Write the balanced reaction Both methyl groups on cadmium can be transferred, giving two molecules of the same ketone. The two chloride groups form cadmium chloride:

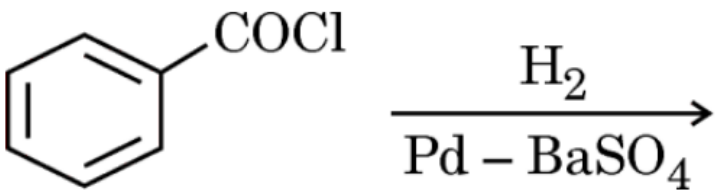
$$(CH_3)_2Cd + 2\,CH_3COCl \longrightarrow 2\,CH_3{-}C(=O){-}CH_3 + CdCl_2.$$

The organocadmium reaction stops at the ketone stage under these conditions.

Step 3: Conclusion The main organic product is propanone (acetone), $CH_3-C(=O)-CH_3$.

Quick Tip to Solve: For an acid chloride plus dialkylcadmium, replace Cl by one alkyl group and retain the C=O bond.

31(a)(i)(III). Complete the following reactions by writing the structure of the main products: [1 mark]



Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen over palladium supported on barium sulphate.
- The deactivated catalyst limits reduction at the aldehyde stage; the benzene ring remains unchanged.

Step 1: Identify the reducible group Benzoyl chloride contains the acyl chloride group $-COCl$ attached to a phenyl group, C_6H_5. Under Rosenmund conditions, chlorine is replaced by hydrogen without removing the carbonyl oxygen.

Quick Tip to Solve: For hydrogen with $Pd/BaSO_4$, replace $-COCl$ by $-CHO$, keeping the carbon skeleton intact.

Step 2: Write the reaction

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

The product retains the carbonyl carbon of the starting acid chloride. Further reduction to benzyl alcohol is suppressed by the low activity of this catalyst.

Step 3: Conclusion The main product is benzaldehyde, with condensed structure $\boxed{C_6H_5{-}C(=O)H}$.

Quick Tip to Solve: For hydrogen with $Pd/BaSO_4$, replace $-COCl$ by $-CHO$, keeping the carbon skeleton intact.

31(a)(ii)(I). Give simple chemical test to distinguish between the following pairs of compounds: Ethyl benzoate and benzoic acid [1 mark]

Solution:

Concept:

- Carboxylic acids react with aqueous sodium hydrogen carbonate to liberate carbon dioxide.
- An ester has no acidic carboxyl hydrogen and does not give this effervescence under the test conditions.

Step 1: Add the distinguishing reagent Take small portions of the two compounds separately and add aqueous $NaHCO_3$ at room temperature. Observe whether a gas is evolved; the test does not require heating or hydrolysis.

Step 2: Compare the observations Benzoic acid gives brisk effervescence of CO_2:

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2\uparrow$$

Ethyl benzoate, $C_6H_5COOC_2H_5$, gives no such effervescence. The evolved gas turns limewater milky.

Step 3: Conclusion The sodium hydrogen carbonate test distinguishes them: benzoic acid evolves CO_2, whereas ethyl benzoate does not.

Quick Tip to Solve: Look for the free $-COOH$ group: it gives bicarbonate effervescence, while $-COOC_2H_5$ does not.

31(a)(ii)(II). Give simple chemical test to distinguish between the following pairs of compounds: Propanal and propanone [1 mark]

Solution:

Concept:

- Tollens' reagent, ammoniacal silver nitrate, oxidises an aldehyde to a carboxylate ion.
- An ordinary ketone does not reduce this reagent; metallic silver is deposited only in a positive test.

Quick Tip to Solve: For an aldehyde–ketone pair, use Tollens' reagent: record the silver mirror for the aldehyde and no mirror for the ketone.

Step 1: Apply Tollens' test Add freshly prepared Tollens' reagent to separate samples in clean test tubes and warm gently in a water bath. Propanal has an aldehyde group, $-\mathrm{CHO}$, whereas propanone has a ketone carbonyl.

Step 2: State both observations Propanal gives a silver mirror as it is oxidised to propanoate:

$$\mathrm{CH_3CH_2CHO} + 2\,[\mathrm{Ag(NH_3)_2}]^+ + 3\,\mathrm{OH^-} \longrightarrow \mathrm{CH_3CH_2COO^-} + 2\,\mathrm{Ag}\downarrow + 4\,\mathrm{NH_3} + 2\,\mathrm{H_2O}$$

Propanone gives no silver mirror because its ketone group is not oxidised by this mild reagent.

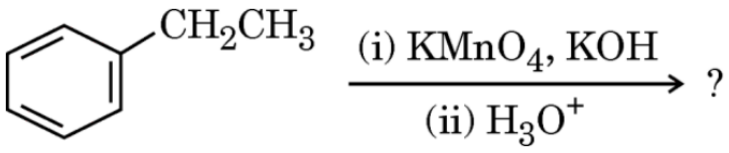
Step 3: Conclusion Propanal gives a positive Tollens' test (silver mirror); propanone gives a negative test.

Quick Tip to Solve: For an aldehyde–ketone pair, use Tollens' reagent: record the silver mirror for the aldehyde and no mirror for the ketone.

OR

31(b)(i)(I). Complete each synthesis by giving missing starting material, reagent or products:

[1 mark]



Solution:

Concept:

- Hot alkaline potassium permanganate oxidises an alkylbenzene side chain to a carboxylate when a benzylic hydrogen is present.
- Acidification converts the resulting carboxylate salt into the free carboxylic acid.

Step 1: Inspect the benzylic carbon Ethylbenzene is $\mathrm{C_6H_5-CH_2-CH_3}$. The carbon directly bonded to the benzene ring bears hydrogen atoms, so vigorous side-chain oxidation is possible. The aromatic ring is retained during this transformation.

Step 2: Apply oxidation and acidification Treatment with $\mathrm{KMnO_4}$ and KOH gives potassium benzoate as the aromatic product. The second step protonates it:

$$\mathrm{C_6H_5COO^-} + \mathrm{H_3O^+} \longrightarrow \mathrm{C_6H_5COOH} + \mathrm{H_2O}$$

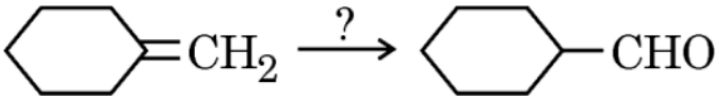
The benzylic carbon becomes the carboxyl carbon, so the original two-carbon side chain does not remain as a two-carbon acid substituent.

Step 3: Conclusion The missing product is benzoic acid, $\boxed{\mathrm{C_6H_5-C(=O)OH}}$.

Quick Tip to Solve: With vigorous side-chain oxidation, check for a benzylic hydrogen and replace the whole alkyl side chain by $-\mathrm{COOH}$ after acidification.

31(b)(i)(II). Complete each synthesis by giving missing starting material, reagent or products:

[1 mark]



Solution:

Concept:

- Hydroboration–oxidation hydrates an alkene in the anti-Markovnikov orientation, placing the hydroxyl group on the less substituted carbon.
- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde without extending oxidation to a carboxylic acid.

Step 1: Make the primary alcohol Treat methylenecyclohexane with BH_3 in THF, followed by alkaline H_2O_2. The terminal $=CH_2$ carbon becomes $-CH_2OH$, and the ring carbon receives hydrogen. This gives cyclohexylmethanol, $C_6H_{11}CH_2OH$.

Step 2: Oxidise to the required aldehyde Treat the primary alcohol with PCC in dry CH_2Cl_2:

$$C_6H_{11}CH_2OH \xrightarrow{PCC} C_6H_{11}CHO$$

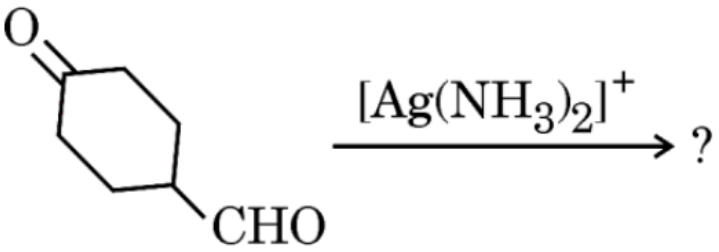
The carbon skeleton is preserved. Direct ozonolysis would cleave the exocyclic double bond and would not give the aldehyde shown in the question.

Step 3: Conclusion The missing reagent sequence is (1) BH_3/THF, (2) H_2O_2/OH^-, and (3) PCC in dry CH_2Cl_2, giving cyclohexanecarbaldehyde.

Quick Tip to Solve: To change terminal $=CH_2$ into $-CHO$ without losing a carbon, first form $-CH_2OH$ by hydroboration–oxidation, then use PCC.

31(b)(i)(III). Complete each synthesis by giving missing starting material, reagent or products:

[1 mark]



Solution:

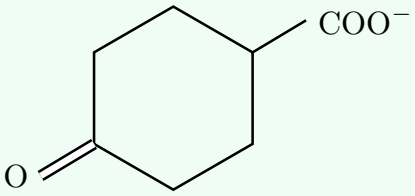
Concept:

- Tollens' reagent, $[Ag(NH_3)_2]^+$ in alkaline solution, selectively oxidises aldehydes to carboxylates.
- An ordinary ketone carbonyl is not oxidised by this reagent, so the ring ketone remains intact.

Quick Tip to Solve: With Tollens' reagent and both aldehyde and ketone groups present, change only $-CHO$; keep the ketone carbonyl exactly where it is.

Step 1: Identify the group that reacts The substrate has an aldehyde substituent $-CHO$ and a ketone group within the cyclohexane ring. Only the aldehyde is readily oxidised; the ring and its carbonyl position are unchanged.

Step 2: Write the selective transformation The attached $-CHO$ becomes $-COO-$ in the alkaline reaction mixture. The product is 4-oxocyclohexane-1-carboxylate: a six-membered ring bearing $-COO-$ at carbon 1 and a ketone carbonyl at carbon 4. On acidification, $-COO-$ becomes $-COOH$, giving 4-oxocyclohexane-1-carboxylic acid.



Product in the alkaline reaction medium

Step 3: Conclusion The aldehyde is oxidised to the carboxyl group while the cyclic ketone stays unchanged: 4-oxocyclohexane-1-carboxylate in the reaction medium, or 4-oxocyclohexane-1-carboxylic acid after acidification.

Quick Tip to Solve: With Tollens' reagent and both aldehyde and ketone groups present, change only $-CHO$; keep the ketone carbonyl exactly where it is.

31(b)(ii)(I). Carry out the following conversions:

Benzaldehyde to Benzophenone [1 mark]

Solution:

Concept:

- A Grignard reagent adds its organic group to the carbonyl carbon of an aldehyde, giving a secondary alcohol after acidic hydrolysis.
- Oxidation of that secondary alcohol gives a ketone with the same two carbon groups attached to its carbonyl carbon.

Step 1: Introduce a second phenyl group React benzaldehyde with phenylmagnesium bromide in dry ether, then hydrolyse with dilute acid:

$$C_6H_5CHO \xrightarrow[\text{dry ether}]{C_6H_5MgBr} (C_6H_5)_2CHOMgBr$$

$$(C_6H_5)_2CHOMgBr \xrightarrow{H_3O^+} (C_6H_5)_2CHOH$$

The intermediate alcohol is diphenylmethanol (benzhydrol).

Step 2: Oxidise the secondary alcohol Use acidified potassium dichromate to oxidise diphenylmethanol:

$$(C_6H_5)_2CHOH + [O] \longrightarrow (C_6H_5)_2CO + H_2O$$

Quick Tip to Solve: Build the extra phenyl–carbon bond with phenylmagnesium bromide first; oxidation alone cannot turn benzaldehyde into benzophenone.

Both phenyl groups remain attached to the same carbon; removal of two hydrogen atoms creates the ketone carbonyl.

Step 3: Conclusion Benzaldehyde is converted to benzophenone, $C_6H_5COC_6H_5$, by C_6H_5MgBr/dry ether, acidic hydrolysis, and oxidation with acidified $K_2Cr_2O_7$.

Quick Tip to Solve: Build the extra phenyl–carbon bond with phenylmagnesium bromide first; oxidation alone cannot turn benzaldehyde into benzophenone.

31(b)(ii)(II). Carry out the following conversions:

Benzaldehyde to 3-phenyl propanol [1 mark]

Solution:

Concept:

- Crossed aldol condensation with ethanal extends the side chain of benzaldehyde by two carbon atoms.
- Catalytic hydrogenation reduces the side-chain carbon-carbon double bond; a hydride reagent reduces the aldehyde group to a primary alcohol.

Step 1: Extend the carbon chain Treat benzaldehyde with ethanal in dilute alkali and heat. Ethanal provides the enolate because benzaldehyde has no alpha-hydrogen. Condensation and dehydration give cinnamaldehyde:

$$C_6H_5CHO + CH_3CHO \xrightarrow[\text{heat}]{\text{dil}\cdot\ NaOH} C_6H_5CH{=}CHCHO + H_2O.$$

Step 2: Reduce the side chain Hydrogenate the side-chain double bond under controlled conditions, then reduce the aldehyde using sodium borohydride:

$$C_6H_5CH{=}CHCHO \xrightarrow{H_2/Pd} C_6H_5CH_2CH_2CHO$$

$$C_6H_5CH_2CH_2CHO \xrightarrow[H_2O]{NaBH_4} C_6H_5CH_2CH_2CH_2OH.$$

The benzene ring is retained, and the alcohol group occupies carbon 1 of the three-carbon side chain.

Step 3: Conclusion Benzaldehyde is converted through cinnamaldehyde and 3-phenylpropanal to 3-phenylpropan-1-ol, $C_6H_5CH_2CH_2CH_2OH$.

Quick Tip to Solve: First count side-chain carbons: crossed aldol condensation with ethanal changes the one-carbon aldehyde chain into the required three-carbon chain.

32(a)(i)(I). Give reasons:

$[Ni(CO)_4]$ is diamagnetic whereas $[NiCl_4]^{2-}$ is paramagnetic. [Atomic number: Ni = 28] [1 mark]

Solution:

Concept:

- A complex with all electrons paired is diamagnetic, whereas unpaired electrons cause paramagnetism.
- The metal oxidation state determines its electron count. Neutral nickel has configuration $[\mathrm{Ar}]3d^8 4s^2$; Ni^{2+} has $3d^8$.

Step 1: Examine the carbonyl complex In $Ni(CO)_4$, the neutral CO ligands give nickel oxidation state zero. In the valence-bond description, the strong-field carbonyl ligands cause the electrons to occupy the $3d$ orbitals as $3d^{10}$, with all electrons paired. The vacant $4s$ and $4p$ orbitals form tetrahedral sp^3 hybrids.

Step 2: Examine the chloride complex In $[NiCl_4]^{2-}$, $x + 4(-1) = -2$ gives $x = +2$, so nickel is $3d^8$. Chloride is a weak-field ligand, and the tetrahedral complex retains two unpaired d electrons. Thus tetrahedral geometry alone does not determine whether a complex is magnetic; electron occupancy must also be considered.

Step 3: Conclusion $Ni(CO)_4$ is diamagnetic because it has no unpaired electrons, while $[NiCl_4]^{2-}$ is paramagnetic because it has two unpaired electrons.

Quick Tip to Solve: Calculate nickel's oxidation state first: it is zero in the carbonyl and $+2$ in the chloride complex, so their electron counts differ.

32(a)(i)(II). Give reasons:

CO is a stronger complexing agent than NH_3. [1 mark]

Solution:

Concept:

- A ligand forms a coordinate sigma bond by donating a lone pair to a suitable vacant orbital of the metal.
- A pi-acceptor ligand can also accept electron density from a filled metal d orbital into its empty antibonding π^* orbital.

Step 1: Identify both interactions of carbon monoxide CO donates a lone pair on carbon to the metal, forming a sigma bond. It also accepts electron density back from filled metal d orbitals into its vacant π^* orbitals. This second interaction is metal-to-ligand pi back-bonding.

Step 2: Compare with ammonia The sigma donation and pi back-bonding in a metal-carbonyl bond reinforce each other; this is the synergic effect. In contrast, NH_3 acts essentially as a sigma donor through the nitrogen lone pair and does not provide comparable pi-acceptor back-bonding. The additional bonding interaction makes carbon monoxide the stronger complexing ligand in this comparison.

Step 3: Conclusion CO is a stronger complexing agent than NH_3 because synergic sigma donation

Quick Tip to Solve: For carbonyl bonding, state both directions of electron flow: ligand-to-metal sigma donation and metal-to-ligand pi back-donation.

and pi back-bonding strengthen the metal-carbonyl bond.

Quick Tip to Solve: For carbonyl bonding, state both directions of electron flow: ligand-to-metal sigma donation and metal-to-ligand pi back-donation.

32(a)(i)(III). Give reasons:

The trans isomer of complex $[Co(en)_2Cl_2]^+$ is optically inactive. [1 mark]

Solution:

Concept:

- Optical isomerism requires a chiral arrangement: the molecule and its mirror image must be non-superimposable.
- A plane of symmetry makes a coordination arrangement achiral. Here en denotes the bidentate ethane-1,2-diamine ligand.

Step 1: Locate the ligands in the trans arrangement In octahedral trans-$[\mathrm{Co(en)_2Cl_2}]^+$, the two chloride ligands occupy opposite positions. The four nitrogen donor atoms of the two ethane-1,2-diamine ligands occupy the remaining four positions around cobalt.

Step 2: Test the arrangement for chirality The trans coordination arrangement has a plane of symmetry through cobalt and the four nitrogen donor positions; reflection exchanges the two identical opposite chloride ligands. Its mirror image is therefore superimposable on the original arrangement. It does not form the pair of optical isomers possible for the cis arrangement.

Step 3: Conclusion The trans isomer of $[\mathrm{Co(en)_2Cl_2}]^+$ is optically inactive because its symmetry makes the coordination arrangement achiral.

Quick Tip to Solve: Place the two chloride ligands opposite one another, then test the remaining donor arrangement for a plane of symmetry before claiming optical isomerism.

32(a)(ii). Using Crystal Field theory, write the number of unpaired electrons in octahedral complexes of Fe^{3+} in the presence of:

(I) Strong field ligand

(II) Weak field ligand

[Atomic number: Fe = 26] [2 marks]

Solution:

Concept:

- Octahedral crystal fields split the five metal d orbitals into lower-energy t_{2g} and higher-energy e_g sets, separated by Δ_o.
- When $\Delta_o > P$, where P is the electron-pairing energy, electrons pair in t_{2g} before occupying e_g. When $\Delta_o < P$, occupation of e_g is preferred to pairing.

Step 1: Determine the d-electron count Iron has atomic number 26 and ground-state configuration

Quick Tip to Solve: Begin with the printed metal charge: ferric iron is d-five, so compare the low-spin occupancy (2,2,1) with five singly occupied orbitals.

$[\mathrm{Ar}]3d^6 4s^2$. Removing the two $4s$ electrons and one $3d$ electron gives

$$\mathrm{Fe}^{3+}: \quad [\mathrm{Ar}]3d^5.$$

Thus five electrons must be placed in the split d orbitals.

Step 2: Fill the orbitals for a strong-field ligand For a strong-field ligand, $\Delta_o > P$. All five electrons occupy the three lower t_{2g} orbitals, with occupancies $(2, 2, 1)$; the two e_g orbitals remain empty. The low-spin configuration is

$$t_{2g}^5 e_g^0.$$

Two orbitals contain paired electrons and one contains a single electron.

Step 3: Fill the orbitals for a weak-field ligand For a weak-field ligand, $\Delta_o < P$. Hund's rule favours single occupation of all five d orbitals before pairing. The high-spin configuration is

$$t_{2g}^3 e_g^2.$$

Each of the three t_{2g} orbitals and each of the two e_g orbitals contains one electron.

Step 4: Conclusion Octahedral Fe^{3+} has (I) one unpaired electron with a strong-field ligand and (II) five unpaired electrons with a weak-field ligand.

Quick Tip to Solve: Begin with the printed metal charge: ferric iron is d-five, so compare the low-spin occupancy (2,2,1) with five singly occupied orbitals.

OR

32(b)(i)(I). Name the type of isomerism exhibited by the following compounds. Also draw their corresponding isomers.

$[Co(NH_3)_6][Cr(CN)_6]$ [1 mark]

Solution:

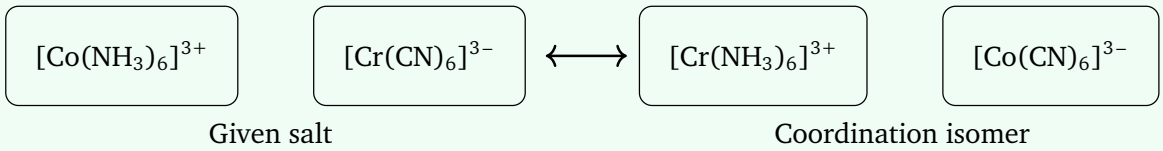
Concept:

- Coordination isomerism occurs when both the cation and the anion are complex ions and ligands are distributed differently between their metal centres.
- The overall chemical composition stays the same, although the metal to which each ligand is bonded changes.

Step 1: Identify the two coordination spheres The given salt contains the complex cation $[Co(NH_3)_6]^{3+}$ and the complex anion $[Cr(CN)_6]^{3-}$. Ammonia is neutral and cyanide has charge -1; thus both cobalt and chromium have oxidation state $+3$.

Step 2: Exchange the ligand sets Coordinate the six ammonia ligands to chromium and the six cyanide ligands to cobalt. This gives the cation $[Cr(NH_3)_6]^{3+}$ and the anion $[Co(CN)_6]^{3-}$, retaining the same numbers of metal atoms and ligands. The two coordination arrangements are drawn below.

Quick Tip to Solve: When both ions contain a metal complex, swap the ligand sets between the two metals and check that the total formula is unchanged.



Ligand distribution in the two coordination isomers

Step 3: Conclusion The compound exhibits **coordination isomerism**; its corresponding isomer is $[Cr(NH_3)_6][Co(CN)_6]$.

Quick Tip to Solve: When both ions contain a metal complex, swap the ligand sets between the two metals and check that the total formula is unchanged.

32(b)(i)(II). Name the type of isomerism exhibited by the following compounds. Also draw their corresponding isomers.

$[Co(en)_3]^{3+}$ [1 mark]

Solution:

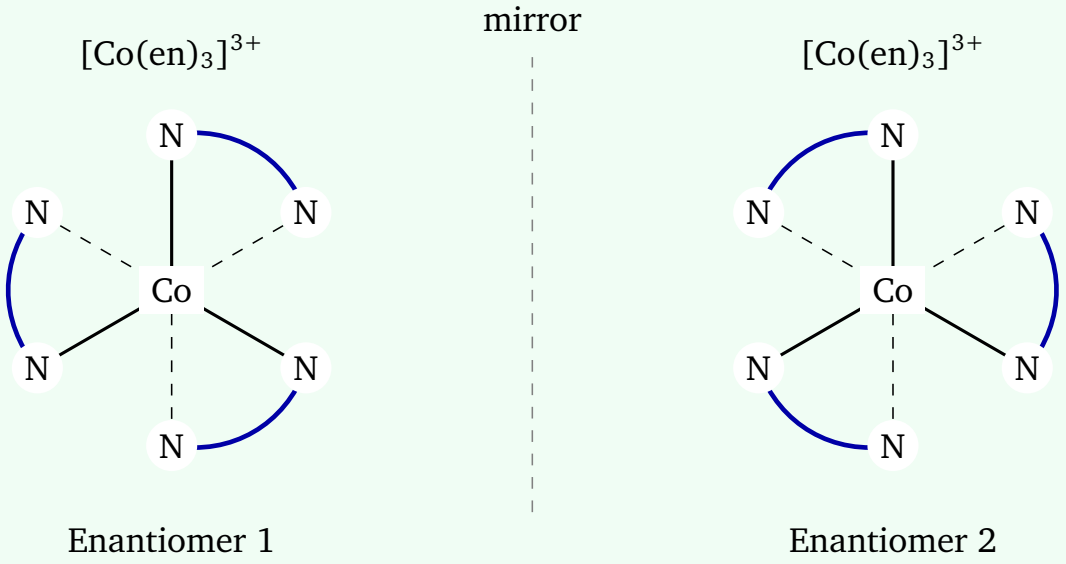
Concept:

- Optical isomers are non-superimposable mirror images; each member of such a pair is called an enantiomer.
- Ethane-1,2-diamine, abbreviated en, is a bidentate ligand. Each en binds through two nitrogen donor atoms to form a chelate ring.

Step 1: Identify the octahedral chelate arrangement In $[Co(en)_3]^{3+}$, three en ligands supply six nitrogen donors around the cobalt centre. The coordination geometry is octahedral, with each en occupying a pair of adjacent coordination positions.

Step 2: Compare the mirror-image structures The three chelate rings can wind around cobalt in two opposite senses. Reflection reverses this winding, and rotation cannot superimpose the two arrangements. In the drawing, each curved N–N link represents one en ligand, with its carbon chain omitted for clarity. Solid and dashed metal–N bonds distinguish the front and rear triangular sets of donors.

Quick Tip to Solve: For an octahedral complex with three bidentate en ligands, track the winding of all three chelate rings to recognise the optical pair.



Non-superimposable mirror-image pair of $[Co(en)_3]^{3+}$; each curved link is one en ligand

Step 3: Conclusion $[Co(en)_3]^{3+}$ exhibits **optical isomerism**. Its two enantiomers are the opposite-handed Δ and Λ forms shown as a mirror-image pair.

Quick Tip to Solve: For an octahedral complex with three bidentate en ligands, track the winding of all three chelate rings to recognise the optical pair.

32(b)(i)(III). Name the type of isomerism exhibited by the following compounds. Also draw their corresponding isomers.

$[Co(NH_3)_3(NO_2)_3]$ [1 mark]

Solution:

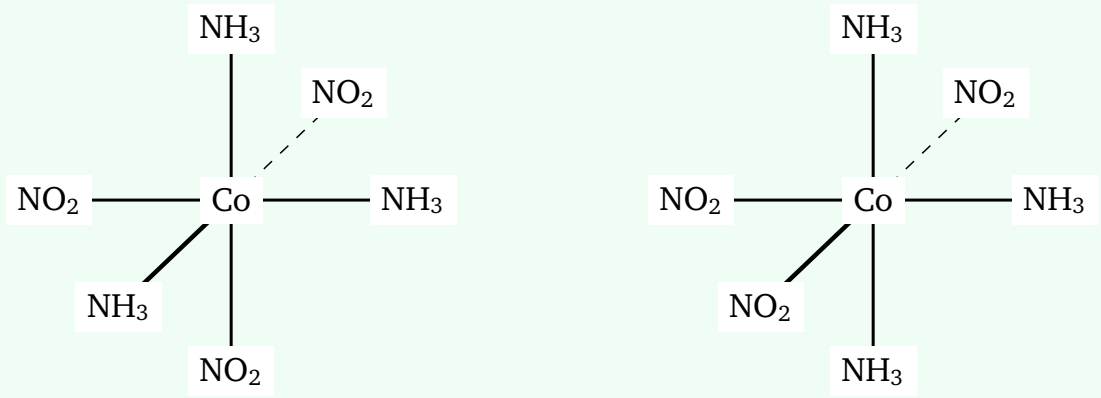
Concept:

- An octahedral complex of the type MA_3B_3, where A and B are different monodentate ligands, has facial (fac) and meridional (mer) geometrical isomers.
- In the fac form, the three identical ligands are mutually cis; in the mer form, two of the three identical ligands are trans.

Step 1: Place three identical ligands on one face In the fac arrangement of $[Co(NH_3)_3(NO_2)_3]$, place the three ammonia ligands at three mutually adjacent vertices of the octahedron. They occupy a triangular face, so all three ammonia–cobalt–ammonia angles are $90°$. The three nitro ligands occupy the opposite face.

Step 2: Place three identical ligands in a meridional plane In the mer arrangement, put two ammonia ligands at opposite vertices and the third at a vertex perpendicular to them. All three lie in a plane through cobalt, with one ammonia–cobalt–ammonia angle of $180°$. The drawings distinguish the two arrangements without changing the identity or attachment of either ligand.

Quick Tip to Solve: Look for a trans pair among the three ammonia ligands: a trans pair means mer; all three mutually cis means fac.



fac (all three NH_3 mutually cis) mer (one trans pair of NH_3)

Facial and meridional geometrical isomers; opposite positions across Co are trans

Step 3: Conclusion The compound exhibits **geometrical isomerism**: the corresponding forms are fac-$[Co(NH_3)_3(NO_2)_3]$ and mer-$[Co(NH_3)_3(NO_2)_3]$.

Quick Tip to Solve: Look for a trans pair among the three ammonia ligands: a trans pair means mer; all three mutually cis means fac.

32(b)(ii). Differentiate between weak field and strong field ligands. How does the strength of the ligand influence the spin of the complex? [2 marks]

Solution:

Concept:

- Ligands split the five initially degenerate metal d-orbitals into groups of different energies. For an octahedral complex, the splitting energy is Δ_o; the energy needed to pair two electrons in one orbital is P.
- The competition between crystal-field splitting and pairing energy determines whether electrons pair in lower orbitals or occupy higher orbitals singly.

Step 1: Compare the field strengths Weak field ligands, such as F^- and Cl^-, produce a relatively small crystal-field splitting. Strong field ligands, such as CN^- and CO, produce a relatively large splitting for a given metal ion and geometry.

Step 2: Relate splitting to spin For octahedral configurations that allow a high-spin/low-spin choice, if $\Delta_o < P$, occupying a higher orbital costs less energy than pairing: weak field ligands favour more unpaired electrons and high spin. If $\Delta_o > P$, electrons pair in the lower t_{2g} orbitals before entering the higher e_g orbitals: strong field ligands favour fewer unpaired electrons and low spin. For example, an octahedral d^5 ion has $t_{2g}^3 e_g^2$ with five unpaired electrons in a weak field, but $t_{2g}^5 e_g^0$ with one unpaired electron in a strong field.

Step 3: Conclusion Weak field ligands cause smaller splitting and favour high-spin complexes; strong field ligands cause larger splitting and favour low-spin complexes when both arrangements are possible.

Quick Tip to Solve: Compare Δ_o with P: smaller splitting favours promotion, while larger splitting favours pairing.

33(a)(i). The initial concentration of N_2O_5 in the first order reaction:

$N_2O_5(g) \rightarrow 2\,NO_2(g) + \frac{1}{2}\,O_2(g)$

was $1.2 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$. The concentration of N_2O_5 after 60 minutes was $0.2 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$. Calculate the rate constant of the reaction at 318 K.

[$\log 6 = 0.778$**]** [3 marks]

Solution:

Concept:

- For a first-order reaction, $k = \dfrac{2.303}{t}\log_{10}\left(\dfrac{[A]_0}{[A]_t}\right)$, where k is the rate constant, $[A]_0$ and $[A]_t$ are reactant concentrations initially and after time t.
- The concentration ratio is dimensionless. A first-order rate constant has units of inverse time, so using time in minutes gives min^{-1}.

Step 1: Identify the reactant concentrations For the decomposition $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, use the measured concentration of N_2O_5 itself in the integrated rate equation. The given quantities are $[A]_0 = 1.2 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$, $[A]_{60} = 0.2 \times 10^{-2}\,\text{mol}\,\text{L}^{-1}$ and $t = 60\,\text{min}$. The product coefficients do not multiply the reactant concentration ratio.

Step 2: Form the concentration ratio Both concentrations have the same units and power of ten, which cancel:

$$\frac{[A]_0}{[A]_{60}} = \frac{1.2 \times 10^{-2}}{0.2 \times 10^{-2}} = 6.$$

Thus the logarithmic term in the integrated first-order equation is $\log_{10} 6 = 0.778$, as supplied.

Step 3: Substitute in the first-order rate equation Using the elapsed time in minutes,

$$\begin{aligned} k &= \frac{2.303}{60}\log_{10} 6 \\ &= \frac{2.303 \times 0.778}{60} \\ &= 0.0298622\,\text{min}^{-1}. \end{aligned}$$

For seconds, divide this value by 60: $k = 4.9770 \times 10^{-4}\,\text{s}^{-1}$. The stated temperature identifies the temperature at which this rate constant applies; no temperature conversion or Arrhenius calculation is needed.

Step 4: Conclusion At $318\,\text{K}$, the rate constant is $\boxed{k = 2.99 \times 10^{-2}\,\text{min}^{-1}}$, or equivalently $\boxed{4.98 \times 10^{-4}\,\text{s}^{-1}}$.

Quick Tip to Solve: Cancel the common 10^{-2} factors first to obtain the ratio 6, and keep the time unit consistent with the unit of k.

33(a)(ii)(I). Account for the following:

We cannot determine the order of a reaction by taking into consideration the balanced chemical equation. [1 mark]

Solution:

Concept:

- The order of a reaction is the sum of the powers of reactant concentrations in its experimentally determined rate law.
- A balanced overall chemical equation expresses stoichiometry and conservation of atoms, but need not describe an elementary reaction step.

Step 1: Distinguish stoichiometry from kinetics If the measured rate law is $r = k[A]^m[B]^n$, the order is $m + n$. The exponents m and n must be found from rate measurements; they are not generally the coefficients of A and B in the overall balanced equation.

Step 2: Explain the role of the mechanism An overall reaction may occur through several elementary steps, and its observed rate depends on the mechanism, including the slow step. The balanced equation does not supply this information. Stoichiometric coefficients can give rate-law powers for an elementary step, but cannot be assumed to do so for an arbitrary overall reaction.

Step 3: Conclusion Therefore, reaction order must be determined experimentally and cannot in general be inferred from the balanced chemical equation alone.

Quick Tip to Solve: Use concentration powers from the measured rate law to find order; use equation coefficients for stoichiometric calculations.

33(a)(ii)(II). Account for the following:

A bimolecular reaction may become kinetically of first order under a specified condition. [1 mark]

Solution:

Concept:

- For a bimolecular process with rate law $r = k[A][B]$, both reactants normally contribute to the observed rate.
- When one reactant is in large excess, its concentration changes negligibly during the reaction and can be absorbed into an observed rate constant.

Step 1: Apply the excess-reactant condition Let B be present in a very large excess compared with A. Although B is consumed, the fractional change in $[B]$ is negligible, so $[B] \approx [B]_0$ remains effectively constant throughout the measurement.

Step 2: Obtain the observed rate law The rate law becomes

$$r = k[A][B] \approx k[B]_0[A] = k_{\text{obs}}[A], \qquad k_{\text{obs}} = k[B]_0.$$

The measured rate therefore varies only with the first power of $[A]$. This is pseudo-first-order behaviour, as in ester hydrolysis when water is present in large excess; the underlying bimolecular process is

Quick Tip to Solve: Check which reactant is in large excess, then combine its nearly constant concentration with k before finding the observed order.

unchanged.

Step 3: Conclusion A bimolecular reaction behaves kinetically as a pseudo-first-order reaction when one reactant is in large excess and its concentration stays practically constant.

Quick Tip to Solve: Check which reactant is in large excess, then combine its nearly constant concentration with k before finding the observed order.

OR

33(b)(i). The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate activation energy (E_a).

[2.303 R = 19.15 J K^{-1} mol^{-1}, log 2 = 0.3] [3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A is the frequency factor, E_a is the activation energy and T is absolute temperature.
- At unchanged reactant concentrations, the ratio of reaction rates equals k_2/k_1. Taking common logarithms at two temperatures gives $\log(k_2/k_1) = \dfrac{E_a}{2.303R}(1/T_1 - 1/T_2)$.

Step 1: Identify the two temperatures and rate ratio The initial temperature is $T_1 = 298\,\text{K}$. The increase of $10\,\text{K}$ makes the final temperature $T_2 = 308\,\text{K}$. Since the rate doubles when only temperature changes, $k_2/k_1 = 2$. The increase itself is not the final temperature; both absolute temperatures enter the Arrhenius relation.

Step 2: Rearrange the two-temperature Arrhenius equation Use the supplied common-logarithm values, with the same frequency factor over this temperature interval:

$$\log 2 = \frac{E_a}{2.303R}\frac{T_2 - T_1}{T_1 T_2},$$
$$E_a = (2.303R)(\log 2)\frac{T_1 T_2}{T_2 - T_1}.$$

Since $T_2 > T_1$, the reciprocal-temperature difference and the activation energy are positive.

Step 3: Substitute the supplied values

$$E_a = 19.15 \times 0.3 \times \frac{298 \times 308}{10}$$
$$= 52729.908\,\text{J mol}^{-1}$$
$$\approx 52.73\,\text{kJ mol}^{-1}.$$

The temperature factor has units of kelvin, cancelling the inverse kelvin in $2.303R$. Division by 1000 converts joules per mole to kilojoules per mole.

Step 4: Conclusion The activation energy is $\boxed{E_a \approx 52.73\,\text{kJ mol}^{-1}}$, using the logarithm value given in the question.

Quick Tip to Solve: For a rate doubling over a temperature rise, set $k_2/k_1 = 2$ and use $T_2 = T_1 + 10$; do not replace either absolute temperature by the rise.

33(b)(ii). For a reaction:

$2\,H_2O_2 \xrightarrow{I^-} 2\,H_2O + O_2$

the proposed mechanism is as given below:

(I) $H_2O_2 + I^- \longrightarrow H_2O + IO^-$ **(slow)**

(II) $H_2O_2 + IO^- \longrightarrow H_2O + I^- + O_2$ **(fast)**

(1) Write rate law for the reaction.

(2) Write the overall order and molecularity of the reaction. [2 marks]

Solution:

Concept:

- The slow elementary step controls the rate of a multistep reaction. Its reacting species determine the rate law.
- Overall order is the sum of concentration powers in the rate law. Molecularity counts reacting particles in an elementary step; it is not assigned to a composite overall reaction.

Step 1: Write the rate law from the slow step Step (I), $H_2O_2 + I^- \longrightarrow H_2O + IO^-$, is slow. It involves one molecule of H_2O_2 and one I^- ion, so

$$\text{Rate} = k[H_2O_2][I^-].$$

Here k is the rate constant. The intermediate IO^- is formed in this step and consumed rapidly in step (II); it does not appear as a reactant in the rate-determining step.

Step 2: Obtain order and interpret molecularity The rate law is first order in H_2O_2 and first order in I^-, giving an overall order of $1 + 1 = 2$. The slow elementary step has two reacting particles and is therefore bimolecular: its molecularity is 2. The fast step is also bimolecular. Strictly, the composite overall reaction has no defined molecularity; the requested value 2 refers to the rate-determining elementary step. Adding the steps cancels IO^- and regenerates the I^- catalyst.

Step 3: Conclusion $\boxed{\text{Rate} = k[H_2O_2][I^-]}$; overall order $= 2$, and molecularity of the slow step $= 2$ (bimolecular).

Quick Tip to Solve: Select the step labelled slow before writing the rate law. Count its reacting particles for molecularity, and add the rate-law powers for order.