CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-4-2

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. 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:

- Acid-catalysed dehydration removes water from an alcohol to form an alkene.
- Protonation converts the poor leaving group $-\mathrm{OH}$ into $-\mathrm{OH}_2^+$, from which water can leave.

Step 1: Identify the initial acid-base reaction The oxygen atom of an alcohol has lone pairs. It accepts a proton from the acidic medium before any carbon-oxygen bond is broken:

$$\mathrm{ROH} + \mathrm{H}^+ \rightleftharpoons \mathrm{ROH}_2^+.$$

Thus the first event is protonation of the alcohol molecule, corresponding to option (C).

Step 2: Distinguish the later steps After protonation, water can leave; in the usual secondary or tertiary alcohol mechanism this produces a carbocation. Subsequent loss of a proton forms the alkene. Therefore carbocation formation (A) and elimination of water (D) follow the initial proton transfer. Ester formation (B) is not the first step in the standard acid-catalysed dehydration mechanism.

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

Quick Tip to Solve: For acid-catalysed alcohol dehydration, first turn the hydroxyl group into water by adding a proton.

2. 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 an organochlorine compound used as an insecticide.
- A non-biodegradable substance persists because biological processes do not readily break it down.

Step 1: Identify the agricultural role DDT is used to kill insect pests, so its relevant agricultural classification is an insecticide. It does not supply essential mineral nutrients to plants and therefore is not a fertilizer, eliminating (B). The greenhouse-gas description in (A) does not identify its characteristic use or environmental behaviour.

Step 2: Assess environmental persistence DDT resists microbial decomposition and remains in the environment for long periods. It can accumulate in fatty tissues and become concentrated along food chains. Thus it is non-biodegradable rather than biodegradable. Option (C) incorrectly states its degradability, whereas option (D) combines its actual use with its persistence.

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

Quick Tip to Solve: Associate DDT with persistent organochlorine insecticides; reject any option calling it biodegradable.

3. 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 the standard alkaline-medium reaction, iodide I^- is oxidised to iodate IO_3^-.

Step 1: Identify the iodine oxidation product In iodide, iodine has oxidation state -1. In iodate, the three oxygen atoms contribute -6, so iodine has oxidation state $+5$. Its oxidation therefore involves

Quick Tip to Solve: Read the medium and the actual formulas: alkaline permanganate gives iodate, which is option D here.

loss of six electrons. The oxidation half-reaction in alkaline solution is

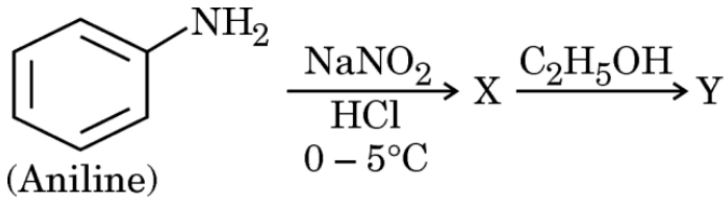
$$I^- + 6OH^- \longrightarrow IO_3^- + 3H_2O + 6e^-.$$

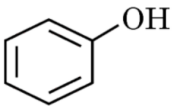
Step 2: Compare all printed options Option (D) is iodate, the required product. Iodine in (B) is the familiar product of oxidation under different conditions, so it must not be selected merely because permanganate oxidises iodide. Hypoiodite in (C) has iodine in oxidation state $+1$, while periodate in (A) has iodine in oxidation state $+7$; neither is the standard product for the stated alkaline permanganate reaction.

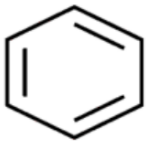
Step 3: Conclusion The oxidation product is IO_3^-, iodate ion. Hence, the correct option is (D).

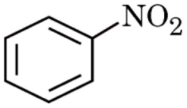
Quick Tip to Solve: Read the medium and the actual formulas: alkaline permanganate gives iodate, which is option D here.

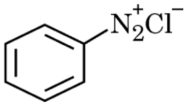
4. In the given reaction sequence, the structure of Y would be: [1 mark]



(A) 

(B) 

(C) 

(D) 

Correct Answer: (B) 

Solution:

Concept:

- Aniline undergoes diazotisation with $NaNO_2/HCl$ at $0-5\,^\circ C$, forming benzenediazonium chloride.
- Ethanol reduces an aromatic diazonium group to hydrogen, releasing nitrogen gas.

Step 1: Identify intermediate X The first reagent combination generates nitrous acid in situ. At the stated low temperature, aniline is converted into benzenediazonium chloride, $C_6H_5N_2^+Cl^-$. Therefore X is the diazonium salt drawn in option (D), but the question asks for Y after the second reaction.

Step 2: Apply the ethanol reaction Ethanol reduces the diazonium salt to benzene and is itself

Quick Tip to Solve: After diazotisation, inspect the second reagent: ethanol replaces the diazonium group by hydrogen.

oxidised to ethanal:

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

Phenol in (A) would be obtained by hydrolysis with warm water. Nitrobenzene in (C) is not produced by either stated reagent, and the diazonium salt in (D) is consumed in the second step. The unsubstituted benzene ring in (B) is therefore Y.

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

Quick Tip to Solve: After diazotisation, inspect the second reagent: ethanol replaces the diazonium group by hydrogen.

5. 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:

- A tetrahedral carbon attached to four different groups is a stereogenic centre.
- The listed bromoalkanes must be checked for identical substituents on each possible asymmetric carbon.

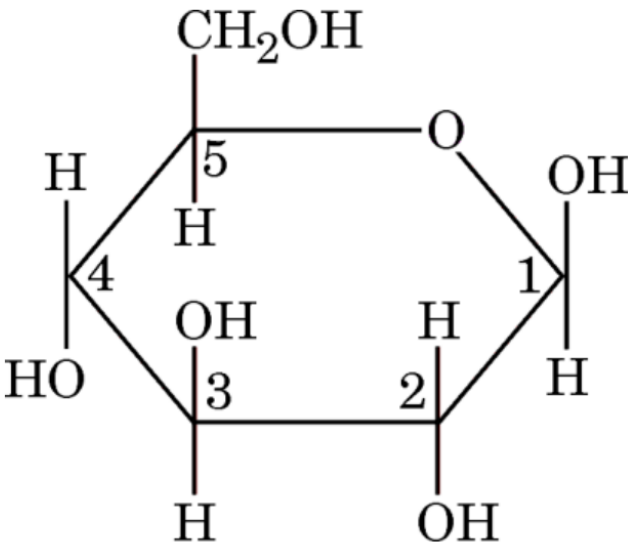
Step 1: Check 2-bromobutane The structure is $CH_3 - CH(Br) - CH_2 - CH_3$. Its second carbon is bonded to Br, H, CH_3 and CH_2CH_3. All four groups differ, so this carbon is asymmetric and the molecule is chiral.

Step 2: Eliminate the remaining molecules In 1-bromobutane and 1-bromopropane, the bromine-bearing carbon is a CH_2 carbon with two identical hydrogen atoms. Neither chain contains another asymmetric carbon. In 2-bromopropane, $CH_3 - CH(Br) - CH_3$, the central carbon has two identical methyl groups. Therefore options (B), (C) and (D) have no stereogenic centre and are achiral.

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

Quick Tip to Solve: List the four groups on the bromine-bearing carbon; methyl and ethyl are different, but two methyls are not.

6. 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 the open-chain sugar that becomes a new stereogenic centre during cyclisation.
- In a cyclic hemiacetal, the anomeric carbon is bonded both to the ring oxygen and to a hydroxyl oxygen.

Step 1: Locate the hemiacetal carbon In the supplied Haworth structure, carbon 1 is directly bonded to the ring oxygen on one side and also carries an OH group. These two oxygen connections identify it as the hemiacetal carbon. It corresponds to the aldehyde carbon of the open-chain form of glucose.

Step 2: Compare the other numbered positions Carbons 2 and 3 carry hydroxyl groups but are not bonded directly to the ring oxygen, so neither is anomeric. Carbon 5 is bonded to the ring oxygen, but it also bears the CH_2OH substituent and lacks the anomeric hydroxyl group. It supplies the oxygen involved in ring formation rather than the original carbonyl carbon. Hence the carbon numbered 1 is the required position.

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 bonded to both the ring oxygen and an OH group to locate the anomeric centre.

7. 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 is $p = K_{\mathrm{H}}x$, where p is the gas partial pressure and x its mole fraction in solution.
- At fixed pressure and temperature, $x = p/K_{\mathrm{H}}$, so solubility is inversely related to this Henry constant.

Step 1: Use the stated Henry-constant convention For a gas dissolved in a liquid, Henry's law gives

$$x = \frac{p}{K_{\mathrm{H}}}.$$

Comparing gases at the same temperature and partial pressure, a greater K_{H} gives a smaller dissolved mole fraction. A smaller mole fraction means lower solubility.

Step 2: Test the options Option (B) correctly associates a greater Henry constant with lower gas solubility. Option (A) reverses the inverse relationship. Option (C) is false because the constant depends on the gas-solvent pair and temperature, and option (D) contradicts Henry's law, which directly relates the constant to the dissolved mole fraction.

Step 3: Conclusion K_{H} is greater for gases with lower solubility. Hence, the correct option is (B).

Quick Tip to Solve: At the same pressure use $x = p/K_{\mathrm{H}}$: increasing the denominator decreases dissolved gas and solubility.

8. 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:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its ions.
- Lanthanoid contraction is the gradual decrease in atomic and ionic radii across the series because 4f electrons shield the nuclear charge poorly.

Step 1: Check statements (A), (B) and (C) La has the configuration $[\mathrm{Xe}]\,5d^1 6s^2$, so it meets the

Quick Tip to Solve: For an incorrect-statement question, check the universal claim first: radioactivity is not shared by all lanthanoids.

transition-element criterion: (A) is correct. Lanthanoid contraction makes the radii of Zr and Hf almost identical, validating (B). The increasing effective nuclear charge contracts the trivalent ions from La^{3+} to Lu^{3+}, validating (C).

Step 2: Check the radioactivity statement Radioactivity is not a general property of all lanthanoids. Promethium has no stable isotope, whereas most lanthanoids possess stable isotopes. Thus the blanket statement that lanthanoids are radioactive is incorrect.

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

Quick Tip to Solve: For an incorrect-statement question, check the universal claim first: radioactivity is not shared by all lanthanoids.

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

$2Ag^+(aq) + Mg(s) \rightarrow 2Ag(s) + Mg^{2+}(aq)$

$E^\circ_{cell} = 2.96$ 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 $[Mg^{2+}]$ increases.

(C) It will increase as $[Ag^+]$ increases.

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

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

Solution:

Concept:

- The Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{RT}{nF}\ln Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solids have unit activity and do not appear in the reaction quotient.

Step 1: Form the reaction quotient For $2Ag^+ + Mg \longrightarrow 2Ag + Mg^{2+}$, magnesium releases two electrons, so $n = 2$. Using concentrations for the dissolved ions,

$$Q = \frac{[Mg^{2+}]}{[Ag^+]^2}.$$

The solid metals are omitted.

Step 2: Follow the voltage as the reaction proceeds As the forward reaction proceeds, $[Mg^{2+}]$ increases and $[Ag^+]$ decreases. Both changes increase Q, so the Nernst correction increases and the cell voltage decreases from its initial value. Option (A) ignores these concentration changes. Option (C) describes an increase of silver-ion concentration, which does not occur during the forward reaction; (D) has the wrong direction of voltage change.

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

Quick Tip to Solve: Write products over reactants in Q; an increasing Q always lowers the potential for the reaction as written.

10. Out of Ti^{3+}, Cr^{3+}, Mn^{2+} and Ni^{2+} ions, the one which has the highest magnetic moment is: [Atomic number: Ti = 22, Cr = 24, Mn = 25, Ni = 28] [1 mark]

(A) Ti^{3+}

(B) Cr^{3+}

(C) Mn^{2+}

(D) Ni^{2+}

Correct Answer: (C) Mn^{2+}

Solution:

Concept:

- The spin-only magnetic moment is $\mu = \sqrt{n(n+2)}\,\mu_B$, where n is the number of unpaired electrons and μ_B is the Bohr magneton.
- When forming transition-metal cations, electrons are removed from the 4s subshell before the 3d subshell.

Step 1: Determine the d configurations The given atomic numbers give Ti^{3+} : $3d^1$, Cr^{3+} : $3d^3$, Mn^{2+} : $3d^5$, and Ni^{2+} : $3d^8$. By Hund's rule, their respective numbers of unpaired electrons are 1, 3, 5 and 2.

Step 2: Compare all four moments Substitution gives $\sqrt{3}\,\mu_B$ for Ti^{3+}, $\sqrt{15}\,\mu_B$ for Cr^{3+}, $\sqrt{35}\,\mu_B$ for Mn^{2+}, and $\sqrt{8}\,\mu_B$ for Ni^{2+}. The half-filled $3d^5$ ion has five unpaired electrons, more than any other listed ion.

Step 3: Conclusion Mn^{2+} has the highest magnetic moment, approximately $5.92\,\mu_B$. Hence, the correct option is (C).

Quick Tip to Solve: Count unpaired d electrons after removing 4s electrons; a half-filled d subshell gives the largest spin-only moment here.

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

(A) CH_3NO_2

(B) CH_3NH_2

(C) CH_3CONH_2

(D) $CH_3CH_2NH_2$

Correct Answer: (C) CH_3CONH_2

Solution:

Concept:

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

Step 1: Identify the functional group required The reactant must contain the primary amide group

Quick Tip to Solve: Look for CONH2 in the starting compound; do not select the amine produced after the one-carbon degradation.

$-CONH_2$. Among the options, only CH_3CONH_2, ethanamide, has this group. CH_3NO_2 is a nitro compound, while CH_3NH_2 and $CH_3CH_2NH_2$ are already amines.

Step 2: Apply the degradation reaction Ethanamide gives methylamine, with loss of the carbonyl carbon. The balanced reaction is

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

Thus methylamine is the product, not the substrate which gives this reaction.

Step 3: Conclusion CH_3CONH_2 undergoes Hofmann bromamide degradation. Hence, the correct option is (C).

Quick Tip to Solve: Look for CONH2 in the starting compound; do not select the amine produced after the one-carbon degradation.

12. What amount of electric charge is required for the oxidation of 1 mole of H_2O to O_2? [1 mark]

(A) 1F

(B) 2F

(C) 3F

(D) 4F

Correct Answer: (B) 2F

Solution:

Concept:

- Faraday's law gives $Q = n_e F$, where n_e is the amount of electrons in moles and F is the charge carried by one mole of electrons.
- Oxygen changes from oxidation state -2 in water to zero in molecular oxygen.

Step 1: Balance the oxidation half-reaction The oxidation half-reaction in acidic notation is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-.$$

Thus two moles of water lose four moles of electrons. Equivalently, each oxygen atom loses two electrons when its oxidation state rises from -2 to zero.

Step 2: Calculate charge for the stated amount The question specifies one mole of water, which requires $4/2 = 2$ moles of electrons. Hence $Q = 2F$, approximately 1.93×10^5 C. The value $4F$ would correspond to two moles of water or one mole of oxygen formed, not the amount of water given. Neither $1F$ nor $3F$ matches the electron balance.

Step 3: Conclusion The required charge is $2F$. Hence, the correct option is (B).

Quick Tip to Solve: Balance the half-reaction, then scale it to moles of water: 4F belongs to two moles of water, not one.

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

Reason (R): In cuprous ion, 3d-orbitals are partially filled. [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:

- A species is diamagnetic when all its electrons are paired; unpaired electrons cause paramagnetism.
- Cuprous means copper(I), Cu^{+}. Copper has the atomic configuration $[Ar]\,3d^{10}4s^{1}$.

Step 1: Judge the assertion Formation of Cu^{+} removes the 4s electron, giving $[Ar]\,3d^{10}$. All five 3d orbitals contain paired electrons. Cuprous salts are therefore diamagnetic, so the assertion is true.

Step 2: Judge the reason The reason says that the 3d orbitals of the cuprous ion are partially filled. This is false: Cu^{+} has a completely filled $3d^{10}$ subshell. Do not confuse it with cupric Cu^{2+}, which has $3d^{9}$ and an unpaired electron.

Step 3: Check whether the reason explains the assertion A false statement about partial filling cannot explain diamagnetism. The correct explanation is the complete pairing of electrons in the filled 3d subshell. Options (A) and (B) require a true reason, while (D) requires a false assertion; none applies.

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

Quick Tip to Solve: Translate cuprous to Cu+ first: removing the single 4s electron leaves a filled, diamagnetic 3d10 subshell.

14. Assertion (A): Acetanilide is more 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- The basicity of an amine depends on the availability of the nitrogen lone pair to accept a proton.

Quick Tip to Solve: Identify acetanilide as an amide: carbonyl resonance ties up the nitrogen lone pair and reduces basicity.

- Acetylation converts aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$.

Step 1: Judge the assertion In acetanilide, the nitrogen lone pair is delocalised towards the carbonyl group by amide resonance. It is less available for proton acceptance than in aniline. Consequently acetanilide is less basic than aniline, so the assertion that it is more basic is false.

Step 2: Judge the reason The acetyl group withdraws electron density from nitrogen through its carbonyl group. Delocalisation of the nitrogen lone pair into the carbonyl system reduces its availability. Therefore the statement that acetylation decreases electron density on nitrogen is true.

Step 3: Check the explanatory relation The true reason supports a decrease, rather than an increase, in basicity after acetylation. Hence it contradicts the comparison made in the false assertion. Options (A) and (B) both demand a true assertion, and option (C) demands a false reason, so all three are excluded.

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

Quick Tip to Solve: Identify acetanilide as an amide: carbonyl resonance ties up the nitrogen lone pair and reduces basicity.

15. 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:

- At the cathode reduction occurs; in aqueous sodium chloride, water is reduced more readily than Na^+.
- Anode products depend on electrode potentials and overpotential. Oxygen evolution from water has a substantial overpotential, allowing chloride oxidation to give chlorine.

Step 1: Evaluate the assertion During electrolysis of aqueous NaCl, hydrogen is released at the cathode and chlorine at the anode under the usual conditions for electrolysis of brine. The electrode reactions are

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

Thus, Assertion (A) is true.

Step 2: Evaluate the reason The reason's comparison of oxidation potentials is false. From standard

Quick Tip to Solve: For aqueous NaCl, remember water gives hydrogen at the cathode; chlorine at the anode is explained by oxygen overpotential.

electrode potentials, oxidation of water to oxygen is thermodynamically favoured over oxidation of chloride to chlorine. Chlorine is actually formed because oxygen evolution requires a higher overpotential, not because chlorine has the stated higher oxidation potential. Hence Reason (R) is false.

Step 3: Match the assertion-reason combination A false reason cannot explain a true assertion. Options (A) and (B) both require a true reason, while option (D) requires a false assertion; these combinations do not match the electrode processes.

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

Quick Tip to Solve: For aqueous NaCl, remember water gives hydrogen at the cathode; chlorine at the anode is explained by oxygen overpotential.

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16. 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:

- Boiling requires overcoming intermolecular attractions, rather than breaking the covalent carbon-halogen bond.
- For the same alkyl group, a larger, more polarizable halogen produces stronger London dispersion forces and generally a higher boiling point.

Step 1: Evaluate the assertion Bromine is larger and more polarizable than chlorine, so $CH_3CH_2CH_2CH_2Br$ has stronger dispersion attractions than $CH_3CH_2CH_2CH_2Cl$. Consequently, n-butyl bromide has the higher boiling point. The assertion, which reverses this order, is false.

Step 2: Evaluate the reason Chlorine is more electronegative than bromine, so the electronegativity difference between carbon and chlorine is greater than that between carbon and bromine. Therefore, the C–Cl bond is more polar than the C–Br bond, and the reason is true.

Step 3: Check the explanatory link Greater bond polarity alone does not determine this boiling-point order. The larger size and stronger dispersion attractions of the bromide prevail. Options (A), (B) and (C) all require the assertion to be true and are therefore excluded.

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

Quick Tip to Solve: For a fixed alkyl group, use the usual boiling-point order chloride below bromide below iodide; do not rank by bond polarity alone.

Section B (10 marks)

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

Solution:

Concept:

- Essential amino acids cannot be synthesized by the human body in sufficient amounts and must be supplied through the diet.
- An amino acid contains an acidic carboxyl group and a basic amino group. An amphoteric substance reacts with both acids and bases.

Step 1: Define essential amino acids Essential amino acids are the amino acids that our body cannot synthesize adequately, so they must be obtained from food. For example, valine and lysine are essential amino acids. This classification concerns their dietary requirement, not whether they occur in proteins: both essential and non-essential amino acids participate in protein formation.

Step 2: Explain the acidic and basic groups In an amino acid, the $-\mathrm{COOH}$ group can donate a proton, whereas the $-\mathrm{NH_2}$ group can accept a proton. In aqueous solution an internal proton transfer gives the zwitterion, which carries both positive and negative charges:

$$\mathrm{H_2N{-}CH(R){-}COOH} \rightleftharpoons \mathrm{H_3N^+{-}CH(R){-}COO^-}.$$

Here R denotes the side chain of the amino acid.

Step 3: Show reaction with an acid and a base The carboxylate group of the zwitterion accepts a proton from an acid, while its ammonium group loses a proton to a base:

$$\mathrm{H_3N^+{-}CH(R){-}COO^- + H^+ \longrightarrow H_3N^+{-}CH(R){-}COOH}$$
$$\mathrm{H_3N^+{-}CH(R){-}COO^- + OH^- \longrightarrow H_2N{-}CH(R){-}COO^- + H_2O}.$$

Thus the same amino acid shows basic behaviour towards an acid and acidic behaviour towards a base.

Step 4: Conclusion Essential amino acids must be supplied by the diet because the body cannot synthesize them adequately. Amino acids are amphoteric because they contain both an acidic carboxyl group and a basic amino group and can react with both acids and bases.

Quick Tip to Solve: Link essential amino acids to dietary supply; link amphoteric behaviour to the two groups, $-\mathrm{COOH}$ and $-\mathrm{NH_2}$.

18(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 is the time required for a reactant concentration to fall to half its current value.
- For a first-order reaction, $t_{1/2} = \ln 2/k$ is independent of the initial concentration, and the rate law is $-d[A]/dt = k[A]$, where k is the rate constant.

Step 1: Compare the successive halving intervals The table shows the sequence

$$0.40 \xrightarrow{1\,\text{h}} 0.20 \xrightarrow{1\,\text{h}} 0.10 \xrightarrow{1\,\text{h}} 0.05\,\text{M}.$$

The concentration halves every hour, even though the concentration at the start of each interval is different. Therefore, the half-life is constant at 1 h.

Step 2: Identify the order and verify it A constant half-life independent of reactant concentration is characteristic of first-order kinetics. The integrated first-order expression gives

$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}.$$

Using the first and second observations relative to time zero gives

$$k = \frac{\ln(0.40/0.20)}{1\,\text{h}} = 0.693\,\text{h}^{-1},$$
$$k = \frac{\ln(0.40/0.10)}{2\,\text{h}} = 0.693\,\text{h}^{-1}.$$

The same constant is obtained at both times, confirming the first-order interpretation.

Step 3: Write the rate law Since the order with respect to the decomposing reactant is one, its disappearance rate is proportional to its concentration:

$$\text{Rate} = -\frac{d[A]}{dt} = k[A].$$

Here $[A]$ is the instantaneous molar concentration. The negative derivative makes the rate positive because $[A]$ decreases with time.

Step 4: Conclusion The reaction is first order, with rate law Rate $= k[A]$, or equivalently $-d[A]/dt = k[A]$.

Quick Tip to Solve: Scan the table for repeated halving in equal time intervals; a constant half-life identifies first-order kinetics directly.

OR

18(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:

- The given experimental rate law, $r = k[H_2][I_2]$, is first order in each reactant and second order overall.
- At constant temperature, the rate constant for a given reaction is independent of reactant concentrations. Increasing a reactant concentration changes the rate through the rate law.

Step 1: Express the initial rate Let the instantaneous concentrations before addition be $[H_2] = a$ and $[I_2] = b$. The initial rate is

$$r = kab.$$

Both reactant concentrations enter linearly, so increasing only the hydrogen concentration increases the rate in the same proportion at the instant of addition.

Step 2: Account for the added hydrogen Let the volume of the reaction chamber be V litres. Adding 1 mol of H_2 to the same chamber raises its concentration by $(1\,\text{mol})/V$, while the iodine concentration is initially unchanged. Thus,

$$r' = k\left(a + \frac{1\,\text{mol}}{V}\right)b, \qquad \frac{r'}{r} = 1 + \frac{1\,\text{mol}}{Va} > 1.$$

The reaction rate therefore increases. A numerical factor cannot be specified without the original hydrogen amount or concentration and the chamber volume; it is not necessarily doubled.

Step 3: Examine the rate constant The temperature is explicitly held constant. Since neither the reaction nor its temperature has changed, adding hydrogen changes its concentration but does not alter k. This is also consistent with the Arrhenius equation $k = Ae^{-E_a/(RT)}$: concentration does not occur in the expression for the rate constant.

Step 4: Conclusion The rate of reaction increases because $[H_2]$ increases. The rate constant remains unchanged at the same temperature.

Quick Tip to Solve: In $r = k[H_2][I_2]$, change the concentration factor when hydrogen is added; keep k fixed if the temperature is fixed.

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

Solution:

Concept:

- Only free chloride ions outside the coordination sphere form a precipitate of AgCl with aqueous $\mathrm{AgNO_3}$.
- The complex ion charge follows from the counterions; its metal oxidation state follows by assigning -1 to each chlorido ligand.

Step 1: Place the chloride ligands No silver chloride precipitate is obtained, so none of the six chlorine atoms in $\mathrm{PtCl_4 \cdot 2KCl}$ occurs as a free chloride counterion. All six belong to the coordination sphere of platinum. The two potassium ions are outside it. Thus the structural formula is

$$\boxed{\mathrm{K_2[PtCl_6]}}.$$

In water it gives $2\mathrm{K^+}$ and $[\mathrm{PtCl_6}]^{2-}$; the bound chlorido ligands do not behave as free chloride ions in this test.

Step 2: Determine the name Let the oxidation state of platinum be x. Since the complex anion has charge -2,

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

There are six chlorido ligands, and an anionic platinum complex uses the metal name platinate. The cation is named before the complex anion.

Step 3: Conclusion The structural formula is $\mathrm{K_2[PtCl_6]}$, and its IUPAC name is **potassium hexachloridoplatinate(IV)**.

Quick Tip to Solve: No AgCl precipitate means no ionisable chloride: put all six Cl atoms inside the brackets before finding the oxidation state.

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

Solution:

Concept:

- A fuel cell is a galvanic cell that converts the chemical energy of a continuously supplied fuel and oxidant directly into electrical energy.
- Unlike a cell containing a fixed store of reactants, a fuel cell can operate continuously while its reactants are supplied and products removed.

Step 1: Define the fuel cell A **fuel cell** is an electrochemical cell in which a fuel, such as hydrogen, and an oxidant, such as oxygen, are continuously fed to the electrodes to generate electricity by a spontaneous redox reaction. In the hydrogen–oxygen fuel cell the net reaction is

$$2\mathrm{H_2}(g) + \mathrm{O_2}(g) \longrightarrow 2\mathrm{H_2O}(l).$$

Quick Tip to Solve: For two advantages, recall efficiency and the hydrogen–oxygen clean water product of the cell; specify the fuel when discussing pollution.

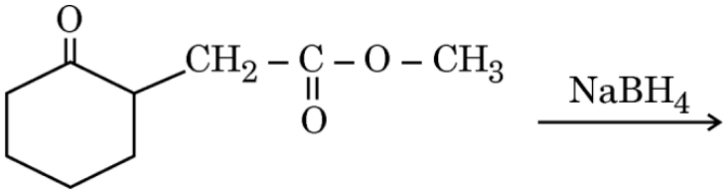
The reaction transfers electrons through the external circuit, producing useful electrical work.

Step 2: State two advantages **First, higher efficiency:** fuel cells convert a larger fraction of the chemical energy directly into electrical energy, so the energy loss is lower than in ordinary cells. **Second, cleaner operation:** the hydrogen–oxygen fuel cell produces water as its reaction product and does not produce polluting combustion gases. This makes this common fuel cell environmentally favourable.

Step 3: Conclusion A fuel cell generates electricity from continuously supplied reactants. Two advantages are **higher efficiency** and, for the hydrogen–oxygen cell, **pollution-free water formation**.

Quick Tip to Solve: For two advantages, recall efficiency and the hydrogen–oxygen clean water product of the cell; specify the fuel when discussing pollution.

21. Write the structures of the main products of the following reactions: (a) $6R_3C{-}OH + 2Al \longrightarrow$**; (b) the ester-substituted cyclohexanone shown below, treated with** $NaBH_4$**.** [2 marks]



Solution:

Concept:

- Aluminium replaces the hydroxyl hydrogen of an alcohol to form an aluminium alkoxide, with liberation of hydrogen gas.
- $NaBH_4$ reduces aldehydes and ketones to alcohols but ordinarily leaves an ester group unchanged.

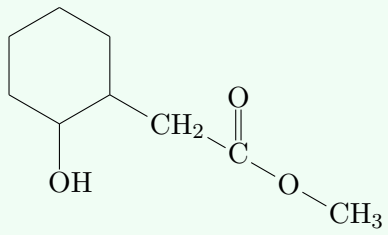
Step 1: Product of the reaction with aluminium The alcohol is tertiary, with structure $R_3C{-}OH$. Its oxygen bonds to aluminium after loss of the hydroxyl hydrogen. Aluminium forms three alkoxide bonds, giving the following balanced reaction:

$$6R_3C{-}OH + 2Al \longrightarrow 2Al[O{-}C(R)_3]_3 + 3H_2 \uparrow .$$

Thus the main organic-containing product is aluminium trialkoxide, $Al[OC(R)_3]_3$, with hydrogen as the gaseous coproduct. The carbon skeleton is retained.

Step 2: Selective reduction of the cyclic ketone The printed reactant has a ketone carbonyl in the cyclohexane ring and an adjacent $-CH_2{-}C(=O){-}OCH_3$ side chain. Sodium borohydride converts the ring $C{=}O$ into $CH{-}OH$; the ester carbonyl is retained. The product structure is

Quick Tip to Solve: With NaBH4, locate the aldehyde or ketone first: change only that carbonyl to an alcohol and retain the ester group.



This is methyl 2-(2-hydroxycyclohexyl)acetate. The hydroxyl group is on the ring carbon next to the side-chain-bearing carbon; no stereochemistry is specified in the question.

Step 3: Conclusion (a) $Al[OC(R)_3]_3$, with H_2 evolution. (b) Methyl 2-(2-hydroxycyclohexyl)acetate: ring ketone reduced to an alcohol, ester unchanged.

Quick Tip to Solve: With NaBH4, locate the aldehyde or ketone first: change only that carbonyl to an alcohol and retain the ester group.

Section C (21 marks)

22(a). Can sodium methoxide and t-butyl bromide be used for the preparation of t-butyl methyl ether? Give suitable reason. Justify your answer by suggesting the appropriate starting material if required for the preparation of t-butyl methyl ether. [2 marks]

Solution:

Concept:

- Williamson ether synthesis is an S_N2 reaction of an alkoxide ion with a preferably primary alkyl halide.
- A tertiary alkyl halide is too hindered for effective S_N2 attack; a strong alkoxide base instead promotes elimination.

Step 1: Test the proposed reactants **No.** Sodium methoxide and tert-butyl bromide are unsuitable for preparing tert-butyl methyl ether. The carbon bearing bromine in $(CH_3)_3CBr$ is tertiary, so backside attack by CH_3O^- is strongly hindered. Methoxide acts as a base and removes a beta hydrogen, favouring elimination:

$$(CH_3)_3CBr + NaOCH_3 \longrightarrow CH_2{=}C(CH_3)_2 + CH_3OH + NaBr.$$

The principal organic product is 2-methylpropene rather than the required ether.

Step 2: Choose the appropriate starting materials Put the bulky tert-butyl group on the alkoxide and the methyl group on the halide. Use **sodium tert-butoxide and methyl bromide** (methyl iodide is also suitable):

$$(CH_3)_3CONa + CH_3Br \longrightarrow (CH_3)_3C{-}O{-}CH_3 + NaBr.$$

Methyl bromide is unhindered and undergoes S_N2 displacement readily. It also has no beta carbon, so competing beta elimination cannot occur.

Step 3: Conclusion Use **sodium tert-butoxide and methyl bromide** to obtain tert-butyl methyl

Quick Tip to Solve: In Williamson synthesis, assign the less hindered group to the halide: methyl bromide plus tert-butoxide gives this ether cleanly.

ether; sodium methoxide with tert-butyl bromide favours elimination.

Quick Tip to Solve: In Williamson synthesis, assign the less hindered group to the halide: methyl bromide plus tert-butoxide gives this ether cleanly.

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

Solution:

Concept:

- Ethers are named as alkoxyalkanes: select the larger carbon framework as the parent alkane and name the smaller group with oxygen as an alkoxy substituent.
- The ether $(CH_3)_3C-O-CH_3$ has a methoxy group attached to the middle carbon of a propane parent chain.

Step 1: Choose the parent chain Write the structure as $CH_3-C(CH_3)(OCH_3)-CH_3$. The longest continuous carbon chain on the tert-butyl side contains three carbons, so the parent is propane. The oxygen interrupts the chain; it is not counted as a carbon in the parent.

Step 2: Identify and locate the substituents The group $-OCH_3$ is methoxy, and the remaining $-CH_3$ branch is methyl. Both are attached to carbon 2 of propane. Combining their locants and substituent names gives the systematic name of the ether.

Step 3: Conclusion The IUPAC name is $\boxed{\text{2-methoxy-2-methylpropane}}$.

Quick Tip to Solve: Expand the tert-butyl group into a propane chain: both methoxy and methyl sit on carbon 2.

23. Arrange the following compounds as asked:

(a) in increasing order of pK_b values

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

(b) in decreasing order of boiling point

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

(c) in decreasing order of solubility in water

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

Solution:

Concept:

- Basic strength increases with K_b and decreases with $pK_b = -\log K_b$. Electron donation, resonance and solvation control the availability of the nitrogen lone pair.
- Intermolecular hydrogen bonding increases boiling point. Hydrogen bonding with water favours solubility, whereas a larger nonpolar hydrocarbon group reduces it.

Step 1: Compare basic strength for part (a) In aqueous solution, diethylamine is more basic than

Quick Tip to Solve: For (a), rank basic strength first and reverse that order for increasing pK_b. For (b) compare hydrogen bonding; for (c) compare the nonpolar group size.

ethylamine because its two ethyl groups increase electron density on nitrogen by the positive inductive effect, while its conjugate acid remains effectively solvated. Both are stronger bases than the aromatic amines: in aniline derivatives the nitrogen lone pair is delocalised into the benzene ring and is less available for protonation. The methyl group in N-methylaniline donates electron density and makes it more basic than aniline. Thus the basic-strength order is $(C_2H_5)_2NH > C_2H_5NH_2 > C_6H_5NHCH_3 > C_6H_5NH_2$. Since a stronger base has a smaller pK_b, the requested increasing order reverses the basic-strength comparison.

Step 2: Compare intermolecular attraction for part (b) Ethanol forms stronger intermolecular hydrogen bonds through its $O-H$ group than these amines form through $N-H$, because oxygen is more electronegative than nitrogen. It therefore has the highest boiling point. Ethylamine and dimethylamine have the same molecular formula and comparable molar masses. Primary ethylamine has two hydrogen atoms bonded to nitrogen and forms more extensive intermolecular hydrogen bonding than secondary dimethylamine, which has only one. Hence ethylamine boils at a higher temperature than dimethylamine.

Step 3: Compare hydration and hydrocarbon size for part (c) All three amines can form hydrogen bonds with water, but their nonpolar groups oppose hydration. Ethylamine has only one small ethyl group and interacts readily with water. Diethylamine has a larger hydrocarbon portion, so its solubility is lower in this comparison. Aniline has a bulky hydrophobic phenyl group and its nitrogen lone pair is delocalised into the ring, making it much less soluble than these lower aliphatic amines.

Step 4: Conclusion The requested orders are:

(a) $(C_2H_5)_2NH < C_2H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$

(b) $C_2H_5OH > C_2H_5NH_2 > (CH_3)_2NH$

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

Quick Tip to Solve: For (a), rank basic strength first and reverse that order for increasing pK_b. For (b) compare hydrogen bonding; for (c) compare the nonpolar group size.

24. Calculate the cell voltage of the voltaic cell which is set up by joining the following half-cells at 25°C:

Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.001 M)

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

Solution:

Concept:

- The electrode with the higher reduction potential is the cathode. Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.
- At 25 °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 the electrodes and balance electron transfer The reduction potential of Ni^{2+}/Ni,

Quick Tip to Solve: Balance the cell reaction before choosing n or writing Q: here $n = 6$, and equal ion concentrations still give $Q = 10^3$.

$-0.25\,\text{V}$, is higher than that of Al^{3+}/Al, $-1.66\,\text{V}$. Thus nickel ions are reduced at the cathode and aluminium is oxidised at the anode. Balance the electron transfer by multiplying the aluminium half-reaction by two and the nickel half-reaction by three:

$$2\,\text{Al(s)} \longrightarrow 2\,\text{Al}^{3+}(\text{aq}) + 6\,\text{e}^-$$
$$3\,\text{Ni}^{2+}(\text{aq}) + 6\,\text{e}^- \longrightarrow 3\,\text{Ni(s)}.$$

Adding gives $2\,\text{Al} + 3\,\text{Ni}^{2+} \longrightarrow 2\,\text{Al}^{3+} + 3\,\text{Ni}$. Hence $n = 6$.

Step 2: Calculate standard cell potential and reaction quotient Using the two given reduction potentials,

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

Omit the solid metals from the reaction quotient, and use the powers from the balanced equation:

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

Equal ion concentrations do not make $Q = 1$, since the two ionic species have different stoichiometric coefficients.

Step 3: Apply the Nernst equation The temperature is $25\,^\circ\text{C}$, so use the base-ten logarithm form:

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}\log(10^3) \\ &= 1.41 - \frac{0.0591}{6} \times 3 \\ &= 1.41 - 0.02955\,\text{V}. \end{aligned}$$

Step 4: Conclusion The cell voltage is $E_{\text{cell}} = 1.38045\,\text{V} \approx \boxed{1.38\,\text{V}}$. Aluminium acts as the anode and nickel as the cathode.

Quick Tip to Solve: Balance the cell reaction before choosing n or writing Q: here $n = 6$, and equal ion concentrations still give $Q = 10^3$.

25(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 intermediates and substitution transition states are stabilised by conjugation with the adjacent carbon-carbon double bond, increasing reactivity compared with ordinary alkyl halides.
- Cyanide is an ambident nucleophile: carbon attack gives a nitrile, $\text{R}-\text{CN}$, whereas nitrogen attack gives an isocyanide, $\text{R}-\text{NC}$.

Quick Tip to Solve: Identify the controlling feature separately: adjacent double bond for allylic reactivity, the free cyanide end for product linkage, and crowding at the reacting carbon for S_N2.

- An S_N2 reaction occurs by a single concerted backside attack. Steric crowding around the carbon bearing the leaving group slows this attack.

Step 1: Explain the greater reactivity of allyl chloride In allyl chloride, $CH_2{=}CH{-}CH_2Cl$, the carbon bearing chlorine lies next to a double bond. During hydrolysis, the allylic substitution intermediate or transition state is stabilised by conjugation with that double bond. In particular, the allyl carbocation has two resonance forms:

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

Positive charge is delocalised over the terminal carbons. By contrast, n-propyl chloride, $CH_3CH_2CH_2Cl$, has no adjacent double bond and cannot obtain this resonance stabilisation. The lower activation barrier in allylic substitution accounts for faster hydrolysis.

Step 2: Explain formation of isocyanides with silver cyanide Silver cyanide, $AgCN$, is predominantly covalent, with silver attached to the carbon end of cyanide. Consequently the nitrogen end is available for attack on the alkyl halide. The new bond forms between the alkyl carbon and nitrogen, yielding the isocyanide linkage:

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

Ionic potassium cyanide supplies free cyanide ions which attack predominantly through carbon to give the nitrile $R{-}CN$.

Step 3: Explain the faster SN2 reaction of methyl chloride The hydroxide ion must approach the carbon bearing chlorine from the side opposite the $C{-}Cl$ bond, while the carbon-chlorine bond breaks in the same step. Methyl chloride has only small hydrogen atoms around this carbon, so backside approach is easy:

$$CH_3Cl + OH^{-} \longrightarrow CH_3OH + Cl^{-}.$$

In tert-butyl chloride, $(CH_3)_3CCl$, three methyl groups crowd the reaction centre and obstruct this approach. Its S_N2 reaction is therefore strongly hindered.

Step 4: Conclusion (i) Allyl chloride hydrolyses faster because allylic substitution is resonance-stabilised. (ii) Covalent $AgCN$ reacts through nitrogen to give $R{-}NC$. (iii) Methyl chloride reacts faster by S_N2 because its carbon is accessible to backside attack, whereas tert-butyl chloride is sterically crowded.

Quick Tip to Solve: Identify the controlling feature separately: adjacent double bond for allylic reactivity, the free cyanide end for product linkage, and crowding at the reacting carbon for S_N2.

OR

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

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

(ii) $CH_3CH_2CH(Cl)CH_3 \xrightarrow[\Delta]{\textbf{alc. KOH}} A \xrightarrow{HBr} B$

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

Solution:

Concept:

- In the presence of peroxide, HBr adds to an unsymmetrical alkene by a radical mechanism in the anti-Markovnikov direction: bromine attaches to the carbon having more hydrogen atoms.
- Aqueous KOH favours substitution of halogen by OH, whereas alcoholic KOH with heat favours elimination of a hydrogen halide. The more substituted alkene is the major product according to Saytzeff's rule.
- Ordinary HBr addition follows Markovnikov's rule. An alkyl chloride reacts with magnesium in dry ether to form a Grignard reagent, which yields the corresponding alkane on hydrolysis.

Step 1: (i) Add HBr with peroxide, then hydrolyse Propene undergoes anti-Markovnikov addition. Bromine attaches to the terminal carbon, so A is 1-bromopropane. Hydroxide from aqueous KOH then replaces bromine to give propan-1-ol:

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2Br,$$
$$CH_3CH_2CH_2Br + KOH(aq.) \longrightarrow CH_3CH_2CH_2OH + KBr.$$

Hence $A = CH_3CH_2CH_2Br$ and $B = CH_3CH_2CH_2OH$.

Step 2: (ii) Eliminate HCl, then add HBr On heating 2-chlorobutane with alcoholic KOH, a beta hydrogen and chlorine are removed. But-2-ene, the more substituted alkene, predominates over but-1-ene:

$$CH_3CH_2CH(Cl)CH_3 + KOH \xrightarrow[\Delta]{\text{alcohol}} CH_3CH{=}CHCH_3 + KCl + H_2O.$$

The double bond of but-2-ene is symmetrically substituted, so HBr addition gives the same constitutional product whichever end receives bromine:

$$CH_3CH{=}CHCH_3 + HBr \longrightarrow CH_3CH(Br)CH_2CH_3.$$

Thus $A = CH_3CH{=}CHCH_3$ and $B = CH_3CH(Br)CH_2CH_3$, namely but-2-ene and 2-bromobutane.

Step 3: (iii) Identify the Grignard precursor and its hydrolysis product Formation of ethylmagnesium chloride requires chloroethane. Magnesium inserts into its carbon–chlorine bond in dry ether; the two-carbon skeleton remains unchanged:

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

Quick Tip to Solve: Read the conditions before choosing the product: peroxide reverses HBr orientation, aqueous KOH substitutes, and hot alcoholic KOH eliminates.

Water supplies a proton to the ethyl group of the Grignard reagent:

$$CH_3CH_2MgCl + H_2O \longrightarrow CH_3CH_3 + Mg(OH)Cl.$$

Therefore A = CH_3CH_2Cl and B = CH_3CH_3; the organic main product is ethane.

Step 4: Conclusion (i) A : $CH_3CH_2CH_2Br$; B : $CH_3CH_2CH_2OH$.
(ii) A : $CH_3CH{=}CHCH_3$; B : $CH_3CH(Br)CH_2CH_3$.
(iii) A : CH_3CH_2Cl; B : CH_3CH_3.

Quick Tip to Solve: Read the conditions before choosing the product: peroxide reverses HBr orientation, aqueous KOH substitutes, and hot alcoholic KOH eliminates.

26. 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 stability of the oxidation state reached after electron transfer, and not merely on the initial number of d electrons.
- In an f-block series, increasing nuclear charge contracts the atomic and ionic radii because f electrons screen nuclear charge poorly.
- Interstitial compounds form when small atoms occupy spaces between metal atoms in a crystal lattice without destroying its basic structure.

Step 1: (a) Compare the states reached by electron transfer Although both ions have a $3d^4$ configuration, manganese(III) readily gains an electron to reach manganese(II), which has the particularly stable half-filled $3d^5$ configuration:

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

By accepting an electron, Mn^{3+} oxidises the other reactant and therefore acts as an oxidising agent. In contrast, chromium(II) readily loses an electron to give chromium(III):

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

The $3d^3$ chromium(III) state is relatively stable; in an octahedral complex it has the favourable t_{2g}^3 arrangement. Electron donation makes Cr^{2+} a reducing agent.

Step 2: (b) Explain the larger actinoid contraction Across the actinoids, electrons enter the $5f$ subshell as nuclear charge increases. The shielding of one $5f$ electron by another is poorer than the shielding of one $4f$ electron by another in the lanthanoids. Therefore the effective nuclear attraction

Quick Tip to Solve: For redox comparisons, write the electron configuration of the ion formed after electron gain or loss; the initial configuration alone is insufficient.

increases more strongly from element to element in the actinoid series. Hence the decrease in radii is larger than for lanthanoids.

Step 3: (c) Explain formation of interstitial compounds The crystal lattices of transition metals contain interstitial spaces between the packed metal atoms. H, B, C and N have sufficiently small atomic sizes to enter these spaces, producing many interstitial compounds while the underlying metal lattice is largely retained. These compounds commonly retain metallic conductivity but become harder and have high melting points.

Step 4: Conclusion (a) Mn^{3+} gains an electron to attain stable $3d^5$, whereas Cr^{2+} loses one to attain stable $3d^3$.

(b) Poorer mutual shielding by $5f$ electrons produces greater actinoid contraction.

(c) Small H, B, C and N atoms occupy interstitial spaces in transition-metal lattices.

Quick Tip to Solve: For redox comparisons, write the electron configuration of the ion formed after electron gain or loss; the initial configuration alone is insufficient.

27. 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 obeys $\pi = iCRT$, where i is the van't Hoff factor, C is the concentration in moles of solute formula units per litre, R is the gas constant and T is the absolute temperature.
- Dissociation increases the number of dissolved particles. Consequently, a molar mass calculated from osmotic pressure without allowing for dissociation is smaller than the true molar mass: $i = M_{\text{true}}/M_{\text{observed}}$.
- For a solute giving n particles on complete dissociation, $i = 1 + (n-1)\alpha$, where α is the fraction of solute dissociated. NaOH produces two ions, so $i = 1 + \alpha$.

Step 1: Calculate the true molar mass of NaOH Add the given atomic masses in the formula NaOH:

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

The value inferred experimentally from osmotic pressure is $M_{\text{observed}} = 25\,\text{g mol}^{-1}$. Its smaller value indicates that dissociation has increased the number of particles exerting osmotic pressure.

Step 2: Obtain the van't Hoff factor from the two molar masses For a mass w of solute in volume V, the actual pressure is $\pi = i(w/M_{\text{true}}V)RT$. The observed molar mass is calculated by treating the same pressure as $\pi = (w/M_{\text{observed}}V)RT$. Equating these expressions cancels w, V, R and T, giving

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

Quick Tip to Solve: Divide the true molar mass by the observed molar mass first; for NaOH, subtract 1 from this ratio and multiply by 100 to obtain percentage dissociation.

The temperature $27\,^{\circ}\text{C}$, approximately $300\,\text{K}$, is common to both expressions and therefore does not enter the ratio.

Step 3: Relate particle number to the dissociated fraction The dissociation is

$$\text{NaOH} \longrightarrow \text{Na}^{+} + \text{OH}^{-}.$$

Starting with one mole of NaOH, a fraction α dissociates. The solution then contains $(1-\alpha)$ mole of undissociated NaOH, α mole of sodium ions and α mole of hydroxide ions. Total particles are $1-\alpha+\alpha+\alpha = 1+\alpha$ moles, so

$$\begin{aligned} i &= 1+\alpha, \\ \alpha &= 1.60 - 1 = 0.60, \\ \text{Percentage dissociation} &= 0.60 \times 100 = 60\%. \end{aligned}$$

The result is consistent with the permitted range $1 \le i \le 2$ for this two-ion dissociation.

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

Quick Tip to Solve: Divide the true molar mass by the observed molar mass first; for NaOH, subtract 1 from this ratio and multiply by 100 to obtain percentage dissociation.

28. A compound 'A' with molecular formula C_4H_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-DNP test identifies an aldehyde or ketone because its carbonyl group forms a 2,4-dinitrophenylhydrazone.
- Ketones do not normally reduce Tollens' or Fehling's reagent. A methyl ketone, containing CH_3CO^-, gives yellow iodoform, CHI_3, with sodium hypoiodite.
- Drastic oxidation of a ketone cleaves carbon-carbon bonds adjacent to its carbonyl group to form smaller carboxylic acids.

Step 1: Identify the carbonyl compound The positive 2,4-DNP test establishes the presence of a carbonyl group. Since A does not react with Tollens' or Fehling's reagent, it is a ketone rather than an aliphatic aldehyde. The molecular formula C_4H_8O fits the four-carbon ketone $CH_3COCH_2CH_3$. Number the chain from the end nearer the carbonyl carbon: the carbonyl group is at position 2. Thus its IUPAC name is butan-2-one.

Step 2: Identify the yellow precipitate A contains the methyl-ketone group CH_3CO^-, so it undergoes the iodoform reaction. The yellow precipitate B has structure $H-C(I)_3$, that is, CHI_3; its IUPAC name

Quick Tip to Solve: Use the negative Tollens test to select a ketone, then the yellow iodoform precipitate to identify its methyl-ketone group.

is triiodomethane. The alkaline reaction can be written as

$$CH_3COCH_2CH_3 + 3\,NaOI \longrightarrow CHI_3\downarrow + CH_3CH_2COONa + 2\,NaOH.$$

The sodium propanoate in this reaction is a soluble coproduct; it is not the yellow precipitate.

Step 3: Identify the oxidation product Under drastic oxidation with $KMnO_4$, butan-2-one undergoes oxidative cleavage to give ethanoic acid. The overall balanced oxidation is

$$CH_3COCH_2CH_3 + 3\,[O] \longrightarrow 2\,CH_3COOH.$$

Hence C has the carboxylic-acid structure $CH_3-C(=O)-OH$. Both acid fragments are the same two-carbon acid in this cleavage, so the acid named here is ethanoic acid.

Step 4: Conclusion A: $CH_3COCH_2CH_3$, butan-2-one; B: CHI_3, triiodomethane; C: CH_3COOH, ethanoic acid.

Quick Tip to Solve: Use the negative Tollens test to select a ketone, then the yellow iodoform precipitate to identify its methyl-ketone group.

Section D (8 marks)

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

29(a). 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:

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

Solution:

Concept:

- Nucleic acids are polymers of nucleotides; complete hydrolysis separates their sugar, phosphate and nitrogenous-base components.
- DNA contains 2-deoxyribose and thymine, whereas RNA contains ribose and uracil.

Step 1: List the products of DNA hydrolysis Complete hydrolysis of DNA yields 2-deoxyribose sugar, phosphoric acid and the nitrogenous bases adenine, guanine, cytosine and thymine. The bases occur in the nucleotides of the original chain; hydrolysis breaks the links that join these components. Adenine and guanine are purines, while cytosine and thymine are pyrimidines. The sugar is specifically 2-deoxyribose, not ribose.

Step 2: Compare the structures of DNA and RNA DNA generally consists of two complementary polynucleotide strands wound into a double helix. RNA is generally a single polynucleotide strand.

Quick Tip to Solve: For a structural comparison, check three features in order: strand arrangement, the sugar at carbon 2, and thymine versus uracil.

DNA has 2-deoxyribose, which has H at the sugar's $2'$ carbon; RNA has ribose, with OH at that carbon. The bases of DNA are adenine, guanine, cytosine and thymine, while RNA has adenine, guanine, cytosine and uracil. Thus thymine is replaced by uracil in RNA.

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

Quick Tip to Solve: For a structural comparison, check three features in order: strand arrangement, the sugar at carbon 2, and thymine versus uracil.

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

Solution:

Concept:

- A nucleoside contains a nitrogenous base attached to a pentose sugar by an N-glycosidic bond.
- A nucleotide is formed when a phosphate group is attached to a nucleoside, commonly at the sugar's $5'$ position.

Step 1: State the composition of a nucleoside A nucleoside has two components: a nitrogenous base and a pentose sugar (ribose or 2-deoxyribose). It contains no phosphate group. For example, adenosine consists of adenine linked to ribose.

Step 2: State the extra component in a nucleotide A nucleotide has a nitrogenous base, a pentose sugar and a phosphate group. It is therefore a phosphorylated nucleoside. For example, adenosine monophosphate is a nucleotide because phosphate is attached to adenosine.

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

Quick Tip to Solve: Check for phosphate: base plus sugar alone is a nucleoside; adding phosphate makes it a nucleotide.

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

Solution:

Concept:

- Nucleic acids are DNA and RNA; their base sequences carry biological information.
- DNA stores hereditary information, while RNA helps express that information through protein synthesis.

Step 1: State the hereditary function DNA stores the genetic information of the cell. It replicates before cell division, allowing the hereditary information to be transmitted from a parent cell to daughter cells and from one generation to the next.

Step 2: State the protein-synthesis function Nucleic acids direct protein synthesis. The DNA sequence supplies the instructions, and RNA carries and translates them: messenger RNA brings the message,

Quick Tip to Solve: Remember the pair: DNA preserves the hereditary message; RNA helps use that message to build proteins.

transfer RNA delivers amino acids, and ribosomal RNA forms part of the ribosome where proteins are assembled.

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

Quick Tip to Solve: Remember the pair: DNA preserves the hereditary message; RNA helps use that message to build proteins.

OR

29(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 the sugar-phosphate backbone.
- RNA contains the bases adenine, guanine, cytosine and uracil; DNA contains thymine in place of uracil.

Step 1: Name the inter-nucleotide linkage Two adjacent nucleotides are joined by a $3'$-$5'$ phosphodiester linkage. A phosphate group forms ester bonds with the $3'$-OH of one sugar and the $5'$-OH of the next sugar, connecting successive nucleotides in the chain.

Step 2: Identify the RNA-specific base The required base is uracil. It occurs in the standard nucleotides of RNA, whereas thymine occupies its corresponding place in DNA. Adenine, guanine and cytosine occur in both, so they do not distinguish RNA from DNA.

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

Quick Tip to Solve: Keep the two bonds distinct: base-to-sugar is glycosidic, but nucleotide-to-nucleotide is phosphodiester.

30(a). 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:

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 the partial vapour pressure of component i as $p_i = x_i p_i^0$, where x_i is its liquid-phase mole fraction and p_i^0 is the pure liquid's vapour pressure at the same temperature.
- Negative deviation occurs when unlike-molecule attractions are stronger than the attractions between like molecules; escape into the vapour becomes less favourable.

Step 1: Identify a suitable liquid pair Acetone (propanone) and chloroform form a miscible liquid pair showing negative deviation. Acetone contains a carbonyl oxygen with lone pairs, while the hydrogen of chloroform is made relatively positive by the three electron-withdrawing chlorine atoms.

Step 2: Explain the lower vapour pressure On mixing, a specific hydrogen-bond interaction develops between the carbonyl oxygen of acetone and the hydrogen of chloroform, written schematically as $(CH_3)_2C = O \cdots H - CCl_3$. These acetone-chloroform attractions are stronger than the corresponding attractions in the pure liquids. The molecules are held more firmly in the liquid, so fewer escape into the vapour at the same temperature. Therefore the partial vapour pressures, and hence the total vapour pressure, lie below the values predicted by Raoult's law.

Step 3: Conclusion Acetone and chloroform show negative deviation from Raoult's law because stronger hydrogen bonding between unlike molecules reduces their escaping tendency.

Quick Tip to Solve: For negative deviation, choose a pair that develops stronger specific attractions on mixing, such as acetone and chloroform.

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

Solution:

Concept:

- For an ideal solution of volatile liquids, each component contributes its own partial vapour pressure to the equilibrium vapour.
- The mole fraction x_i refers to component i in the liquid, and p_i^0 is the vapour pressure of that pure component at the same temperature.

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

Step 1: State the proportionality Raoult's law states that the partial vapour pressure of each volatile component of a solution is directly proportional to its mole fraction in the solution. The proportionality constant is the vapour pressure of the pure component:

$$p_i = x_i p_i^0.$$

Step 2: Apply the law to two components For a binary ideal solution of volatile liquids A and B, $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$. Since both liquids are volatile, both contributions are included: $p_{\text{total}} = x_A p_A^0 + x_B p_B^0$, with $x_A + x_B = 1$.

Step 3: Conclusion Raoult's law is $p_i = x_i p_i^0$: each volatile component's partial vapour pressure equals its liquid mole fraction times its pure vapour pressure.

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

OR

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

Solution:

Concept:

- Henry's law has the form $p = K_H x$, where p is the partial pressure of the component, x its mole fraction in solution and K_H the Henry's law constant.
- Raoult's law has the form $p = p^0 x$, where p^0 is the vapour pressure of the pure volatile component at the same temperature.

Step 1: Compare the two equations Both equations describe a linear relationship between partial pressure and liquid mole fraction. Henry's law uses the constant K_H, which depends on the solute, solvent and temperature; Raoult's law uses the pure component's vapour pressure p^0.

Step 2: Identify the special condition If $K_H = p^0$, substituting this value into $p = K_H x$ gives $p = p^0 x$, exactly the expression for Raoult's law. Thus the general proportionality becomes the ideal-solution relation under this condition.

Step 3: Conclusion Raoult's law is a special case of Henry's law when $K_H = p^0$, the pure component's vapour pressure.

Quick Tip to Solve: Compare the constants in the two pressure-versus-mole-fraction equations: the special case requires their equality.

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

Solution:

Concept:

- An ideal solution obeys Raoult's law over the entire range of composition at a given temperature.
- For ideal mixing, attractions between unlike molecules are effectively equal to those between like molecules, so mixing produces no net energetic or volume change.

Step 1: State the enthalpy characteristic The enthalpy of mixing is zero: $\Delta_{\text{mix}}H = 0$. Replacing A-A and B-B interactions by A-B interactions does not produce a net absorption or release of heat because these intermolecular attractions have essentially the same strength.

Step 2: State the volume characteristic The volume of mixing is zero: $\Delta_{\text{mix}}V = 0$. The final volume is therefore the sum of the initial volumes of the components; ideal mixing causes neither contraction nor expansion.

Step 3: Conclusion Two characteristics are $\Delta_{\text{mix}}H = 0$ and $\Delta_{\text{mix}}V = 0$.

Quick Tip to Solve: Remember the two zero changes for ideal mixing: zero heat of mixing and zero volume change.

Section E (15 marks)

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

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

was 1.2×10^{-2} mol L^{-1}. The concentration of N_2O_5 after 60 minutes was 0.2×10^{-2} mol 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, $k = \dfrac{2.303}{t}\log_{10}\dfrac{[A]_0}{[A]_t}$, where k is the rate constant, t the elapsed time and $[A]_0, [A]_t$ the initial and remaining reactant concentrations.
- A first-order rate constant has units of inverse time; concentration units cancel in the ratio. Use the concentration of the same reactant at both times.

Step 1: Record the reactant concentrations At 318 K, the initial concentration is $[N_2O_5]_0 = 1.2 \times 10^{-2}$ mol L^{-1}, and after $t = 60$ min it is $[N_2O_5]_t = 0.2 \times 10^{-2}$ mol L^{-1}. The ratio of initial to remaining concentration is

$$\frac{[N_2O_5]_0}{[N_2O_5]_t} = \frac{1.2 \times 10^{-2}}{0.2 \times 10^{-2}} = 6.$$

The denominator is the concentration remaining, not the amount decomposed.

Quick Tip to Solve: Cancel the common concentration power first; the logarithm is of 6, and using 60 minutes gives inverse-minute units.

Step 2: Substitute into the integrated rate equation Using the supplied value $\log_{10} 6 = 0.778$,

$$\begin{aligned} k &= \frac{2.303}{60} \log_{10} 6 \\ &= \frac{2.303 \times 0.778}{60} \\ &= \frac{1.791734}{60} \text{ min}^{-1}. \end{aligned}$$

The temperature labels the conditions at which this rate constant applies; no extra temperature factor is needed because the concentration data already refer to $318\,\text{K}$.

Step 3: Express the value in inverse seconds if required To convert an inverse-minute rate constant to inverse seconds, divide by 60, because one minute equals $60\,\text{s}$. Thus $k = (1.791734/3600)\,\text{s}^{-1}$. Either time unit is acceptable when stated consistently with the calculation.

Step 4: Conclusion The rate constant at $318\,\text{K}$ is $k = 2.99 \times 10^{-2}\,\text{min}^{-1}$, equivalent to $4.98 \times 10^{-4}\,\text{s}^{-1}$.

Quick Tip to Solve: Cancel the common concentration power first; the logarithm is of 6, and using 60 minutes gives inverse-minute units.

31(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:

- Reaction order is the sum of the powers of reactant concentrations in the experimentally determined rate law, such as $r = k[A]^m[B]^n$, whose overall order is $m + n$.
- A balanced overall equation specifies stoichiometric proportions and conservation of atoms; it does not specify the reaction mechanism or the concentration dependence of the rate.

Step 1: Distinguish stoichiometry from rate dependence The coefficients in an overall balanced equation tell us how much of each substance is consumed or produced. The exponents in a rate law tell us how changing concentrations affects the reaction rate. These two kinds of information need not coincide.

Step 2: Explain why experimental evidence is needed An overall reaction may occur through several elementary steps, with its rate controlled by a slow step and possibly other mechanistic conditions. The overall equation hides these steps, so its coefficients alone cannot give the rate-law exponents. Order must therefore be determined experimentally; coefficients can be used as exponents only for a verified elementary reaction.

Step 3: Conclusion The order cannot generally be obtained from a balanced overall equation because it is an experimental kinetic property, whereas the equation expresses only overall stoichiometry.

Quick Tip to Solve: Use experimentally measured rate-law exponents for order; do not automatically add the balanced-equation coefficients.

31(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 elementary reaction involving reactants A and B, the rate law is $r = k[A][B]$, where k is the rate constant.
- When one reactant is in large excess, its concentration changes negligibly and can be included in an observed rate constant.

Step 1: Apply the excess-reactant condition Consider $A + B \rightarrow$ products. If B is present in a very large excess over A, consumption of B during the reaction is too small to change $[B]$ appreciably. Hence, $[B]$ remains effectively constant.

Step 2: Rewrite the observed rate law The rate becomes

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

It therefore depends on the first power of the concentration of the reactant that is not in excess. The number of reacting species in the elementary event has not changed; only the observed concentration dependence has changed.

Step 3: Conclusion A bimolecular reaction behaves as a pseudo-first-order reaction when one reactant is present in large excess, so its concentration is effectively constant.

Quick Tip to Solve: Look for a reactant in large excess and absorb its nearly constant concentration into k_{obs}.

OR

31(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 E_a is activation energy, R the gas constant, T absolute temperature and A the pre-exponential factor.
- At fixed reactant concentrations, the rate changes in the same ratio as the rate constant. The two-temperature form is $\log(k_2/k_1) = \dfrac{E_a}{2.303R}(1/T_1 - 1/T_2)$.

Step 1: Identify the temperature and rate ratios The initial temperature is $T_1 = 298\,\text{K}$. A rise of $10\,\text{K}$ gives $T_2 = 308\,\text{K}$. Since the rate doubles for the same reaction conditions and concentrations, $k_2/k_1 = 2$. Use the supplied values $\log 2 = 0.3$ and $2.303R = 19.15\,\text{J K}^{-1}\text{mol}^{-1}$.

Step 2: Rearrange the Arrhenius relation Subtracting the logarithmic Arrhenius expressions at the

Quick Tip to Solve: Use $T_1T_2/(T_2 - T_1) = 298 \times 308/10$; do not substitute the temperature rise alone for either absolute temperature.

two temperatures eliminates $\log A$:

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right),$$
$$E_a = \frac{(2.303R)\log(k_2/k_1)T_1T_2}{T_2 - T_1}.$$

The reciprocal-temperature difference is positive, consistent with an increase of rate on heating.

Step 3: Substitute the given values

$$E_a = \frac{19.15 \times 0.3 \times 298 \times 308}{308 - 298}$$
$$= 52728.708\,\text{J mol}^{-1}$$
$$= 52.728708\,\text{kJ mol}^{-1}.$$

Temperature must be in kelvin in the reciprocal terms. The energy unit is joules per mole because $2.303R$ was supplied in joules per kelvin per mole; divide by 1000 to express the result in kilojoules per mole.

Step 4: Conclusion The activation energy is $E_a \approx 52.7\,\text{kJ mol}^{-1}$ (about $5.27 \times 10^4\,\text{J mol}^{-1}$), using the supplied logarithm.

Quick Tip to Solve: Use $T_1T_2/(T_2 - T_1) = 298 \times 308/10$; do not substitute the temperature rise alone for either absolute temperature.

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

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

the proposed mechanism is as given below:

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

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

(1) Write rate law for the reaction.

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

Solution:

Concept:

- For an elementary slow step, the rate law contains the concentrations of the reacting species in that step, each raised to its stoichiometric power.
- Overall order is the sum of concentration exponents in the rate law. Molecularity counts reacting species in an elementary event; it is not assigned to an overall multistep reaction.

Step 1: Write the rate law from the slow step The rate-determining step is $H_2O_2 + I^- \rightarrow H_2O + IO^-$. One hydrogen peroxide molecule and one iodide ion react in this elementary step. Thus,

$$r = k[H_2O_2][I^-].$$

Quick Tip to Solve: Read concentrations from the slow elementary step; count its reactant species for molecularity instead of using the net equation.

The fast step consumes IO^- and regenerates iodide; therefore IO^- is an intermediate and I^- is a catalyst.

Step 2: Find order and identify the relevant molecularity The sum of exponents is $1 + 1 = 2$, so the overall kinetic order is two. The slow, rate-determining elementary step is bimolecular because it involves two reacting species; the fast elementary step is also bimolecular. Strictly, the overall reaction consists of two steps and has no single molecularity. The molecularity quoted from this mechanism is two for its rate-determining step, not a value inferred from the net equation.

Step 3: Conclusion Rate law: $r = k[H_2O_2][I^-]$; overall order: 2. Molecularity of the rate-determining step: 2 (bimolecular); molecularity of the overall multistep reaction is not defined.

Quick Tip to Solve: Read concentrations from the slow elementary step; count its reactant species for molecularity instead of using the net equation.

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

Cyclohexanone + $H_2NCONH–NH_2$ $\rightarrow$ [1 mark]



Solution:

Concept:

- Aldehydes and ketones condense with semicarbazide, $H_2N - NH - C(= O) - NH_2$, to form semicarbazones with elimination of water.
- The terminal amino group forms a semicarbazone linkage:

$$C = N - NH - C(= O) - NH_2.$$

Step 1: Identify the reactive group Cyclohexanone contains a ketonic carbonyl in its six-membered ring. The terminal $-NH_2$ group of semicarbazide attacks this carbonyl carbon. The amino group attached directly to the semicarbazide carbonyl is resonance-stabilised and does not form the new imine bond.

Step 2: Write the product structure Condensation removes one molecule of water and leaves the ring intact. A condensed structural formula that explicitly shows ring closure is

$$\underbrace{(CH_2)_5C}_{\text{six-membered ring}} = N - NH - C(= O) - NH_2.$$

Both ends of the $(CH_2)_5$ chain are attached to the imine carbon, which is the original carbonyl carbon.

Quick Tip to Solve: Replace the ketone oxygen by $= N - NH - C(= O) - NH_2$ while retaining every carbon of the cyclohexane ring.

Step 3: Conclusion The main product is cyclohexanone semicarbazone:

$$\underbrace{(CH_2)_5C}_{\text{ring}} = N - NH - C(=O) - NH_2.$$

Water is the by-product.

Quick Tip to Solve: Replace the ketone oxygen by $= N - NH - C(=O) - NH_2$ while retaining every carbon of the cyclohexane ring.

32(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 compounds react with acid chlorides to form ketones by replacing the chloride with an alkyl group.
- Dimethylcadmium supplies two methyl groups; each methyl group reacts with one molecule of acetyl chloride.

Step 1: Identify the acyl and alkyl fragments Acetyl chloride supplies the $CH_3 - C(=O)-$ fragment, and dimethylcadmium supplies $-CH_3$. Joining these fragments at the acyl carbon gives $CH_3 - C(=O) - CH_3$. The carbonyl group is retained in this acyl substitution.

Step 2: Balance the reaction The two methyl groups on cadmium convert two acetyl chloride molecules into two ketone molecules:

$$(CH_3)_2Cd + 2CH_3COCl \rightarrow 2CH_3C(=O)CH_3 + CdCl_2.$$

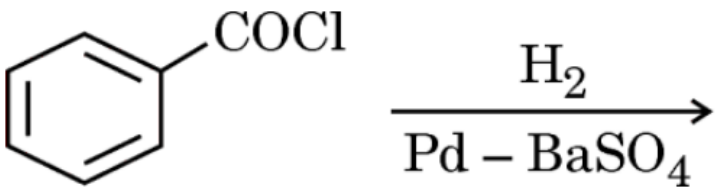
Organocadmium reagents form ketones in this reaction; the product is not the tertiary alcohol associated with further addition of a more reactive organometallic reagent.

Step 3: Conclusion The main organic product is propanone (acetone), $CH_3 - C(=O) - CH_3$; two molecules are formed per molecule of dimethylcadmium.

Quick Tip to Solve: For an acid chloride with dialkylcadmium, replace Cl by one alkyl group and retain the carbonyl to obtain a ketone.

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

$C_6H_5COCl \xrightarrow[Pd-BaSO_4]{H_2}$ [1 mark]



Solution:

Concept:

- Rosenmund reduction converts an acid chloride into an aldehyde using hydrogen over palladium supported on barium sulphate.
- The controlled catalyst prevents extensive reduction of the aldehyde to the corresponding primary alcohol.

Step 1: Recognise the selective reduction The substrate is benzoyl chloride, $C_6H_5 - C(=O) - Cl$. Hydrogen in the presence of $Pd - BaSO_4$ replaces the acyl chloride chlorine with hydrogen. The benzene ring and the carbonyl group remain intact.

Step 2: Write the main product and equation The reaction is

$$C_6H_5COCl + H_2 \xrightarrow{Pd-BaSO_4} C_6H_5C(=O)H + HCl.$$

The product has an aldehydic $-CHO$ group directly attached to the phenyl group. The selective conditions stop at the aldehyde rather than producing benzyl alcohol.

Step 3: Conclusion The main product is benzaldehyde, with structure $C_6H_5 - C(=O) - H$ (C_6H_5CHO).

Quick Tip to Solve: Identify $H_2/Pd - BaSO_4$ as Rosenmund conditions and replace $-COCl$ by $-CHO$.

32(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 liberate carbon dioxide from aqueous sodium hydrogencarbonate because they are stronger acids than carbonic acid.
- An ester has no acidic carboxyl hydrogen and does not give this effervescence test.

Step 1: Add sodium hydrogencarbonate Add a little aqueous $NaHCO_3$ separately to the two samples at room temperature. Benzoic acid reacts with brisk effervescence of CO_2; the gas turns limewater milky.

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

Quick Tip to Solve: Use aqueous hydrogencarbonate at room temperature: gas evolution distinguishes the acid directly from its ester.

Step 2: Compare the ester sample Ethyl benzoate, $C_6H_5COOC_2H_5$, does not evolve CO_2 under the same conditions. Its ester group cannot supply the proton needed to decompose hydrogencarbonate.

Step 3: Conclusion Benzoic acid gives brisk CO_2 effervescence with aqueous $NaHCO_3$; ethyl benzoate gives no effervescence.

Quick Tip to Solve: Use aqueous hydrogencarbonate at room temperature: gas evolution distinguishes the acid directly from its ester.

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

Solution:

Concept:

- Tollens' reagent is ammoniacal silver nitrate containing $[Ag(NH_3)_2]^+$. Aldehydes reduce it to metallic silver.
- Simple ketones do not reduce Tollens' reagent under the test conditions, so aldehydes can be distinguished from them.

Step 1: Test propanal with Tollens' reagent Warm propanal gently with freshly prepared Tollens' reagent in a clean test tube. A silver mirror forms on the tube as propanal is oxidised to propanoate in the alkaline medium.

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

Step 2: Compare the propanone sample Propanone, CH_3COCH_3, gives no silver mirror with Tollens' reagent. Unlike the aldehyde group in propanal, its ketone group is not readily oxidised by this mild reagent.

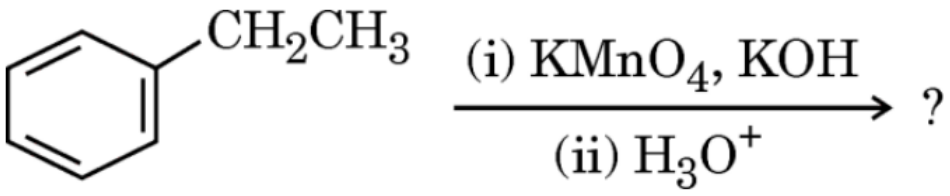
Step 3: Conclusion Propanal gives a silver mirror with Tollens' reagent; propanone does not.

Quick Tip to Solve: For this aldehyde–ketone pair, use the silver-mirror test and state the observation for each sample.

OR

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

[1 mark]



Solution:

Concept:

- Hot alkaline potassium permanganate oxidises an alkyl side chain attached to benzene to a carboxylate group if the benzylic carbon has a hydrogen.
- Acidification converts the intermediate benzoate ion into benzoic acid; the benzene ring remains intact.

Step 1: Identify the oxidisable side chain The printed starting compound is ethylbenzene, $C_6H_5CH_2CH_3$. Its benzylic CH_2 group contains hydrogen, so vigorous oxidation converts the side chain into $-COO^-$, irrespective of its original length.

Step 2: Apply oxidation and acidification First $KMnO_4/KOH$ gives potassium benzoate, C_6H_5COOK. The subsequent H_3O^+ treatment protonates the carboxylate:

$$C_6H_5COO^- + H_3O^+ \longrightarrow C_6H_5COOH + H_2O.$$

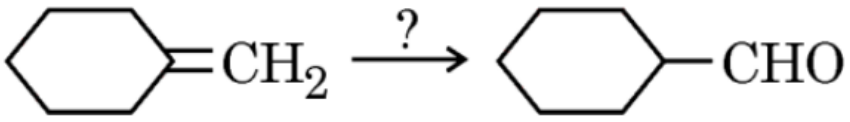
The terminal side-chain carbon is removed during the vigorous oxidation.

Step 3: Conclusion The missing product is benzoic acid, $\boxed{C_6H_5COOH}$.

Quick Tip to Solve: For an alkylbenzene with a benzylic hydrogen, hot alkaline permanganate followed by acidification gives $-COOH$ at the original side-chain position.

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

[1 mark]



Solution:

Concept:

- Hydroboration followed by alkaline hydrogen peroxide gives anti-Markovnikov hydration of an alkene.
- Pyridinium chlorochromate (PCC) oxidises a primary alcohol to an aldehyde under anhydrous

Quick Tip to Solve: For terminal methylene to $-CHO$ without breaking the carbon skeleton, make the primary alcohol by hydroboration, then use PCC.

conditions.

Step 1: Place the alcohol group on the terminal carbon The starting alkene is methylenecyclohexane, with an exocyclic $=CH_2$ group. Treat it first with $BH_3 \cdot THF$, then with H_2O_2/OH^-. Hydroboration places boron on the less substituted terminal carbon; oxidation replaces the carbon-boron bond by a carbon-oxygen bond. The product is cyclohexylmethanol, $C_6H_{11}CH_2OH$.

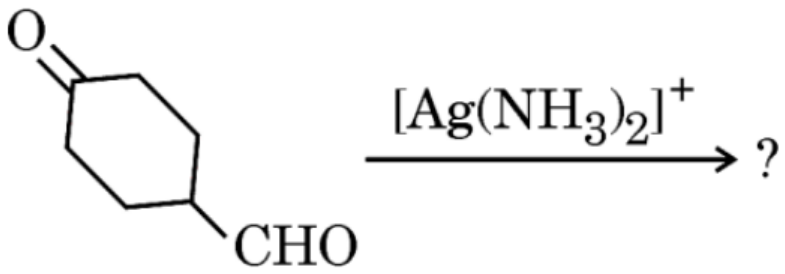
Step 2: Oxidise only to the aldehyde Use PCC in dry CH_2Cl_2 to convert $C_6H_{11}CH_2OH$ into $C_6H_{11}CHO$, the printed cyclohexanecarbaldehyde. A strong aqueous oxidant would instead risk forming the carboxylic acid. Ozonolysis would cleave the exocyclic double bond and give cyclohexanone, so it does not accomplish this synthesis.

Step 3: Conclusion The missing reagent sequence is $\boxed{(1)\ BH_3 \cdot THF;\ (2)\ H_2O_2/OH^-;\ (3)\ PCC}$ (PCC in dry dichloromethane).

Quick Tip to Solve: For terminal methylene to $-CHO$ without breaking the carbon skeleton, make the primary alcohol by hydroboration, then use PCC.

32(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, oxidises an aldehyde group to a carboxylate ion.
- An ordinary ketone group does not undergo this oxidation, so the ring carbonyl group is retained.

Step 1: Identify the group that reacts The printed substrate contains both a cyclic ketone group and a $-CHO$ substituent. Tollens reagent distinguishes the aldehyde from the ketone: only the aldehyde is oxidised. Its aldehydic carbon stays attached at the same ring position, and the ring ketone remains $C=O$.

Step 2: Write the selective transformation Replacing the side group $-CHO$ by $-COO^-$ gives 4-oxocyclohexane-1-carboxylate in the alkaline reaction mixture. For an aldehyde RCHO, the ionic equation is

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCOO^- + 2Ag + 4NH_3 + 2H_2O.$$

Metallic silver is deposited. On acidification, the carboxylate gives the corresponding carboxylic acid.

Quick Tip to Solve: When a molecule has both aldehyde and ordinary ketone groups, Tollens reagent changes only $-CHO$ into carboxylate; acid work-up gives $-COOH$.

Step 3: Conclusion The product has the original ring ketone intact and $-CHO$ replaced by $-COO^-$: 4-oxocyclohexane-1-carboxylate. Its acid form after acidification is 4-oxocyclohexane-1-carboxylic acid ($-COOH$).

Quick Tip to Solve: When a molecule has both aldehyde and ordinary ketone groups, Tollens reagent changes only $-CHO$ into carboxylate; acid work-up gives $-COOH$.

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

Benzaldehyde to Benzophenone [1 mark]

Solution:

Concept:

- Phenylmagnesium bromide adds a phenyl group to an aldehyde carbonyl; acidic hydrolysis of the adduct gives a secondary alcohol.
- Oxidation of a secondary alcohol gives a ketone without changing the carbon skeleton.

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

$$C_6H_5CHO \xrightarrow[\text{dry ether}]{C_6H_5MgBr} (C_6H_5)_2CHOMgBr \xrightarrow{H_3O^+} (C_6H_5)_2CHOH.$$

The alcohol is diphenylmethanol. Dry conditions are essential during Grignard addition because water destroys the reagent.

Step 2: Oxidise the secondary alcohol Treat diphenylmethanol with acidified potassium dichromate. Its $-CHOH-$ unit loses two hydrogen atoms and becomes $> C = O$:

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

Both phenyl groups remain attached to the carbonyl carbon, producing benzophenone.

Step 3: Conclusion $\boxed{C_6H_5CHO \xrightarrow[2.\ H_3O^+]{1.\ C_6H_5MgBr,\ \text{dry ether}} (C_6H_5)_2CHOH \xrightarrow{K_2Cr_2O_7/H^+} (C_6H_5)_2CO}$.

Quick Tip to Solve: Add the missing phenyl group with phenylmagnesium bromide first; then oxidise the resulting secondary alcohol to benzophenone.

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

Benzaldehyde to 3-phenyl propanol [1 mark]

Solution:

Concept:

- Benzaldehyde has no alpha-hydrogen, whereas ethanal has alpha-hydrogens and can provide the enolate for crossed aldol condensation.

Quick Tip to Solve: Use crossed aldol condensation with ethanal to add two carbons, then reduce both side-chain unsaturation and the aldehyde to obtain 3-phenylpropan-1-ol.

- Aldol condensation adds the two-carbon ethanal unit; catalytic hydrogenation can reduce both the alkene and aldehyde groups.

Step 1: Extend the carbon chain by two carbon atoms Condense benzaldehyde with ethanal in dilute NaOH, using excess benzaldehyde to favour the crossed product. The ethanal enolate attacks benzaldehyde, initially forming $\mathrm{C_6H_5CH(OH)CH_2CHO}$. Warming dehydrates this beta-hydroxy aldehyde to cinnamaldehyde:

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

Step 2: Reduce the side chain to the primary alcohol Hydrogenate cinnamaldehyde with sufficient $\mathrm{H_2}$ over Ni under conditions for side-chain reduction. One equivalent reduces $\mathrm{C = C}$, and another reduces $-\mathrm{CHO}$ to $-\mathrm{CH_2OH}$:

$$\mathrm{C_6H_5CH = CHCHO + 2H_2 \xrightarrow{Ni} C_6H_5CH_2CH_2CH_2OH.}$$

The benzene ring is retained. The hydroxyl carbon is carbon 1, so the phenyl substituent is at carbon 3.

Step 3: Conclusion Crossed aldol condensation with ethanal gives cinnamaldehyde. Hydrogenation with $\mathrm{2H_2/Ni}$ then gives $\boxed{\mathrm{C_6H_5CH_2CH_2CH_2OH}}$, 3-phenylpropan-1-ol.

Quick Tip to Solve: Use crossed aldol condensation with ethanal to add two carbons, then reduce both side-chain unsaturation and the aldehyde to obtain 3-phenylpropan-1-ol.

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

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

Solution:

Concept:

- Magnetic behaviour depends on unpaired electrons: a complex with none is diamagnetic, whereas a complex with unpaired electrons is paramagnetic.
- Neutral CO and anionic $\mathrm{Cl^-}$ give different nickel oxidation states and therefore different d-electron counts in these complexes.

Step 1: Examine nickel tetracarbonyl In $\mathrm{Ni(CO)_4}$, nickel has oxidation state zero. Free nickel is $[\mathrm{Ar}]\,3d^8 4s^2$. In forming this complex with the strong-field ligand CO, the electrons pair to give a filled $3d^{10}$ set. The tetrahedral complex uses sp^3 hybrid orbitals and has no unpaired electron.

Step 2: Examine tetrachloridonickelate(II) In $[\mathrm{NiCl_4}]^{2-}$, let the nickel oxidation state be x. Then $x - 4 = -2$, so $x = +2$, giving $\mathrm{Ni^{2+}}$ the configuration $[\mathrm{Ar}]\,3d^8$. The weak-field ligand $\mathrm{Cl^-}$ forms a tetrahedral sp^3 complex with two unpaired d electrons; its tetrahedral occupancy is $e^4 t_2^4$.

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

Quick Tip to Solve: Determine nickel's oxidation state first: neutral carbonyl gives Ni(0), while four chloride ligands give Ni(II).

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

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

Solution:

Concept:

- A ligand forms a coordinate bond by donating an electron pair to a vacant orbital of the metal: ligand-to-metal σ donation.
- Carbon monoxide also accepts electron density from filled metal d orbitals into its vacant antibonding π^* orbitals: metal-to-ligand π back-bonding.

Step 1: Compare electron-pair donation Both CO and NH_3 donate a lone pair to the central metal to form a σ bond. Carbon monoxide coordinates through carbon, whereas ammonia coordinates through nitrogen. This donation alone does not account for the particularly strong metal-carbonyl bond.

Step 2: Identify the additional bonding in a carbonyl In a metal-carbonyl complex, a filled metal d orbital can donate electron density into a suitable vacant π^* orbital of CO. The σ donation and π back-donation reinforce each other; this synergic bonding strengthens the metal-CO bond. Ammonia does not provide comparable π-acceptor back-bonding.

Step 3: Conclusion CO is a stronger complexing agent than NH_3 because it forms both a σ bond and a reinforcing π back-bond with the metal.

Quick Tip to Solve: For a metal-carbonyl bonding question, mention both directions: CO donates to the metal and the metal back-donates to CO.

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

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

Solution:

Concept:

- Optical isomers are non-superimposable mirror images. A complex is optically active only when its molecular arrangement is chiral.
- Ethane-1,2-diamine, denoted en, is bidentate: its two nitrogen donors bind to the same metal and form a chelate ring.

Step 1: Examine the trans arrangement In octahedral trans-$[Co(en)_2Cl_2]^+$, the two chloride ligands occupy opposite positions. The four nitrogen donors of the two en ligands occupy the remaining four positions around the cobalt ion.

Step 2: Apply the symmetry criterion The trans coordination arrangement possesses a plane of symmetry. Reflection in this plane preserves the arrangement of the identical chloride ligands and the chelating ligands. Consequently, its mirror image can be superimposed on the original arrangement; it cannot form a pair of distinct optical isomers.

Step 3: Conclusion The trans isomer of $[Co(en)_2Cl_2]^+$ is optically inactive because its plane of symmetry makes it achiral.

Quick Tip to Solve: For optical activity, test mirror-image superimposability; the trans dichloro arrangement here has a plane of symmetry.

33(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 splitting places the three t_{2g} orbitals below the two e_g orbitals. The splitting energy is Δ_o, and P denotes the electron-pairing energy.
- Strong-field ligands give $\Delta_o > P$, favouring a low-spin configuration. Weak-field ligands give $\Delta_o < P$, favouring a high-spin configuration.

Step 1: Obtain the configuration of the printed metal ion For iron, $Z = 26$, so the neutral-atom configuration is $[Ar]3d^6 4s^2$. On forming Fe^{3+}, the two $4s$ electrons and one $3d$ electron are removed. Hence the ion has configuration $[Ar]3d^5$; five electrons must be distributed among the split d orbitals.

Step 2: (I) Place the electrons with a strong-field ligand Because $\Delta_o > P$, pairing in the lower t_{2g} orbitals is energetically preferable to occupying e_g. The configuration is

$$t_{2g}^5 e_g^0, \qquad t_{2g} : (\uparrow\downarrow)\ (\uparrow\downarrow)\ (\uparrow).$$

Two orbitals contain electron pairs, while the third contains a single electron. Therefore there is one unpaired electron.

Step 3: (II) Place the electrons with a weak-field ligand Because $\Delta_o < P$, the electrons occupy all five orbitals singly before pairing, as required by Hund's rule. The configuration is

$$t_{2g}^3 e_g^2, \qquad t_{2g} : (\uparrow)\ (\uparrow)\ (\uparrow), \quad e_g : (\uparrow)\ (\uparrow).$$

All five d electrons are unpaired in this high-spin arrangement.

Step 4: Conclusion For octahedral Fe^{3+}: (I) strong-field ligand gives $\boxed{1}$ unpaired electron; (II) weak-field ligand gives $\boxed{5}$ unpaired electrons.

Quick Tip to Solve: Determine the ionic d-electron count first: Fe3+ is d5, so its low-spin and high-spin unpaired counts are 1 and 5.

OR

33(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]

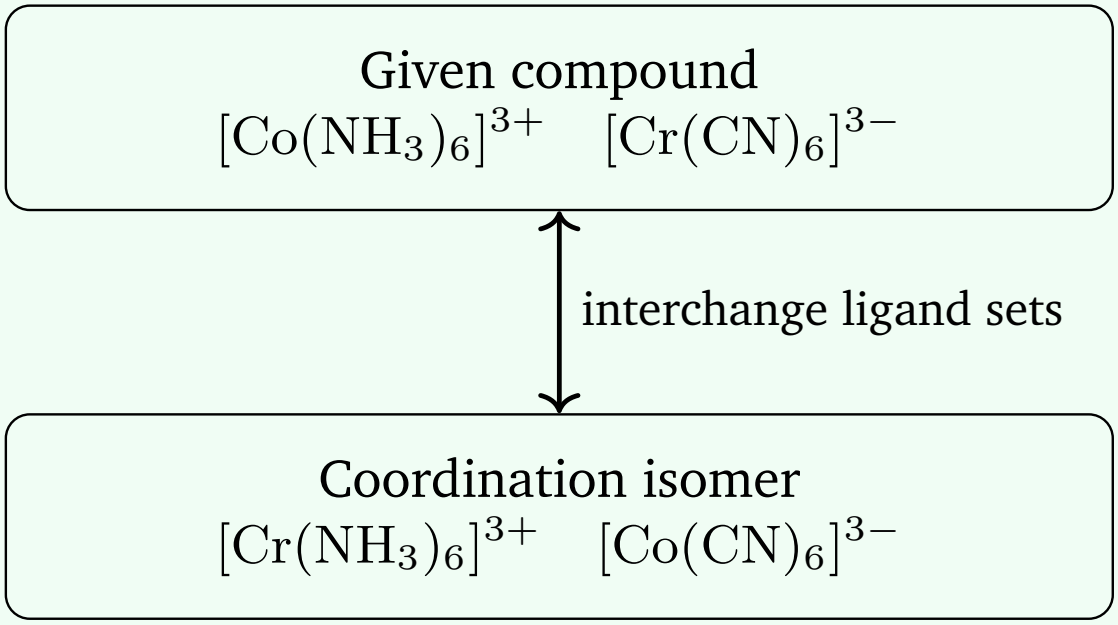
Solution:

Concept:

- Coordination isomerism occurs when both the cation and anion are complex ions and their ligands are interchanged between the two metal centres.
- A coordination isomer retains the overall composition but changes which ligands surround each metal.

Step 1: Identify the two coordination spheres In $[Co(NH_3)_6][Cr(CN)_6]$, the cation is $[Co(NH_3)_6]^{3+}$, and the anion is $[Cr(CN)_6]^{3-}$. The ammonia ligands are neutral, while each cyanide ligand has charge -1; both metals are in oxidation state $+3$.

Step 2: Interchange the ligand sets Transfer the six ammonia ligands to chromium and the six cyanide ligands to cobalt. The resulting salt contains $[Cr(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$. The total numbers of cobalt atoms, chromium atoms, ammonia ligands and cyanide ligands remain unchanged, but their distribution between the coordination spheres differs.



Coordination-sphere representations of the given salt and its coordination isomer

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 are complexes, exchange their ligand sets and verify that the new cation and anion charges still balance.

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

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

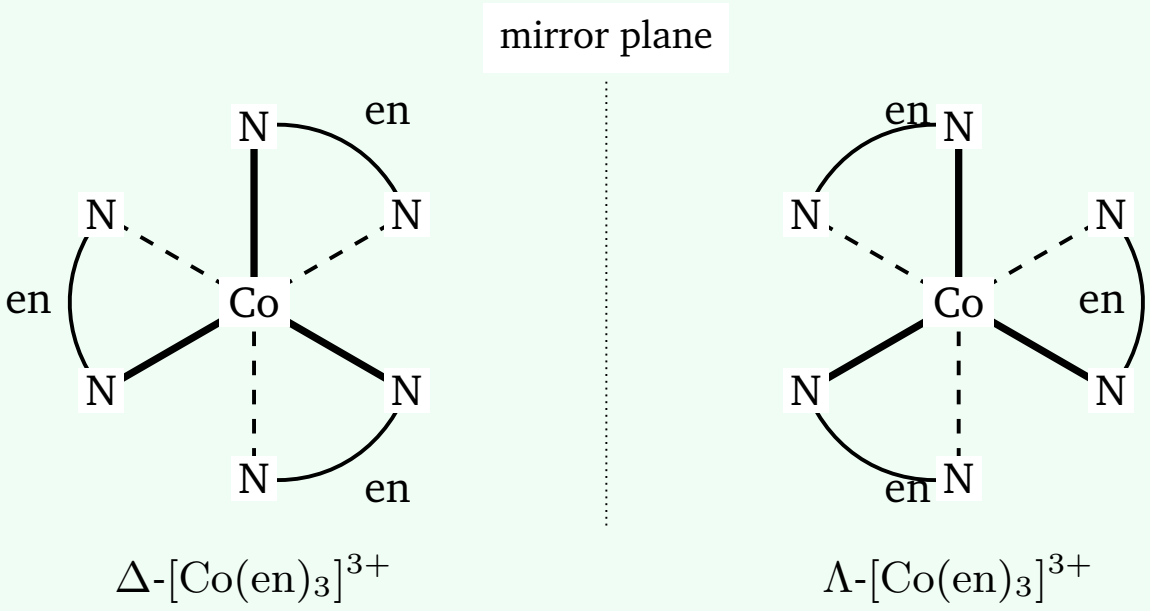
Solution:

Concept:

- Optical isomerism arises from non-superimposable mirror images, called enantiomers.
- Each ethane-1,2-diamine ligand, en, binds through two nitrogen donors. Three such bidentate ligands give an octahedral coordination number of six.

Step 1: Identify the chiral chelate arrangement In $[Co(en)_3]^{3+}$, the three chelate rings wind around the cobalt centre in a helical arrangement. Although the three ligands are identical, their spatial arrangement has no plane of symmetry that makes the complex identical to its reflected image.

Step 2: Draw the two enantiomers The right-handed helical arrangement is denoted Δ, and its mirror image has the left-handed arrangement denoted Λ. In the drawings, each outer curved connection joins the two nitrogen donors of one en ligand. Solid metal-donor bonds point towards the viewer; dashed bonds point away. Reflection reverses all three chelate connections, producing a non-superimposable mirror image.



Mirror-image octahedral chelate arrangements; each curved N-to-N connection represents one en ligand

Step 3: Conclusion $[Co(en)_3]^{3+}$ exhibits optical isomerism; its optical isomers are Δ-$[Co(en)_3]^{3+}$ and Λ-$[Co(en)_3]^{3+}$.

Quick Tip to Solve: Three bidentate en ligands form a pair of opposite helical arrangements; use Delta and Lambda to label their handedness.

33(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]

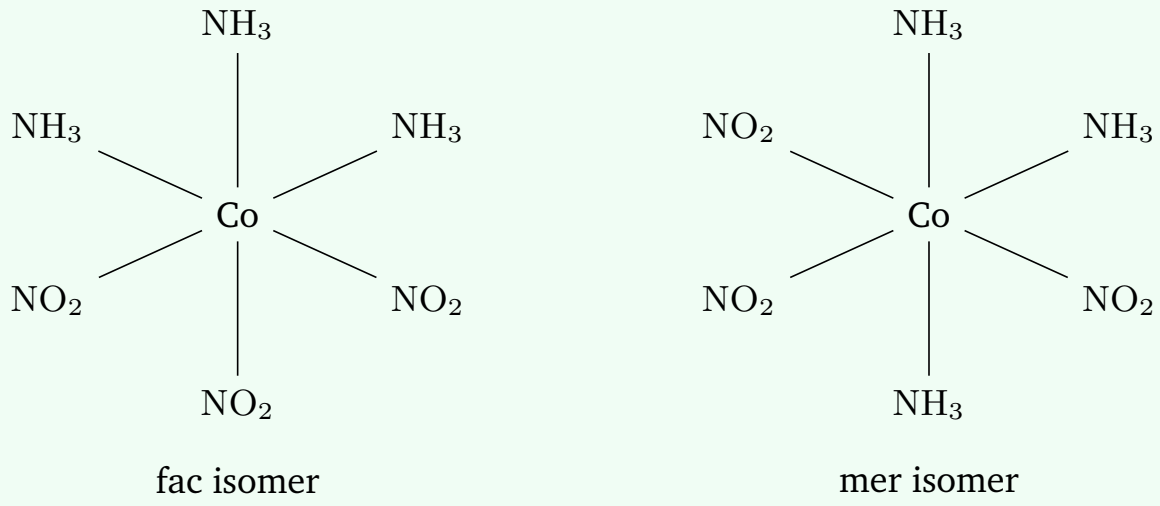
Solution:

Concept:

- An octahedral complex of the form $[MA_3B_3]$ shows geometrical isomerism because the three identical ligands can occupy different relative positions.
- In the facial (fac) isomer the three identical ligands occupy one triangular face and are mutually cis; in the meridional (mer) isomer they lie in a plane through the metal, with one pair trans.

Step 1: Identify the octahedral arrangement In $[Co(NH_3)_3(NO_2)_3]$, three ammonia ligands and three nitro ligands surround the central cobalt ion. Its six coordination positions give an octahedral $[MA_3B_3]$ arrangement, so the relative positions of the ligands must be compared.

Step 2: Draw and distinguish the two arrangements The sketches show all six metal–ligand bonds. The vertical endpoints are opposite, as are the two endpoints of each diagonal through Co. In fac, each pair of NH_3 ligands is cis, at $90°$. In mer, the two axial NH_3 ligands are trans, at $180°$, while the third is cis to both. Thus the two sketches cannot be made identical by rotating the complex.



Octahedral facial and meridional isomers; opposite endpoints through Co are trans.

Step 3: Conclusion The complex exhibits geometrical isomerism: its corresponding isomers are facial (fac) and meridional (mer), as drawn.

Quick Tip to Solve: For an octahedral $[MA_3B_3]$ complex, inspect one ligand set: no trans pair means fac; one trans pair means mer.

33(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:

- In an octahedral crystal field, the five metal d orbitals split into lower-energy t_{2g} and higher-energy e_g orbitals. Their energy separation is the crystal-field splitting energy, Δ_o.
- The pairing energy P is the energy cost of pairing two electrons in one orbital. Whether electrons pair or occupy the higher set depends on the comparison of Δ_o with P.

Step 1: Differentiate the two kinds of ligand Weak field ligands, such as F^- and Cl^-, produce a relatively small splitting of the metal d orbitals. Strong field ligands, such as CN^- and CO, produce a relatively large splitting. Thus ligand strength here refers to the size of the crystal-field splitting, rather than simply the charge on the ligand.

Step 2: Relate splitting to electron pairing and spin With weak field ligands, $\Delta_o < P$. It is energetically preferable for an electron to occupy a higher-energy orbital rather than pair in a lower one, giving a high-spin complex with more unpaired electrons. With strong field ligands, $\Delta_o > P$; electrons pair in the lower t_{2g} orbitals before occupying e_g, giving a low-spin complex with fewer unpaired electrons. 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. This high-spin/low-spin choice applies when alternative occupancies are possible, notably octahedral d^4 to d^7 configurations.

Step 3: Conclusion Weak field ligands give small splitting and favour high spin; strong field ligands give large splitting and favour low spin, because the balance between splitting energy and pairing energy controls electron pairing.

Quick Tip to Solve: Compare Δ_o with P: a small splitting favours promotion and high spin; a large splitting favours pairing and low spin.