CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-4-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

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

General Instructions

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

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

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

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

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

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

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

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

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

(x) Use of calculator is not allowed.

Section A (16 marks)

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

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

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

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

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

(A) Voltage will remain constant.

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

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

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

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

Solution:

Concept:

- The Nernst equation relates cell potential to the reaction quotient: $E = E^{\circ} - (0.0591/n)\log Q$ at 298 K.
- Pure solids have unit activity; dissolved species determine Q.

Step 1: Write the reaction quotient Zinc loses two electrons, so $n = 2$. For the printed reaction,

$$Q = \frac{[Zn^{2+}]}{[Cu^{+}]^2}, \qquad E = 1.28 - \frac{0.0591}{2}\log Q.$$

Concentrations are expressed relative to the standard concentration.

Step 2: Track reaction progress As the reaction proceeds, zinc ions accumulate and copper(I) ions are consumed. Both changes increase Q, making the subtraction in the Nernst equation larger. The voltage therefore falls. Option (A) ignores changing concentrations. Option (C) describes an increase in copper(I) concentration, whereas this reactant is consumed. Option (D) reverses the effect of zinc-ion accumulation.

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

Quick Tip to Solve: Put products above reactants in Q; an increasing quotient lowers cell voltage.

2. Out of Ti^{3+}, Cr^{3+}, Fe^{2+} and Ni^{2+} ions, the one which is the most stable ion in aqueous solution is: [Atomic number: Ti = 22, Cr = 24, Fe = 26, Ni = 28] [1 mark]

(A) Ti^{3+}

(B) Cr^{3+}

(C) Fe^{2+}

(D) Ni^{2+}

Correct Answer: (B) Cr^{3+}

Solution:

Concept:

- Remove outer $4s$ electrons before $3d$ electrons when writing transition-metal ion configurations.
- In an octahedral aqueous complex, the d orbitals split into lower t_{2g} and higher e_g sets.

Step 1: Find the ionic configurations The configurations are Ti^{3+} : $3d^1$, Cr^{3+} : $3d^3$, Fe^{2+} : $3d^6$, and Ni^{2+} : $3d^8$. Thus these ions have different occupancies of the split d orbitals in their hydrated complexes.

Step 2: Compare aqueous stability For Cr^{3+}, the three electrons occupy the three lower t_{2g} orbitals singly, giving $t_{2g}^3 e_g^0$. This favourable configuration gives chromium(III) pronounced stability in aqueous solution and resistance to further oxidation or reduction. Titanium(III) and iron(II) are readily oxidised to higher states; nickel(II) lacks the characteristic t_{2g}^3 configuration. Therefore the other listed ions are not the intended most stable choice.

Step 3: Conclusion The most stable listed ion in aqueous solution is Cr^{3+}. Hence, the correct option is (B).

Quick Tip to Solve: Recognise aqueous chromium(III) by its stable $3d^3$, t_{2g}^3 arrangement.

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

(A) R–NO_2

(B) R–NH_2

(C) R–CH_2–NH_2

(D) R–CO–NH_2

Correct Answer: (D) R–CO–NH_2

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide into a primary amine using Br_2 and aqueous alkali.
- The product contains one fewer carbon atom because the amide carbonyl carbon is removed.

Step 1: Identify the required starting group The substrate must contain the primary amide group

Quick Tip to Solve: For Hofmann degradation, identify $-CONH_2$ in the reactant before choosing an amine product.

$-CONH_2$. Its general reaction is

$$RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O.$$

The group R is retained in the amine, while the carbonyl carbon is lost.

Step 2: Check the alternatives Option (A), RNO_2, is a nitro compound, not an amide. Options (B) and (C) are amines and lack the carbonyl group needed for this degradation. Option (B) resembles the product of the reaction, which is why it is tempting, but the question asks which compound gives the reaction. Only option (D) supplies the required primary amide.

Step 3: Conclusion $R - CO - NH_2$ gives Hofmann bromamide degradation. Hence, the correct option is (D).

Quick Tip to Solve: For Hofmann degradation, identify $-CONH_2$ in the reactant before choosing an amine product.

4. 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 $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution.
- Compare solubilities at the same temperature and gas pressure.

Step 1: Rearrange Henry's law From $p = K_H x$,

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

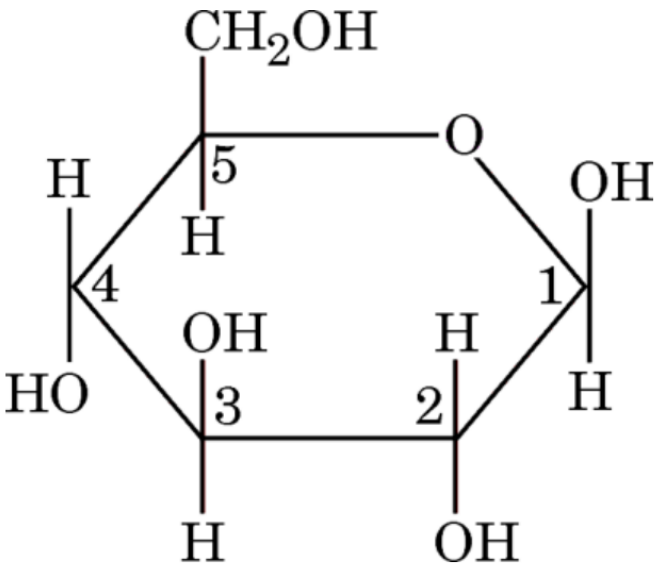
At a fixed pressure, a larger Henry constant gives a smaller mole fraction of dissolved gas. Hence the gas has lower solubility in the liquid.

Step 2: Eliminate the other statements Option (A) reverses the inverse relationship between x and K_H. Option (C) is incorrect because different gases have different interactions with a given solvent and therefore different Henry constants. Option (D) is incorrect because Henryś law directly connects the constant with dissolved mole fraction. Temperature must be kept the same when making this comparison.

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

Quick Tip to Solve: Rearrange $p = K_H x$ to $x = p/K_H$ before comparing gas solubilities.

5. 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 former carbonyl carbon of the open-chain sugar.
- In a cyclic hemiacetal, this carbon is bonded to both the ring oxygen and a hydroxyl oxygen.

Step 1: Locate the hemiacetal centre In the printed Haworth structure, the carbon labelled 1 lies next to the ring oxygen and also carries an OH group. It therefore has bonds to two oxygen atoms, identifying the newly formed hemiacetal centre. This is the carbon derived from the aldehyde group of the open-chain aldose.

Step 2: Check the numbered alternatives Carbons 2 and 3 carry hydroxyl groups but are not directly bonded to the ring oxygen. Carbon 5 is bonded to the ring oxygen and carries the CH_2OH substituent, but it is not the former aldehyde carbon and does not have an anomeric hydroxyl group. Thus none of these three labels identifies the anomeric centre. Changing the orientation of the hydroxyl on carbon 1 distinguishes the two anomers.

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

Quick Tip to Solve: Find the carbon bonded to the ring oxygen and an OH oxygen together.

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

(A) La is actually not an element of transition series.

(B) Zr and Hf have almost identical atomic radii.

(C) Lanthanoids are radioactive.

(D) Ionic radius increases from La^{3+} to Lu^{3+}.

Correct Answer: (B) Zr and Hf have almost identical atomic radii.

Solution:

Concept:

- Lanthanoid contraction is the gradual decrease in size across the lanthanoid series caused by poor shielding by $4f$ electrons.
- This contraction makes corresponding elements of the second and third transition series unusually similar in size.

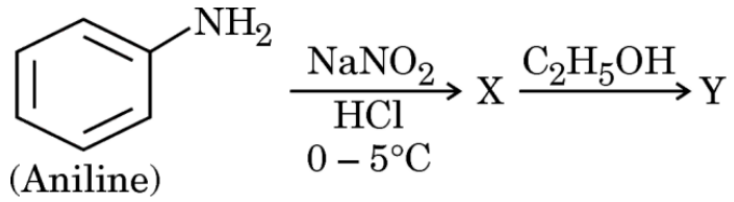
Step 1: Apply lanthanoid contraction Hafnium follows the lanthanoids. The increasing effective nuclear attraction across the intervening $4f$ series contracts its size enough to offset the increase expected from an additional shell. Consequently, zirconium and hafnium have almost identical atomic radii, supporting option (B).

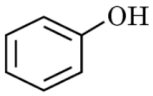
Step 2: Check each remaining statement Lanthanum has configuration $[Xe]5d^16s^2$ and has an incompletely filled d subshell in its atom, so option (A) is false. The lanthanoids are not all radioactive; promethium is the characteristic radioactive member, so (C) is false. The ionic radius of Ln^{3+} decreases from La^{3+} to Lu^{3+}, contrary to (D).

Step 3: Conclusion Zr and Hf have almost identical atomic radii. Hence, the correct option is (B).

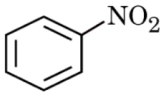
Quick Tip to Solve: Associate the nearly equal sizes of Zr and Hf with contraction across the intervening $4f$ series.

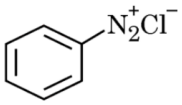
7. In the given reaction sequence, the structure of Y would be: [1 mark]



(A) 

(B) 

(C) 

(D) 

(A) Phenol

(B) Benzene

(C) Nitrobenzene

(D) Benzenediazonium chloride

Correct Answer: (B) Benzene

Solution:

Concept:

- Aniline reacts with $NaNO_2/HCl$ at 0–5 °C to form benzenediazonium chloride.
- Ethanol reduces the diazonium group to hydrogen, releasing nitrogen gas.

Step 1: Identify intermediate X The cold mixture generates nitrous acid, which diazotises aniline:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Thus X is benzenediazonium chloride, the species drawn in option (D). It is an intermediate rather than the final product.

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

$$C_6H_5N_2^+Cl^- + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Hence Y is benzene. Phenol in (A) is obtained by hydrolysis with warm water, not this ethanol treatment. Nitrobenzene in (C) would require introducing a nitro group and is not formed by the stated sequence.

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

Quick Tip to Solve: For an aryl diazonium salt, ethanol replaces $-N_2^+$ with hydrogen.

8. 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 is a chiral centre when it is bonded to four different groups.
- A molecule with such a centre and no internal symmetry can exist as non-superimposable mirror images.

Step 1: Examine 2-bromobutane In $CH_3CH(Br)CH_2CH_3$, carbon-2 carries H, Br, CH_3 and CH_2CH_3. All four substituents differ, so this carbon is asymmetric and the molecule is chiral.

Step 2: Reject the other choices In 1-bromobutane and 1-bromopropane, the carbon bonded to bromine is CH_2Br, with two identical hydrogen atoms. Neither molecule has an asymmetric carbon. In 2-bromopropane, carbon-2 has two identical methyl groups, so it also fails the four-different-groups test.

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

Quick Tip to Solve: Inspect the carbon carrying bromine and compare its two carbon-chain substituents.

9. Which of the following properties of transition metals enables them to behave as catalysts? [1 mark]

(A) High melting point

(B) High ionisation enthalpy

(C) Alloy formation

(D) Variable oxidation states

Correct Answer: (D) Variable oxidation states

Solution:

Concept:

- A catalyst offers a reaction pathway with a lower activation energy and is regenerated at the end.
- Transition metals can adopt different oxidation states because their valence electrons have comparable energies.

Step 1: Identify the catalytic property Variable oxidation states allow a transition metal to accept and donate electrons during successive steps of a reaction. It can form a reactive intermediate and then return to its original oxidation state, completing a catalytic cycle.

Step 2: Compare the alternatives A high melting point describes thermal stability, while a high ionisation enthalpy concerns the energy needed to remove an electron. Alloy formation describes

Quick Tip to Solve: For transition-metal catalysis, look for reversible changes in oxidation state.

mixing with other metals. These properties do not directly explain the reversible electron transfer involved in catalytic action; variable oxidation states do.

Step 3: Conclusion Variable oxidation states enable catalytic behaviour. Hence, the correct option is (D).

Quick Tip to Solve: For transition-metal catalysis, look for reversible changes in oxidation state.

10. What amount of electric charge is required for the oxidation of 1 mole of FeO to Fe_2O_3? [1 mark]

(A) 1F

(B) 2F

(C) 3F

(D) 4F

Correct Answer: (A) 1F

Solution:

Concept:

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

Step 1: Find the oxidation-state change Oxygen has oxidation state -2. Thus iron is $+2$ in FeO and $+3$ in $\mathrm{Fe_2O_3}$. Each iron atom loses one electron:

$$\mathrm{Fe^{2+} \longrightarrow Fe^{3+} + e^-}.$$

Step 2: Count electrons for the stated amount One mole of FeO contains one mole of iron atoms. Its complete oxidation therefore releases one mole of electrons, even though the product formula contains two iron atoms. Hence $Q = (1\,\mathrm{mol})F = 96485\,\mathrm{C}$, conventionally written as $1F$. The values $2F$, $3F$ and $4F$ overcount the electrons for the given one mole of FeO.

Step 3: Conclusion The required charge is $1F$. Hence, the correct option is (A).

Quick Tip to Solve: Count iron atoms in the given FeO amount before using the product formula.

11. 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 converts an alcohol to an alkene by removing the elements of water.
- Protonation converts the poor leaving group $-\mathrm{OH}$ into the better leaving group $-\mathrm{OH}_2^+$.

Step 1: Activate the alcohol The lone pair on the oxygen atom accepts a proton from the acid. This is the first step:

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

The resulting protonated alcohol can subsequently lose neutral water more readily than an unprotonated alcohol can lose hydroxide.

Step 2: Place the other processes in order Loss of water and, for suitable alcohols, formation of a carbocation follow protonation. Removal of a beta hydrogen then gives the alkene. Carbocation formation and water elimination therefore are not the first step. Ester formation is not the first step of the standard acid-catalysed dehydration mechanism asked here.

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

Quick Tip to Solve: In acid-catalysed dehydration, protonate oxygen first to make water the leaving group.

12. 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 a chlorinated organic compound historically used to kill insect pests.
- A non-biodegradable substance resists breakdown by biological processes and can persist in the environment.

Step 1: Identify the use of DDT DDT acts as an insecticide: its agricultural use is to control insects,

Quick Tip to Solve: Pair DDT with insect control and environmental persistence when comparing the options.

not to supply mineral nutrients to plants. It is therefore not a fertilizer. The relevant classification here is a pesticide rather than a greenhouse gas.

Step 2: Identify its environmental behaviour DDT resists biological degradation and remains in the environment for long periods. Its persistence allows accumulation in organisms and increasing concentration along food chains. Consequently, describing it as a biodegradable insecticide is incorrect; the non-biodegradable insecticide description includes both its use and its persistence.

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

Quick Tip to Solve: Pair DDT with insect control and environmental persistence when comparing the options.

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

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

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

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

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

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

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

Solution:

Concept:

- Basicity depends on the availability of a lone pair to accept a proton.
- Acetylation converts aniline, $C_6H_5NH_2$, into the amide acetanilide, $C_6H_5NHCOCH_3$.

Step 1: Judge the assertion Acetanilide is less basic than aniline. In acetanilide, the nitrogen lone pair is strongly delocalised towards the adjacent carbonyl group, so it is less available for proton acceptance. The assertion is true.

Step 2: Judge the reason The acetyl group withdraws electron density from nitrogen through the carbonyl group and resonance involving the nitrogen lone pair. Acetylation therefore decreases the electron density available on nitrogen. The reason is true.

Step 3: Connect the statements The decrease in available electron density reduces the ability of nitrogen to accept a proton, which directly explains the lower basicity of acetanilide. Thus the reason explains the assertion; the choices calling either statement false or denying the explanatory connection are excluded.

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

Quick Tip to Solve: After acetylation, check whether the nitrogen lone pair is delocalised into a carbonyl group.

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

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

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

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

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

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

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

Solution:

Concept:

- A species with all electrons paired is diamagnetic; unpaired electrons produce paramagnetism.
- Cuprous means copper in the $+1$ oxidation state, represented by Cu^{+}.

Step 1: Judge the assertion Neutral copper has configuration $[\mathrm{Ar}]\,3d^{10}4s^{1}$. Formation of Cu^{+} removes the $4s$ electron, leaving $[\mathrm{Ar}]\,3d^{10}$. There are no unpaired electrons, so cuprous salts are diamagnetic. The assertion is true.

Step 2: Judge the reason The $3d^{10}$ configuration fills all five $3d$ orbitals, each with a pair of electrons. Thus the statement that the cuprous ion has completely filled $3d$ orbitals is true.

Step 3: Connect the statements A completely filled $3d$ subshell has no unpaired electrons. This explains the diamagnetism of cuprous salts directly. Both statements are true and their explanatory connection holds, excluding the remaining assertion-reason options.

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

Quick Tip to Solve: For Cu+, remove the 4s electron first and count unpaired electrons in 3d10.

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

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

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

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

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

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

Solution:

Concept:

- Boiling point depends on the strength of intermolecular attractions; stronger attractions require more energy for vaporisation.
- For comparable alkyl halides, the larger, more polarisable halogen strengthens London dispersion forces. Bond polarity alone does not determine the boiling-point order.

Step 1: Judge the assertion n-Butyl bromide has a larger molar mass and a more readily polarisable electron cloud than n-butyl chloride. Its dispersion forces are stronger, so n-butyl bromide has the higher boiling point. The assertion states the reverse order and is false.

Step 2: Judge the reason Chlorine is more electronegative than bromine. The electronegativity difference between carbon and chlorine is therefore greater than that between carbon and bromine, making the C–Cl bond more polar. The reason is true.

Step 3: Check the explanation and the options A true statement about bond polarity cannot explain a false boiling-point order. Options (A) and (B) wrongly treat the assertion as true; option (C) also wrongly treats the reason as false.

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

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

16. 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; at the anode, oxidation occurs. Aqueous salt electrolysis involves competition between the ions and water.
- Observed electrode products depend on electrode potentials, ion concentration and overpotential. Oxygen evolution has a substantial overpotential.

Step 1: Judge the assertion In the usual electrolysis of aqueous sodium chloride (brine), water is reduced in preference to sodium ions, giving hydrogen at the cathode. Chloride ions give chlorine at the anode. Thus the assertion is true.

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

$$2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$$

Step 2: Judge the reason The stated oxidation-potential order is false. Thermodynamically, water oxidation to oxygen is favoured over chloride oxidation under the standard comparison. Chlorine evolution is observed in brine because oxygen evolution has a high overpotential, together with the high chloride concentration; it is not explained by chlorine having a higher oxidation potential than water.

Step 3: Choose the matching option Options (A) and (B) both require a true reason, whereas (D) requires a false assertion. None of these matches the independently checked truth values.

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 hydrogen and chlorine as the usual products, and use oxygen overpotential to explain the anode product.

Section B (10 marks)

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

Solution:

Concept:

- Amino acids contain both an acidic carboxyl group, $-\mathrm{COOH}$, and a basic amino group, $-\mathrm{NH_2}$.
- Essential amino acids must be obtained from food because the human body cannot synthesise them in sufficient amounts.

Step 1: Define essential amino acids Essential amino acids are amino acids that the human body cannot synthesise in amounts adequate for its needs and must therefore obtain through the diet. For example, valine and lysine are essential amino acids. Their presence in proteins does not imply that the body can manufacture them.

Step 2: Explain the amphoteric behaviour The carboxyl group can donate a proton and hence behaves as an acid; the amino group can accept a proton and hence behaves as a base. Consequently an amino acid reacts with both bases and acids. In aqueous solution, internal proton transfer produces a zwitterion containing both positive and negative charges:

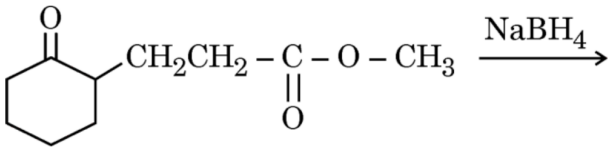
$$\mathrm{H_2N{-}CH(R){-}COOH} \rightleftharpoons \mathrm{H_3N^+{-}CH(R){-}COO^-}$$

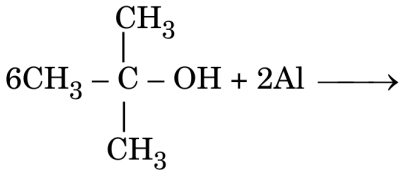
Here R denotes the side chain. In acidic medium, the carboxylate group accepts a proton; in basic medium, the ammonium group loses a proton.

Step 3: Conclusion Essential amino acids must be supplied by the diet. Amino acids are amphoteric because they have an acidic carboxyl group and a basic amino group.

Quick Tip to Solve: Identify both functional groups: proton donation by carboxyl and proton acceptance by amino explain amphoterism together.

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

(a) 

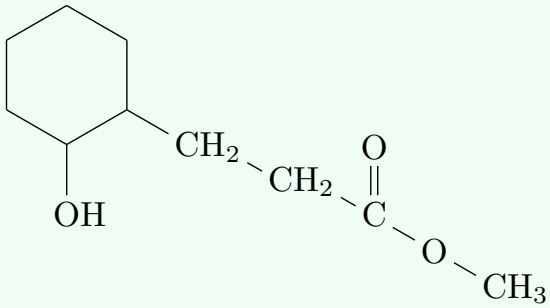
(b) 

Solution:

Concept:

- $NaBH_4$ reduces aldehyde and ketone carbonyl groups to alcohols; under ordinary conditions it does not reduce an ester group.
- Alcohols react with aluminium to form aluminium alkoxides and hydrogen. Each aluminium atom binds three alkoxide groups.

Step 1: Reduce the ketone in part (a) The substrate has a ketone carbonyl in the cyclohexane ring and an ester group in the side chain. Sodium borohydride converts the ring C=O into CH−OH, leaving $-CH_2CH_2COOCH_3$ unchanged. The product is methyl 3-(2-hydroxycyclohexyl)propanoate. The structure below shows the hydroxyl group adjacent to the ring carbon bearing the ester-containing side chain; no stereochemical configuration is specified in the question.



Product of reaction (a)

Step 2: Form the aluminium alkoxide in part (b) The alcohol is tert-butyl alcohol, $(CH_3)_3COH$. Aluminium replaces its hydroxyl hydrogen to form aluminium tert-butoxide. The oxygen remains bonded to the tert-butyl carbon and also bonds to aluminium. The balanced reaction, retaining the printed coefficients, is

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

Each product molecule has three $-OC(CH_3)_3$ groups around aluminium; six alcohol molecules supply the six hydrogen atoms needed for three hydrogen molecules.

Step 3: Conclusion (a) Methyl 3-(2-hydroxycyclohexyl)propanoate, with the ester group unchanged. (b) Aluminium tert-butoxide, $Al[OC(CH_3)_3]_3$, and H_2.

Quick Tip to Solve: With NaBH4, change the ketone to an alcohol and leave the ester intact; with aluminium, replace the alcohol hydrogen by Al.

19. Name and define the cell which was used for providing electric power in the Apollo space programme. Also write its one advantage. [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.
- In the hydrogen–oxygen fuel cell, the overall reaction is $2\,H_2 + O_2 \longrightarrow 2\,H_2O$; the reactants are supplied to the electrodes during operation.

Step 1: Name and define the cell The Apollo space programme used the hydrogen–oxygen fuel cell to provide electrical power. It is a galvanic cell in which hydrogen is the fuel and oxygen is the oxidant, and their chemical energy is converted directly into electrical energy. Unlike a cell whose reactants are all stored inside it, the fuel cell receives a continuing external supply of reactants.

Step 2: State an advantage The hydrogen–oxygen fuel cell produces water as its reaction product:

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

This gives clean operation, with no polluting combustion exhaust from the cell reaction. In the Apollo spacecraft, the water produced was also useful as a source of drinking water for astronauts. Continuous supply of hydrogen and oxygen allows the cell to keep providing electricity while fuel and oxidant remain available.

Step 3: Conclusion The cell was the hydrogen–oxygen fuel cell: a galvanic cell converting continuously supplied fuel and oxidant directly into electrical energy. One advantage is its clean water product, which was also used by the astronauts.

Quick Tip to Solve: Associate Apollo with the hydrogen–oxygen fuel cell: the same reaction supplies electric power and produces useful water.

20. $PdCl_2{\cdot}2KCl$ does not give precipitate of AgCl with $AgNO_3$ solution. Write the structural formula and IUPAC name of the complex. [2 marks]

Solution:

Concept:

- Silver nitrate detects free chloride ions: $Ag^+ + Cl^- \longrightarrow AgCl(s)$. Chlorido ligands inside the coordination sphere are not free chloride ions.
- The coordination sphere is written in square brackets. The oxidation state of the central metal is found by balancing ligand charges with the charge on the complex ion.

Step 1: Locate the chloride ions The composition contains four chlorine atoms per palladium atom. Since no AgCl precipitate is obtained, none is present as an ionisable chloride counter-ion. All four are coordinated to Pd; the two potassium ions remain outside the coordination sphere. Thus the coordination formula is $K_2[PdCl_4]$, containing $[PdCl_4]^{2-}$. The four Pd–Cl bonds have a square-planar arrangement around Pd(II).

Quick Tip to Solve: No AgCl precipitate means chloride belongs inside the square brackets, not among the counter-ions.

Step 2: Assign the oxidation state and name If the oxidation state of Pd is x, charge balance gives

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

Four chlorido ligands give the prefix tetrachlorido. As the complex is anionic, the metal name becomes palladate, followed by its oxidation state (II). The cation is named first.

Step 3: Conclusion Structural formula: $\boxed{K_2[PdCl_4]}$ (square-planar complex). IUPAC name: $\boxed{\text{potassium tetrachloridopalladate(II)}}$.

Quick Tip to Solve: No AgCl precipitate means chloride belongs inside the square brackets, not among the counter-ions.

21(a). The reaction between $A_2(g)$ and $B_2(g)$ was carried out in a sealed isothermal container. The rate law for the reaction was found to be:

Rate = $k[A_2][B_2]$

If 1 mole of $A_2(g)$ 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 rate law is $r = k[A_2][B_2]$: the reaction is first order in each reactant and second order overall.
- At fixed temperature, the rate constant k for the same reaction is independent of reactant concentrations. Concentration changes affect the rate through the rate law.

Step 1: Compare the concentrations immediately after addition For the reaction chamber of fixed volume V litres, let the initial concentrations be $a = [A_2]$ and $b = [B_2]$, in mol L^{-1}. Addition of $1\,\text{mol}$ of A_2 increases its concentration by $\Delta a = (1\,\text{mol})/V$, while the concentration of B_2 immediately after addition remains b.

Step 2: Apply the rate law at unchanged temperature The old and new instantaneous rates are

$$r = kab, \qquad r' = k(a + \Delta a)b.$$

Therefore $r'/r = (a + \Delta a)/a > 1$: the rate increases. A numerical multiplication factor cannot be specified without the initial amount of A_2. Since the temperature is held constant, the value of k remains unchanged; the increase in rate is due to the increased reactant concentration.

Step 3: Conclusion The reaction rate increases, while the rate constant k remains unchanged.

Quick Tip to Solve: Compare instantaneous rates with the same k; adding one mole does not automatically double the concentration.

OR

21(b). Reactant 'A' underwent a decomposition reaction. The concentration of 'A' was measured periodically and recorded in the table given below. Based on the above data, predict the order of the reaction and write the expression for the rate law. [2 marks]

Time / Hours	[A]/M
0	0·88
1	0·44
2	0·22
3	0·11

Solution:

Concept:

- A first-order reaction has a concentration-independent half-life: $t_{1/2} = \ln 2/k$, where k is its rate constant.
- For decomposition of A with first-order kinetics, the rate law is $-d[\mathrm{A}]/dt = k[\mathrm{A}]$; its integrated form is $\ln([\mathrm{A}]_0/[\mathrm{A}]_t) = kt$.

Step 1: Identify the concentration pattern The concentration changes from 0.88 to $0.44\,\mathrm{M}$ during the first hour, from 0.44 to $0.22\,\mathrm{M}$ during the next hour, and from 0.22 to $0.11\,\mathrm{M}$ during the third hour. Each equal interval of $1\,\mathrm{h}$ halves the concentration. Thus the half-life stays constant even as the starting concentration of each interval decreases.

Step 2: Infer the order and write the rate law A constant half-life identifies first-order kinetics. A zero-order reaction instead loses equal amounts in equal time intervals; here the decreases are 0.44, 0.22 and $0.11\,\mathrm{M}$, which are unequal. For first order,

$$k = \frac{\ln 2}{1\,\mathrm{h}} = 0.693\,\mathrm{h}^{-1}.$$

This same value fits each halving interval and gives the rate expression $r = k[\mathrm{A}]$.

Step 3: Conclusion The reaction is $\boxed{\text{first order}}$, with rate law $\boxed{-\frac{d[\mathrm{A}]}{dt} = k[\mathrm{A}]}$.

Quick Tip to Solve: Look for equal fractional decreases: halving in every one-hour interval reveals a constant first-order half-life.

Section C (21 marks)

22. Give explanation for each of the following observations:

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

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

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

Solution:

Concept:

- Redox behaviour depends on the relative stability of the initial and final electronic configurations, not only on the initial number of d electrons.
- Poor shielding by f electrons increases effective nuclear attraction across an f-block series, decreasing atomic and ionic radii.
- Interstitial compounds form when small atoms occupy spaces within a metal crystal lattice without replacing the metal atoms.

Step 1: (a) Explain the opposite redox tendencies Both Mn^{3+} and Cr^{2+} have a $3d^4$ configuration, but their favoured products differ. Manganese(III) gains an electron:

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

The half-filled $3d^5$ configuration of Mn^{2+} is especially stable, so Mn^{3+} accepts electrons and acts as an oxidising agent. Chromium(II) loses an electron:

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

The $3d^3$ configuration is particularly stable in the usual octahedral environment, with three singly occupied t_{2g} orbitals. Hence Cr^{2+} donates electrons and acts as a reducing agent.

Step 2: (b) Compare the contractions Across each series, nuclear charge increases while electrons enter f orbitals. These electrons shield the increased nuclear charge poorly, so the outer electrons experience increasing effective nuclear attraction. The $5f$ electrons of actinoids shield less effectively than the $4f$ electrons of lanthanoids. Consequently the element-to-element decrease in size, or contraction, is greater among actinoids.

Step 3: (c) Explain interstitial-compound formation Transition metals have crystal lattices with interstitial spaces. The small atoms H, B, C and N can fit into these spaces, giving many interstitial compounds without greatly changing the basic metal framework. Such compounds are often non-stoichiometric because different fractions of the spaces may be occupied. Their formation depends on the small size of the inserted atoms relative to the available lattice voids.

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

Quick Tip to Solve: For redox behaviour, write the product configuration; for contraction compare shielding, and for interstitial compounds compare atomic size.

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

Solution:

Concept:

- A positive 2,4-dinitrophenylhydrazine (2,4-DNP) test indicates a carbonyl group of an aldehyde or ketone.
- The iodoform test detects the methyl ketone group $-COCH_3$; its yellow precipitate is CHI_3.
- An aromatic methyl ketone can undergo drastic oxidation to a carboxylic acid containing the same phenyl group.

Step 1: Identify the carbonyl compound A The molecular formula is C_8H_8O, and the compound is aromatic. The positive 2,4-DNP test confirms an aldehyde or ketone. Since neither Tollens' reagent nor Fehling' reagent reacts with A, and the iodoform test is positive, A must contain the methyl ketone group. Joining a phenyl group to this group gives $C_6H_5 - C(=O) - CH_3$, which has exactly eight carbon atoms, eight hydrogen atoms and one oxygen atom. This is acetophenone; its IUPAC name is 1-phenylethan-1-one.

Step 2: Identify the yellow precipitate B Sodium hypoiodite converts the methyl ketone into benzoate and yellow iodoform. The reaction may be represented using iodine in alkaline medium as

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

Thus B has the structure $H - C(I)_3$. Its IUPAC name is triiodomethane, and its common name is iodoform.

Step 3: Identify the oxidation product C Under drastic oxidation with $KMnO_4$, the acetyl side chain is oxidised to the carboxyl group attached directly to the benzene ring. The acid obtained is $C_6H_5 - C(=O) - OH$. Its IUPAC retained name is benzoic acid. This product is consistent with the aromatic ring of A and the oxidation behaviour stated in the question.

Step 4: Conclusion A: $C_6H_5COCH_3$, 1-phenylethan-1-one; B: CHI_3, triiodomethane; C: C_6H_5COOH, benzoic acid.

Quick Tip to Solve: Use the yellow iodoform precipitate to recognise a methyl ketone before applying the molecular formula.

24. Arrange the following compounds as asked:

(a) in decreasing order of pK_b values

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

(b) increasing order of boiling point

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

(c) increasing order of solubility in water

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

Solution:

Concept:

- $pK_b = -\log K_b$: a larger pK_b means a weaker base. Resonance in aromatic amines lowers availability of the nitrogen lone pair.
- Intermolecular hydrogen bonding affects boiling point; O–H hydrogen bonds are stronger than comparable N–H hydrogen bonds.
- Water solubility reflects hydrogen bonding with water and the opposing effect of hydrophobic alkyl or phenyl groups.

Step 1: (a) Compare basicity and reverse it for pKb Aniline, $C_6H_5NH_2$, has its nitrogen lone pair delocalised into the benzene ring and is therefore a weak base. The methyl group in N-methylaniline, $C_6H_5NHCH_3$, supplies electron density by its positive inductive effect, making it more basic than aniline. Both aromatic amines are weaker bases than the aliphatic amines. In water, diethylamine is more basic than ethylamine because the electron-donating effect of two ethyl groups, together with adequate solvation, favours protonation. Since larger basicity means smaller pK_b, the requested decreasing order is

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

Step 2: (b) Compare intermolecular attraction Ethylamine and dimethylamine have the same molecular formula and comparable molecular masses. Primary ethylamine has two N–H bonds and forms more extensive intermolecular hydrogen bonding than secondary dimethylamine, which has only one. Ethanol forms stronger O–H hydrogen bonds than the N–H hydrogen bonds of these amines. Therefore the increasing boiling-point order is

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

Step 3: (c) Compare the hydrophobic portions All three amines can interact with water through hydrogen bonding. Aniline has a large hydrophobic phenyl group and is least soluble. Diethylamine has two ethyl groups, whereas ethylamine has only one and a greater proportion of hydrophilic amino character. Therefore the increasing order of solubility in water is

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

Step 4: Conclusion The displayed orders give decreasing pK_b, increasing boiling point, and increasing water solubility, respectively.

Quick Tip to Solve: Write the basicity order first, then reverse it for pKb; compare hydrogen bonding and hydrophobic size separately.

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 delocalisation involving the adjacent carbon–carbon double bond.
- Cyanide is an ambident nucleophile: attachment through carbon gives a nitrile $R-CN$, while attachment through nitrogen gives an isocyanide $R-NC$.
- An S_N2 reaction involves simultaneous backside nucleophilic attack and leaving-group departure; steric crowding at the reacting carbon slows it.

Step 1: (i) Hydrolysis of allyl chloride Allyl chloride is $CH_2=CH-CH_2Cl$. Its carbon bearing chlorine is next to a double bond. During substitution the developing positive charge can be stabilised by delocalisation; if ionisation occurs, the allyl carbocation has two resonance forms:

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

The adjacent double bond also stabilises the transition state for nucleophilic substitution. In contrast, $CH_3CH_2CH_2Cl$ has no adjacent double bond to provide resonance stabilisation. The lower activation barrier makes allyl chloride hydrolyse more readily.

Step 2: (ii) Formation of isocyanides with silver cyanide Silver cyanide, $AgCN$, is predominantly covalent. Its carbon end is bonded to silver, so nitrogen is the available attacking end of this ambident group. Consequently the alkyl group bonds to nitrogen, producing an isocyanide:

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

This differs from ionic KCN, whose cyanide ion normally attacks through carbon and gives $R-CN$. The bonding in the cyanide reagent therefore determines the point of attachment.

Step 3: (iii) Faster SN2 reaction of methyl chloride In S_N2 substitution, OH^- must approach the carbon bearing chlorine from the side opposite the C–Cl bond. Methyl chloride, CH_3Cl, has only small hydrogen atoms around this carbon, allowing easy backside approach. In tert-butyl chloride, $(CH_3)_3CCl$, three methyl groups shield the reaction centre and severely hinder that approach and the crowded transition state. Thus methyl chloride undergoes S_N2 reaction much faster; tert-butyl chloride is practically unreactive by this mechanism.

Step 4: Conclusion (i) Allylic resonance stabilisation facilitates hydrolysis; (ii) covalent AgCN attacks through nitrogen to give isocyanide; (iii) methyl chloride has far less steric hindrance to backside S_N2 attack than tert-butyl chloride.

Quick Tip to Solve: For substitution explanations, check resonance at the reaction centre, the attacking atom of the reagent, and steric access.

OR

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

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

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

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

[3 marks]

Solution:

Concept:

- In the presence of peroxide, HBr adds to propene by the free-radical mechanism in the anti-Markovnikov orientation; bromine attaches to the terminal carbon.
- Aqueous KOH replaces halogen by hydroxyl, whereas hot alcoholic KOH eliminates a hydrogen halide. The more substituted alkene is the major product (Saytzeff rule).
- An alkyl chloride reacts with Mg in dry ether to form a Grignard reagent, $RMgCl$. Water protonates its carbon to give RH.

Step 1: (i) Addition followed by hydrolysis The peroxide effect gives 1-bromopropane, not 2-bromopropane. Hydroxide then substitutes bromide to give propan-1-ol:

$$CH_3CH{=}CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br \xrightarrow{\text{aq. KOH}} CH_3CH_2CH_2OH.$$

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

Step 2: (ii) Elimination followed by addition Heating 2-chlorobutane with alcoholic KOH removes HCl from adjacent carbon atoms. But-2-ene is the major alkene because its double bond is more substituted than that of but-1-ene. Addition of HBr across its double bond gives 2-bromobutane:

$$CH_3CH_2CH(Cl)CH_3 \xrightarrow[\Delta]{\text{alc. KOH}} CH_3CH{=}CHCH_3 \xrightarrow{HBr} CH_3CH(Br)CH_2CH_3.$$

Here $A = CH_3CH{=}CHCH_3$ and $B = CH_3CH(Br)CH_2CH_3$.

Step 3: (iii) Formation and hydrolysis of the Grignard reagent The ethyl group and chloride in the given Grignard reagent identify the starting halide as chloroethane. Preparation requires dry ether because moisture would destroy the reagent. Its hydrolysis forms ethane:

$$CH_3CH_2Cl \xrightarrow[\text{dry ether}]{Mg} CH_3CH_2MgCl \xrightarrow[H^+]{H_2O} CH_3CH_3.$$

Hence $A = CH_3CH_2Cl$ and the main organic product $B = CH_3CH_3$.

Step 4: Conclusion The required pairs (A, B) are: (i) 1-bromopropane and propan-1-ol; (ii) but-2-ene and 2-bromobutane; (iii) chloroethane and ethane. Their condensed structural formulae are given above.

Quick Tip to Solve: First distinguish aqueous KOH (substitution) from hot alcoholic KOH (elimination); peroxide changes the orientation only of HBr addition.

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

Solution:

Concept:

- Williamson ether synthesis is an S_N2 reaction of an alkoxide ion with an alkyl halide. Primary halides permit backside attack readily.
- A tertiary halide is sterically hindered; a strong alkoxide base favours elimination instead of ether formation.

Step 1: Assess the proposed reagents No. Sodium propoxide, $CH_3CH_2CH_2ONa$, cannot suitably prepare the desired ether with tert-butyl chloride, $(CH_3)_3CCl$. The tertiary carbon blocks the backside attack required for S_N2. Propoxide instead abstracts a beta hydrogen and the halide undergoes elimination, producing 2-methylpropene:

$$(CH_3)_3CCl + NaOCH_2CH_2CH_3 \longrightarrow (CH_3)_2C{=}CH_2 + HOCH_2CH_2CH_3 + NaCl.$$

Step 2: Choose the appropriate Williamson partners Place the bulky tert-butyl group in the alkoxide and use a primary propyl halide as the electrophile. Sodium tert-butoxide and 1-bromopropane are suitable:

$$(CH_3)_3CONa + BrCH_2CH_2CH_3 \longrightarrow (CH_3)_3COCH_2CH_2CH_3 + NaBr.$$

The unhindered primary carbon allows displacement of bromide by the alkoxide ion, forming tert-butyl propyl ether.

Step 3: Conclusion Use sodium tert-butoxide, $(CH_3)_3CONa$, with 1-bromopropane, $CH_3CH_2CH_2Br$, instead of sodium propoxide with tert-butyl chloride.

Quick Tip to Solve: For an unsymmetrical ether, put the more hindered group in the alkoxide and choose the less hindered alkyl halide.

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

Solution:

Concept:

- Ethers are named as alkoxyalkanes: the oxygen-linked substituent is an alkoxy group on the chosen carbon parent.
- The tert-butyl skeleton is 2-methylpropane; in this ether its central carbon bears the propoxy group.

Step 1: Write the ether structure The ether from part (a) is $(CH_3)_3C{-}O{-}CH_2CH_2CH_3$. The oxygen joins a tert-butyl group to a straight-chain propyl group. The tert-butyl carbon skeleton contains four carbons and is selected as the parent side.

Step 2: Assign the substituents and locants The parent is propane with a methyl substituent at carbon 2. The $-OCH_2CH_2CH_3$ substituent is propoxy, also attached at carbon 2. Listing methyl before

Quick Tip to Solve: Draw the central tert-butyl carbon first: both methyl and propoxy receive locant 2 on the propane parent.

propoxy gives the substitutive IUPAC name below; the oxygen is part of propoxy, not of the parent carbon chain.

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

Quick Tip to Solve: Draw the central tert-butyl carbon first: both methyl and propoxy receive locant 2 on the propane parent.

27. An aqueous solution of NaOH was made and its molar mass from the measurement of osmotic pressure at 25°C was found to be 28 g mol^{-1}. Calculate the percentage dissociation of NaOH in this solution.

[Atomic mass: Na = 23.0 u, O = 16.0 u, H = 1.0 u] [3 marks]

Solution:

Concept:

- Osmotic pressure obeys $\pi = iCRT$, where i is the van't Hoff factor, C is formula-unit molarity, R the gas constant and T absolute temperature.
- For an apparent molar mass obtained by ignoring dissociation, $i = M_{\text{true}}/M_{\text{apparent}}$. For $\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$, $i = 1 + \alpha$, where α is the fraction dissociated.

Step 1: Calculate the true molar mass Using the supplied atomic masses, the formula molar mass is

$$M_{\text{true}} = 23.0 + 16.0 + 1.0 = 40.0\,\text{g mol}^{-1}.$$

The measured apparent molar mass is only $28\,\text{g mol}^{-1}$. Dissociation increases the number of solute particles, raising osmotic pressure and consequently lowering the inferred molar mass.

Step 2: Determine the particle multiplication factor If mass w is dissolved in volume V, then $\pi = i(w/M_{\text{true}}V)RT$. Interpreting the same measurement without dissociation gives $\pi = (w/M_{\text{apparent}}V)RT$. Equating these expressions cancels the common mass, volume and temperature factors:

$$i = \frac{M_{\text{true}}}{M_{\text{apparent}}} = \frac{40}{28} = \frac{10}{7}.$$

Thus no separate substitution of 25°C is needed.

Step 3: Relate the factor to dissociation Begin with one mole of NaOH formula units. At fraction α dissociated, the amounts are $(1-\alpha)$ mol undissociated NaOH, α mol Na^+, and α mol OH^-. The total is $1+\alpha$ mol particles. Hence

$$\alpha = i - 1 = \frac{10}{7} - 1 = \frac{3}{7}, \qquad 100\alpha = \frac{300}{7}\% = 42.86\%.$$

The result lies between zero and complete dissociation, as expected from $1 < i < 2$.

Step 4: Conclusion The percentage dissociation of NaOH inferred from the osmotic-pressure measurement is $\boxed{42.86\%}$.

Quick Tip to Solve: For a solute yielding two ions, compute percentage dissociation directly as $100(M_{\text{true}}/M_{\text{apparent}} - 1)$.

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

Al/Al^{3+} (0.002 M) and Ni/Ni^{2+} (0.002 M)

Given: $E^\circ_{Ni^{2+}/Ni} = -0.25$ V, $E^\circ_{Al^{3+}/Al} = -1.66$ V, log 5 = 0.6990 [3 marks]

Solution:

Concept:

- The electrode with the higher standard reduction potential acts as the cathode in a voltaic cell. The 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 in the balanced reaction and Q is its reaction quotient. Pure solid metals have unit activity.

Step 1: Identify the electrodes and balance the reaction Nickel has the higher reduction potential, so nickel ions undergo reduction while aluminium undergoes oxidation. Balancing electrons gives

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

Hence the overall reaction is $2\text{Al} + 3\text{Ni}^{2+} \longrightarrow 2\text{Al}^{3+} + 3\text{Ni}$, with $n = 6$.

Step 2: Calculate the standard potential and reaction quotient

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

Using the concentrations specified in the question,

$$Q = \frac{[\text{Al}^{3+}]^2}{[\text{Ni}^{2+}]^3} = \frac{(0.002)^2}{(0.002)^3} = 500.$$

The concentrations do not cancel completely because their stoichiometric powers are different. From the supplied logarithm, $\log 500 = 2 + \log 5 = 2.6990$.

Step 3: Apply the Nernst equation Substituting the balanced electron count and reaction quotient,

$$\begin{aligned} E_{\text{cell}} &= 1.41 - \frac{0.0591}{6}(2.6990) \\ &= 1.41 - 0.02659 \\ &= 1.38341\,\text{V}. \end{aligned}$$

Since $Q > 1$, the concentration correction reduces the potential below its standard value, consistent with the calculated result.

Step 4: Conclusion The voltage of the voltaic cell at 25°C is $\boxed{E_{\text{cell}} \approx 1.383\,\text{V}}$.

Quick Tip to Solve: Balance the overall redox reaction first: here six electrons are transferred, and equal ion concentrations still give $Q = 500$, not unity.

Section D (8 marks)

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

29(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 $p_i = x_i p_i^\circ$, where p_i is the partial vapour pressure of component i, x_i its liquid-phase mole fraction and p_i° its pure-liquid vapour pressure at the same temperature.
- Negative deviation occurs when unlike-molecule attractions are stronger than the attractions in the pure liquids, reducing the tendency of molecules to escape into the vapour.

Step 1: Give a suitable miscible liquid pair A mixture of acetone and chloroform shows negative deviation from Raoult's law. These liquids are miscible, and their mixture has a lower vapour pressure than predicted by the ideal-solution relation at the same temperature and composition.

Step 2: Explain the intermolecular interaction The hydrogen atom of chloroform forms a hydrogen bond with the oxygen atom of the carbonyl group of acetone. Thus, acetone–chloroform attractions are stronger than the corresponding attractions between like molecules. Molecules are held more firmly in the liquid and escape less readily into the vapour, so the partial vapour pressures fall below their Raoult-law values.

Step 3: Conclusion $\boxed{\text{Acetone and chloroform}}$ show negative deviation because stronger unlike-molecule hydrogen bonding lowers their escaping tendency and vapour pressure.

Quick Tip to Solve: Link negative deviation to stronger unlike-molecule attraction; for acetone and chloroform, explicitly identify hydrogen bonding.

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

Solution:

Concept:

- For an ideal solution containing volatile components, each component contributes a partial pressure to the vapour above the solution.
- x_i denotes the mole fraction of component i in the liquid, and p_i° denotes the vapour pressure of its pure liquid at the same temperature.

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

Step 2: Express the law for a binary solution For components A and B,

$$p_A = x_A p_A^\circ, \qquad p_B = x_B p_B^\circ.$$

Their total vapour pressure is $P = p_A + p_B = x_A p_A^\circ + x_B p_B^\circ$. The mole fractions here belong to the liquid solution, not the vapour mixture.

Step 3: Conclusion Raoult's law is $\boxed{p_i = x_i p_i^\circ}$ for each volatile component at a fixed temperature.

Quick Tip to Solve: In the statement, say partial vapour pressure and liquid mole fraction; use the pure-liquid vapour pressure at the same temperature.

OR

29(b). 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 dissolved species, x its mole fraction in the liquid and K_H the Henry constant at a specified temperature.
- Raoult's law is $p = p^\circ x$, where p° is the vapour pressure of the pure liquid at that temperature.

Step 1: Compare the mathematical forms Both laws express the partial pressure as a linear function of the liquid-phase mole fraction. The difference in their expressions is the proportionality constant: Henry's law uses K_H, whereas Raoult's law uses p°.

Step 2: Specify the condition for equivalence If the Henry constant for a component equals its pure-component vapour pressure, $K_H = p^\circ$, then substituting this value into $p = K_H x$ gives $p = p^\circ x$, exactly the Raoult-law expression.

Step 3: Conclusion Raoult's law is the special case of Henry's law in which $\boxed{K_H = p^\circ}$.

Quick Tip to Solve: Compare the constants in $p = K_H x$ and $p = p^\circ x$; the required comment is their equality, not merely that both laws are linear.

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

Solution:

Concept:

- An ideal solution has comparable intermolecular attractions between like and unlike molecules and obeys Raoult's law over the entire composition range.
- ΔH_{mix} is the enthalpy change on mixing, and ΔV_{mix} is the volume change on mixing at the specified temperature and pressure.

Step 1: State the enthalpy characteristic An ideal solution has $\Delta H_{\text{mix}} = 0$. Mixing the components causes neither heat absorption nor heat evolution because replacing like-molecule interactions by unlike-molecule interactions produces no net change in interaction energy.

Step 2: State the volume characteristic An ideal solution has $\Delta V_{\text{mix}} = 0$. The volume of the mixture equals the sum of the volumes of its components before mixing, so there is neither contraction nor expansion on forming the solution.

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

Quick Tip to Solve: Use the two zero mixing changes: no heat change and no volume change; do not confuse ideal mixing with zero entropy of mixing.

30(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:

- DNA is a polynucleotide whose repeating units contain a sugar, phosphate and a nitrogenous base.
- Hydrolysis breaks the covalent bonds joining the components. DNA contains 2-deoxyribose, whereas RNA contains ribose.

Step 1: Identify the hydrolysis products On complete hydrolysis, DNA yields phosphoric acid, 2-deoxyribose sugar and the nitrogenous bases adenine, guanine, cytosine and thymine. These are the components of its nucleotides; hydrolysis separates the phosphate, sugar and base constituents.

Step 2: Compare the structures of DNA and RNA DNA generally consists of two complementary polynucleotide strands wound into a double helix, whereas RNA is generally single-stranded. DNA has 2-deoxyribose sugar, which lacks the hydroxyl group at the $2'$ carbon; RNA has ribose with a $2'$-OH group. The bases in DNA are A, G, C and T; RNA has A, G, C and U, with uracil replacing thymine.

Step 3: Conclusion DNA hydrolysis produces phosphoric acid, 2-deoxyribose and A, G, C, T. Struc-

Quick Tip to Solve: For DNA versus RNA, compare three features together: sugar, thymine versus uracil, and number of strands.

turally, DNA is generally double-stranded with deoxyribose and thymine, whereas RNA is generally single-stranded with ribose and uracil.

Quick Tip to Solve: For DNA versus RNA, compare three features together: sugar, thymine versus uracil, and number of strands.

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

Solution:

Concept:

- A nitrogenous base attached to a pentose sugar forms a nucleoside.
- Adding a phosphate group to a nucleoside forms a nucleotide.

Step 1: Describe a nucleoside A nucleoside contains only a nitrogenous base and a pentose sugar, joined through an N-glycosidic bond. It has no phosphate group; adenosine is an example.

Step 2: Describe a nucleotide A nucleotide contains a nitrogenous base, a pentose sugar and a phosphate group. The phosphate is attached to the sugar, usually at its $5'$ position. Adenosine monophosphate is an example. Thus the extra phosphate group is the decisive structural distinction.

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

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

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

Solution:

Concept:

- Nucleic acids are polynucleotides that carry biological information in their base sequence.
- DNA and RNA perform complementary roles in heredity and protein synthesis.

Step 1: State the hereditary function DNA stores genetic information in the sequence of its nitrogenous bases. Replication passes this information to daughter cells and thereby transmits hereditary characteristics from one generation to the next.

Step 2: State the protein-synthesis function Nucleic acids direct the synthesis of proteins. The information in DNA is transcribed into RNA; messenger RNA carries the code, while transfer RNA and ribosomal RNA help translate it into a specific amino-acid sequence.

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

Quick Tip to Solve: Recall the two linked roles: DNA preserves the genetic code, and RNA helps express that code as proteins.

OR

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

Solution:

Concept:

- The sugar-phosphate backbone of a nucleic acid joins successive nucleotide units.
- RNA contains uracil in place of the thymine present in DNA.

Step 1: Name the internucleotide linkage Two adjacent nucleotides are joined by a $3'$-$5'$ phosphodiester linkage. A phosphate group connects the $3'$-oxygen of one sugar to the $5'$-oxygen of the next sugar, forming the polynucleotide backbone.

Step 2: Identify the RNA-specific base The base is uracil, a pyrimidine. In the standard base composition of RNA, adenine, guanine, cytosine and uracil are present; DNA contains thymine instead of uracil. The linkage joins nucleotide units, whereas the base is a constituent of each nucleotide.

Step 3: Conclusion The linkage is a $3'$-$5'$ phosphodiester linkage; the RNA base absent from DNA is uracil.

Quick Tip to Solve: Keep the two names separate: phosphodiester is the backbone bond; uracil is the RNA-specific base.

Section E (15 marks)

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

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

Solution:

Concept:

- A complex is diamagnetic when all electrons are paired and paramagnetic when it contains unpaired electrons.
- Nickel has atomic number 28; its oxidation state determines the metal d-electron count.

Step 1: Explain the carbonyl complex In $Ni(CO)_4$, CO is neutral, so nickel has oxidation state zero. In the valence-bond description, its electrons rearrange to give a filled $3d^{10}$ set and vacant orbitals for sp^3 bonding. All electrons are paired, so the tetrahedral complex is diamagnetic.

Step 2: Explain the chloride complex In $[NiCl_4]^{2-}$, each chloride has charge -1, hence nickel is $+2$ with configuration $3d^8$. Chloride is a weak-field ligand, and this tetrahedral sp^3 complex retains two unpaired d electrons. These unpaired electrons cause paramagnetism.

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

Quick Tip to Solve: Find the nickel oxidation state first: neutral CO gives Ni(0), while four chloride ligands give Ni(II).

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

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

Solution:

Concept:

- A coordinate bond can involve ligand-to-metal donation and metal-to-ligand back donation.
- CO can act as both a sigma donor and a pi acceptor, whereas ammonia principally donates its nitrogen lone pair.

Step 1: Identify donation by CO CO donates a lone pair on carbon into a vacant metal orbital, forming a metal-carbon sigma bond. Like ammonia, it can therefore supply an electron pair to the metal ion.

Step 2: Explain the additional back bonding CO also has vacant antibonding π^* orbitals that accept electron density from filled metal d orbitals. This creates metal-to-CO pi back bonding. Sigma donation and pi back donation reinforce each other through a synergic effect, strengthening the metal-carbon bond. Ammonia lacks comparable pi-acceptor bonding and principally forms a sigma coordinate bond.

Step 3: Conclusion CO is a stronger complexing agent because synergic sigma donation and pi back bonding strengthen its metal-ligand bond; ammonia principally provides sigma donation.

Quick Tip to Solve: For CO versus ammonia, name both directions of electron flow: CO to metal donation and metal to CO back donation.

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

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

Solution:

Concept:

- Optical activity requires chirality: a complex and its mirror image must be non-superimposable.
- A plane of symmetry makes a coordination complex achiral; en denotes the bidentate ligand ethane-1,2-diamine.

Step 1: Identify the trans arrangement In octahedral $\text{trans-}[\text{Co(en)}_2\text{Cl}_2]^+$, the two chloride ligands occupy opposite positions. The two en ligands occupy the remaining four coordination sites.

Step 2: Check the symmetry The trans arrangement has a plane of symmetry through cobalt and the four nitrogen donor sites, which interchanges the two identical chloride ligands. Reflection therefore gives a superimposable image. The complex does not form a pair of optical enantiomers.

Step 3: Conclusion The trans isomer is optically inactive because it possesses a plane of symmetry and is achiral.

Quick Tip to Solve: For this octahedral trans complex, put the two Cl ligands opposite each other and check the plane containing the four N donors.

31(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 produces three lower-energy t_{2g} orbitals and two higher-energy e_g orbitals. Δ_o is the splitting energy and P is the pairing energy.
- Strong-field ligands favour pairing when $\Delta_o > P$; weak-field ligands favour high spin when $\Delta_o < P$.

Step 1: Find the configuration of the metal ion For iron, $Z = 26$ and the neutral configuration is $[Ar]3d^6 4s^2$. Formation of Fe^{3+} removes the two $4s$ electrons first and then one $3d$ electron, giving $[Ar]3d^5$. Thus five electrons must be distributed among the split d orbitals.

Step 2: Strong-field ligand: low spin When $\Delta_o > P$, electrons pair in the lower t_{2g} set before entering e_g. The distribution is $t_{2g}^5 e_g^0$. The three t_{2g} orbitals contain two pairs and one single electron: $(\uparrow\downarrow)(\uparrow\downarrow)(\uparrow)$. Hence there is one unpaired electron.

Step 3: Weak-field ligand: high spin When $\Delta_o < P$, occupying the higher orbitals costs less energy than pairing. Hund's rule gives $t_{2g}^3 e_g^2$, with one electron in each of the five d orbitals. Therefore all five electrons remain unpaired.

Step 4: Conclusion (I) Strong-field ligand: $\boxed{1}$ unpaired electron. (II) Weak-field ligand: $\boxed{5}$ unpaired electrons.

Quick Tip to Solve: Read the ionic charge first: Fe3+ is d5. For d5, low spin leaves one single electron and high spin leaves five.

OR

31(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:

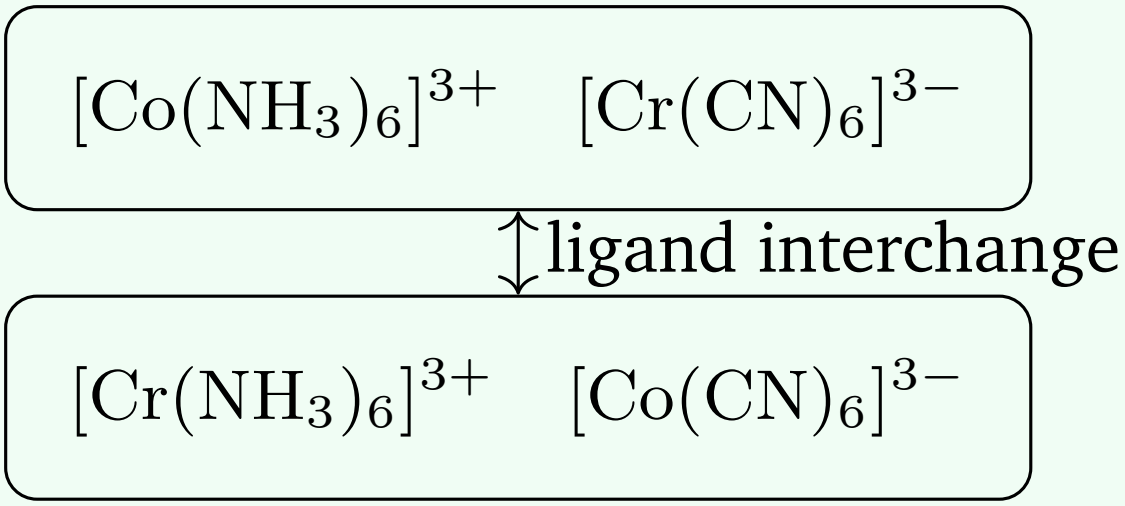
- Coordination isomerism arises when both the cation and anion are complex ions and ligands interchange between their metal centres.
- An isomer must preserve the total metal and ligand inventory while changing their distribution.

Step 1: Identify the complex ions The compound contains $[Co(NH_3)_6]^{3+}$ and $[Cr(CN)_6]^{3-}$. Both ions have their own coordination spheres; this permits coordination isomerism.

Step 2: Interchange the ligand sets Exchange the six ammonia ligands and six cyanide ligands

Quick Tip to Solve: Exchange the ligands between the two metal centres; retain six NH3, six CN and one atom of each metal overall.

between cobalt and chromium. The resulting compound is $[Cr(NH_3)_6][Co(CN)_6]$. Both metal ions remain in the +3 oxidation state; the ammonia complex is the cation and the cyanide complex is the anion. The drawing shows the two coordination formulations.



Coordination isomers: exchange of ligand sets between metal centres

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

Quick Tip to Solve: Exchange the ligands between the two metal centres; retain six NH3, six CN and one atom of each metal overall.

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

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

Solution:

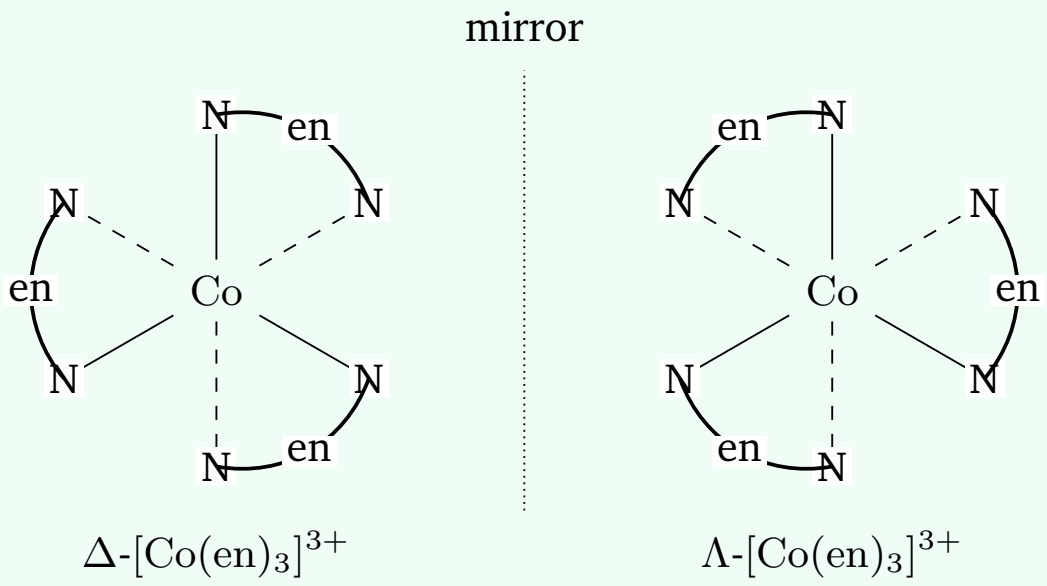
Concept:

- Optical isomers are non-superimposable mirror images, called enantiomers.
- Three bidentate en ligands chelate an octahedral metal centre; opposite helicities are designated Δ and Λ.

Step 1: Identify the arrangement In $[Co(en)_3]^{3+}$, each en ligand binds through two nitrogen atoms. Three chelate rings wind around cobalt in a chiral arrangement. There is no plane of symmetry making this arrangement identical to its reflection.

Step 2: Draw the corresponding mirror images The two forms are Δ-$[Co(en)_3]^{3+}$ and Λ-$[Co(en)_3]^{3+}$. The diagram is an octahedral projection along a threefold axis. Each curved en connection joins the two N donors of one ligand; solid and dashed Co–N lines distinguish the two sets of three donor sites. Reflection reverses the winding of the three chelate rings, giving non-superimposable mirror images.

Quick Tip to Solve: Join adjacent N donor sites into three en chelate rings; reflect all three connections together to obtain the opposite optical isomer.



Mirror-image octahedral arrangements of the three en chelate rings

Step 3: Conclusion The complex exhibits optical isomerism: the corresponding isomers are the Δ and Λ enantiomers shown in the diagram.

Quick Tip to Solve: Join adjacent N donor sites into three en chelate rings; reflect all three connections together to obtain the opposite optical isomer.

31(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:

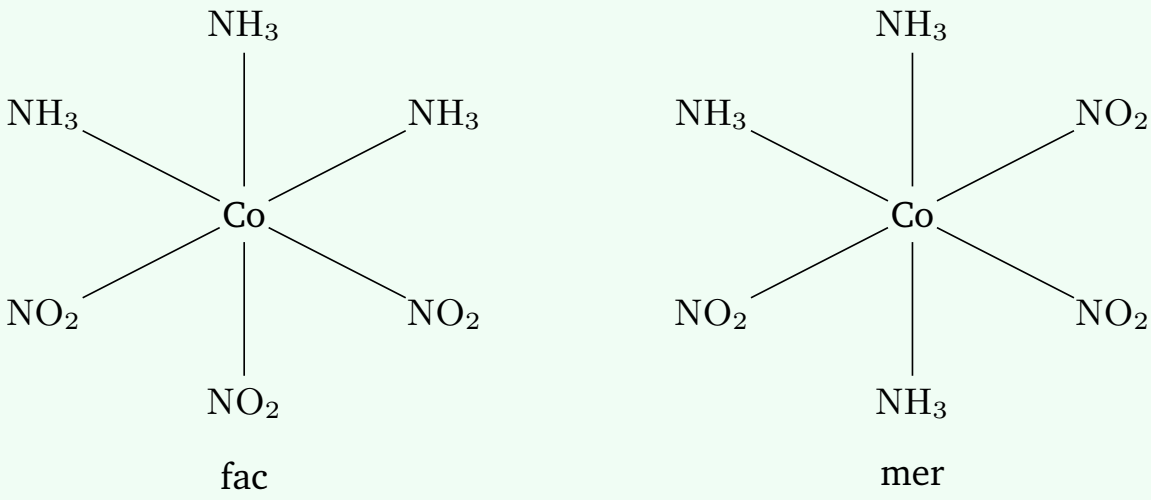
Concept:

- An octahedral complex of the form MA_3B_3 exhibits geometrical isomerism: facial (fac) and meridional (mer).
- In the fac isomer, the three identical ligands occupy one triangular face; in the mer isomer, they lie in a plane passing through the metal centre.

Step 1: Identify the coordination geometry The six monodentate ligands, three NH_3 and three NO_2^-, surround cobalt in an octahedral arrangement. Keeping the identity and bonding of the ligands fixed, their positions can differ.

Step 2: Arrange the identical ligands In fac, every pair of NH_3 ligands is cis ($90°$); the same holds for the three nitro ligands. In mer, two NH_3 ligands form a trans pair ($180°$), and the third is cis to both. The drawings show all six sites, with the vertical and the two opposite diagonal pairs representing the three trans axes.

Quick Tip to Solve: For an octahedral MA_3B_3 complex, look for a trans pair of identical ligands: present means mer; absent means fac.



Facial and meridional isomers; opposite sites on each line are trans.

Step 3: Conclusion The complex exhibits geometrical (fac–mer) isomerism, with the two corresponding isomers drawn below.

Quick Tip to Solve: For an octahedral MA_3B_3 complex, look for a trans pair of identical ligands: present means mer; absent means fac.

31(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:

- Crystal-field splitting Δ_o is the energy gap between the lower t_{2g} and upper e_g orbitals in an octahedral complex.
- Pairing energy P is the energy needed to pair two electrons in one orbital. The relative sizes of Δ_o and P determine whether electrons pair or occupy higher orbitals.

Step 1: Weak-field ligands and high spin Weak-field ligands such as F^-, Cl^- and H_2O produce comparatively small splitting. When $\Delta_o < P$, it costs less energy to occupy an upper e_g orbital than to pair in t_{2g}. Electrons therefore retain as many unpaired spins as possible, giving a high-spin complex. For octahedral d^5, the distribution is $t_{2g}^3 e_g^2$, with five unpaired electrons.

Step 2: Strong-field ligands and low spin Strong-field ligands such as CN^- and CO produce comparatively large splitting. When $\Delta_o > P$, electrons pair in the lower t_{2g} orbitals before entering e_g. This gives fewer unpaired electrons and a low-spin complex; octahedral d^5 then has $t_{2g}^5 e_g^0$, with one unpaired electron. The metal ion and its oxidation state also affect splitting. The high-spin/low-spin distinction is relevant especially for octahedral d^4 to d^7 configurations.

Step 3: Conclusion Weak-field ligands favour high spin when $\Delta_o < P$; strong-field ligands favour low spin when $\Delta_o > P$.

Quick Tip to Solve: Compare the splitting energy with pairing energy before deciding spin; strong field does not mean every electron is necessarily paired.

32(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, the integrated rate law is $k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$, where $[A]_0$ and $[A]_t$ are the reactant concentrations initially and after time t.
- The rate constant of a first-order reaction has dimensions of inverse time. Concentrations must use the same units so their ratio is dimensionless.

Step 1: Identify the concentration ratio At 318 K, the given 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}. Thus

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

The final concentration is the amount remaining, so it is used directly in the denominator, rather than the concentration consumed.

Step 2: Substitute in the first-order law The reaction is specified as first order, so using the supplied value $\log 6 = 0.778$,

$$\begin{aligned} k &= \frac{2.303}{60} \log 6 \\ &= \frac{2.303 \times 0.778}{60} \\ &= \frac{1.791734}{60} = 0.0298622 \text{ min}^{-1}. \end{aligned}$$

The product coefficients do not enter this integrated law for the decay of the measured reactant.

Step 3: Express and check the unit As the time was inserted in minutes, the calculated unit is min^{-1}. In seconds,

$$k = \frac{0.0298622}{60} = 4.977 \times 10^{-4} \text{ s}^{-1}.$$

Both values represent the same rate constant at the stated temperature. A positive value is expected because the reactant concentration falls with time; the initial-to-final ratio exceeds unity and its logarithm is positive.

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

Quick Tip to Solve: Cancel the common power of ten before taking the logarithm, and retain the time unit used in the substitution.

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

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

Solution:

Concept:

- The order of a reaction is the sum of the exponents of reactant concentrations in its experimentally determined rate law.
- A balanced overall equation expresses conservation of atoms and stoichiometric proportions; it does not specify the reaction mechanism.

Step 1: Separate stoichiometry from rate For an experimentally observed rate law $r = k[A]^m[B]^n$, the overall order is $m + n$. The powers m and n need not equal the coefficients of A and B in the balanced overall reaction.

Step 2: Explain the mechanistic reason An overall reaction can proceed through several elementary steps, and its rate depends on the mechanism and the rate-determining step. These details are absent from the balanced equation. Stoichiometric coefficients can be used as concentration powers for an elementary mass-action step, but cannot generally be used for an overall reaction.

Step 3: Conclusion The order must be determined experimentally from the rate law; the balanced chemical equation alone is insufficient.

Quick Tip to Solve: Use coefficients to balance matter; use experimentally measured concentration exponents to calculate reaction order.

32(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 an elementary bimolecular reaction $A + B \rightarrow$ products, the rate law is $r = k[A][B]$.
- If one reactant is present in large excess, its concentration remains practically constant during the reaction.

Step 1: Consider a large excess of B When $[B]_0 \gg [A]_0$, consumption of B is very small compared with its initial amount. Thus $[B] \simeq [B]_0$, even while the concentration of A changes appreciably.

Step 2: Absorb the constant concentration into the rate constant The rate becomes $r = k[B]_0[A] = k_{\text{obs}}[A]$, where $k_{\text{obs}} = k[B]_0$. The measured rate therefore varies only with the first power of the concentration of A. The underlying elementary event still involves two reactant particles.

Step 3: Conclusion A bimolecular reaction shows pseudo-first-order kinetics when one reactant is in sufficiently large excess that its concentration is practically constant.

Quick Tip to Solve: Look for a reactant in large excess; include its nearly constant concentration in the observed rate constant.

OR

32(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 the activation energy and R is the gas constant.
- At unchanged reactant concentrations, the ratio of reaction rates equals the ratio of rate constants.

Step 1: Identify both temperatures and the rate ratio 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, $k_2/k_1 = 2$. Both temperatures must be used on the absolute scale; the temperature difference alone cannot be substituted for either temperature.

Step 2: Apply the two-temperature Arrhenius relation Taking common logarithms and subtracting the Arrhenius equations at the two temperatures gives

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

Hence

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

The supplied values are $2.303R = 19.15\,\text{J K}^{-1}\text{mol}^{-1}$ and $\log 2 = 0.3$.

Step 3: Substitute and convert the energy unit

$$\begin{aligned} E_a &= \frac{19.15 \times 0.3 \times 298 \times 308}{10}\,\text{J mol}^{-1} \\ &= 52730.508\,\text{J mol}^{-1} \\ &\simeq 52.73\,\text{kJ mol}^{-1}. \end{aligned}$$

The sign is positive because both $\log(k_2/k_1)$ and $1/T_1 - 1/T_2$ are positive. The energy unit follows from multiplying R by a temperature.

Step 4: Conclusion The activation energy is $\boxed{E_a \simeq 52.73\,\text{kJ mol}^{-1}}$, using the supplied value $\log 2 = 0.3$.

Quick Tip to Solve: For a rate increase, pair the positive logarithm with $1/T_1 - 1/T_2$; use 298 K and 308 K, then divide joules by 1000.

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

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

the proposed mechanism is as given below:

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

- The slow elementary step controls the rate of a multistep reaction.
- Reaction order is the sum of the powers in the rate law; molecularity counts reacting particles in an elementary step.

Step 1: Write the rate law from the slow step The slow step is $H_2O_2 + I^- \rightarrow H_2O + IO^-$. It involves one hydrogen peroxide molecule and one iodide ion, so

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

The intermediate IO^- belongs to the fast step and does not appear in this rate law. Iodide is regenerated in the second step and acts as a catalyst.

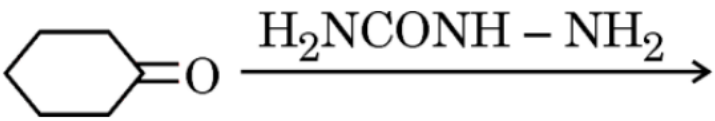
Step 2: Determine order and state the relevant molecularity The rate is first order in H_2O_2 and first order in I^-, so the overall order is $1 + 1 = 2$. The rate-determining elementary step contains two reacting particles and is bimolecular: molecularity $= 2$. Each given elementary step is bimolecular. Strictly, molecularity is defined for elementary steps, not for the combined multistep equation; the value requested here refers to the slow step.

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

Quick Tip to Solve: Use the slow elementary equation for the rate law; count its particles for molecularity and add concentration exponents for order.

33(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:

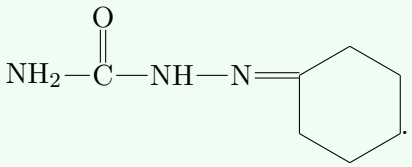
- Ketones condense with semicarbazide, $H_2N - NH - C(= O) - NH_2$, to give semicarbazones.

Quick Tip to Solve: Replace only the ketone oxygen by $N - NH - CO - NH_2$; retain both the ring and the semicarbazide amide carbonyl.

- The terminal amino group attached to NH reacts with the ketone carbonyl; the amide carbonyl remains intact.

Step 1: Identify the reacting amino group The terminal $-NH_2$ of $H_2N-NH-CO-NH_2$ attacks cyclohexanone. The amide amino group is less nucleophilic because its lone pair is delocalised into its carbonyl group.

Step 2: Write the condensation product structure Loss of water replaces the ring carbonyl $C=O$ by $C=N-NH-C(=O)-NH_2$, leaving the six-membered carbon ring intact. The main product structure is



One molecule of water is formed in the condensation.

Step 3: Conclusion The main product is cyclohexanone semicarbazone, with the ring carbon bearing $=N-NH-C(=O)-NH_2$.

Quick Tip to Solve: Replace only the ketone oxygen by $N-NH-CO-NH_2$; retain both the ring and the semicarbazide amide carbonyl.

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

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

Solution:

Concept:

- Dialkylcadmium reagents react with acid chlorides to form ketones.
- Each methyl group of dimethylcadmium replaces the chlorine attached to the acyl carbon.

Step 1: Identify the product of methyl transfer Acetyl chloride has the acyl group CH_3CO-. Transfer of a methyl group from $(CH_3)_2Cd$ gives $CH_3-C(=O)-CH_3$, a ketone with three carbon atoms.

Step 2: Balance the reaction for both methyl groups Both methyl groups react with two molecules of acetyl chloride:

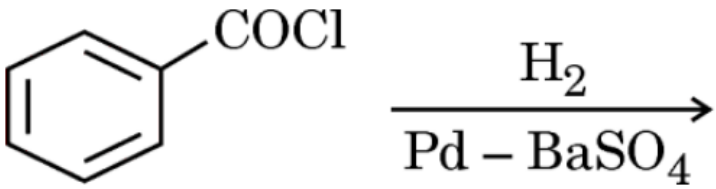
$$(CH_3)_2Cd + 2CH_3COCl \longrightarrow 2CH_3C(=O)CH_3 + CdCl_2.$$

The organic product is propanone (acetone). Organocadmium reagents permit ketone formation without the further addition characteristic of more reactive organometallic reagents.

Step 3: Conclusion The main organic product is $\boxed{CH_3-C(=O)-CH_3}$, propanone; two molecules form per molecule of dimethylcadmium.

Quick Tip to Solve: Join the methyl group from cadmium to the acetyl carbonyl carbon, and use both methyl groups to balance the equation.

33(a)(i)(III). Complete the following reaction by writing the structure of the main product: [1 mark]



Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde using hydrogen and poisoned palladium catalyst.
- $Pd-BaSO_4$ controls catalytic activity so that reduction stops at the aldehyde stage.

Step 1: Identify the functional group Benzoyl chloride, C_6H_5COCl, is an aromatic acyl chloride. The benzene ring is retained; the carbonyl carbon attached to the ring remains in the product.

Step 2: Apply the selective reduction The chlorine attached to the carbonyl carbon is replaced by hydrogen. The reaction is

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

The poisoned catalyst prevents further reduction of the aldehyde to benzyl alcohol.

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

Quick Tip to Solve: For hydrogen over poisoned palladium, replace the acyl chloride group $-COCl$ by $-CHO$.

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

Solution:

Concept:

- Carboxylic acids react with aqueous sodium hydrogencarbonate to liberate carbon dioxide.
- Esters do not show this immediate acid-carbonate reaction.

Step 1: Add sodium hydrogencarbonate Take separate small samples of ethyl benzoate and benzoic acid, and add aqueous $NaHCO_3$ to each. Perform the test at room temperature; heating or hydrolysing the ester beforehand is unnecessary.

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

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

Ethyl benzoate, $C_6H_5COOC_2H_5$, gives no such effervescence because it has no free carboxylic acid proton.

Step 3: Conclusion Brisk effervescence with aqueous $NaHCO_3$ identifies benzoic acid; ethyl benzoate

Quick Tip to Solve: Test the free $-COOH$ group with bicarbonate: visible carbon dioxide separates the acid from its ester.

gives no effervescence.

Quick Tip to Solve: Test the free $-COOH$ group with bicarbonate: visible carbon dioxide separates the acid from its ester.

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

Solution:

Concept:

- Tollens' reagent, alkaline $[Ag(NH_3)_2]^+$, oxidises ordinary aldehydes to carboxylate ions.
- The silver complex is reduced to metallic silver; ordinary ketones do not give this test.

Step 1: Treat both samples with Tollens reagent Add freshly prepared Tollens' reagent to separate samples of propanal and propanone, then warm gently in a water bath. Propanal contains the $-CHO$ group, whereas propanone contains an internal ketone carbonyl.

Step 2: Record the silver-mirror observation Propanal gives a silver mirror, or a grey deposit of silver, while propanone gives no silver mirror. The aldehyde reaction is

$$\begin{aligned} &CH_3CH_2CHO + 2\,[Ag(NH_3)_2]^+ + 3\,OH^- \\ &\longrightarrow CH_3CH_2COO^- + 2\,Ag + 4\,NH_3 + 2\,H_2O \end{aligned}$$

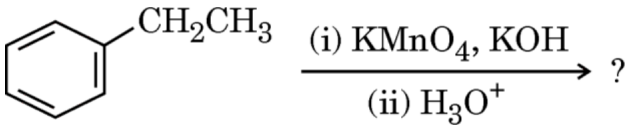
Propanone is not oxidised by this mild reagent.

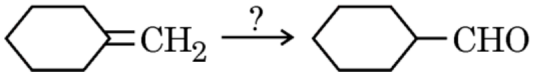
Step 3: Conclusion Propanal gives a silver mirror with Tollens' reagent; propanone does not.

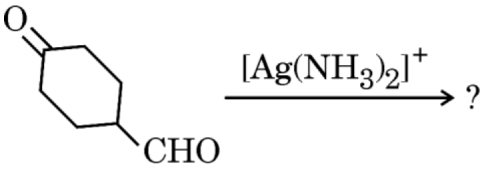
Quick Tip to Solve: Choose Tollens' reagent to distinguish these two carbonyl compounds: an aldehyde gives silver, an ordinary ketone does not.

OR

33(b)(i). Complete each synthesis by giving missing starting material, reagent or products: [3 marks]

(I) 

(II) 

(III) 

Solution:

Concept:

- Hot alkaline $KMnO_4$ oxidises an alkylbenzene side chain containing a benzylic hydrogen to carboxylate; acidification gives the acid.
- Hydroboration-oxidation gives anti-Markovnikov hydration of an alkene; PCC oxidises a primary alcohol to an aldehyde.
- Tollens' reagent selectively oxidises an aldehyde group while leaving an ordinary ketone group unchanged.

Step 1: (I): Oxidise the ethylbenzene side chain The printed starting material is ethylbenzene, $C_6H_5CH_2CH_3$. Its benzylic carbon has hydrogen atoms, so vigorous oxidation gives potassium benzoate; subsequent acidification gives benzoic acid.

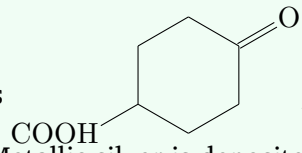
$$C_6H_5CH_2CH_3 \xrightarrow[\text{heat}]{KMnO_4,\,KOH} C_6H_5COOK \xrightarrow{H_3O^+} C_6H_5COOH.$$

The aromatic ring is retained, and the two-carbon side chain is shortened to a carboxyl group.

Step 2: (II): Convert the exocyclic methylene group into an aldehyde First carry out hydroboration with BH_3 in THF, followed by alkaline hydrogen peroxide, H_2O_2/OH^-. Boron attaches to the less substituted terminal carbon, so oxidation gives cyclohexylmethanol, $C_6H_{11}CH_2OH$. Oxidise this primary alcohol using PCC in dry dichloromethane to obtain cyclohexanecarbaldehyde, $C_6H_{11}CHO$. Thus the missing reagent sequence is (1) BH_3/THF, (2) H_2O_2/OH^-, (3) PCC. The original six-membered ring is retained.

Step 3: (III): Oxidise only the aldehyde group The starting compound contains a cyclohexanone carbonyl and a formyl group on the opposite ring carbon. Tollens' reagent changes $-CHO$ into $-COO-$ in its alkaline medium, leaving the ketone unchanged. The immediate product is 4-oxocyclohexane-1-carboxylate; on acidification it is 4-oxocyclohexane-1-carboxylic acid. The acid

Quick Tip to Solve: Check the functional group that each reagent attacks: alkaline permanganate oxidises the side chain, hydroboration targets the alkene, and Tollens reagent targets the aldehyde.

structure is  ; replace its COOH by COO^- for the product in the alkaline reagent solution. Metallic silver is deposited.

Step 4: Conclusion (I) Benzoic acid, C_6H_5COOH. (II) BH_3/THF, then H_2O_2/OH^-, then PCC in dry dichloromethane. (III) 4-Oxocyclohexane-1-carboxylate, with the ring ketone unchanged; acidification gives the corresponding carboxylic acid.

Quick Tip to Solve: Check the functional group that each reagent attacks: alkaline permanganate oxidises the side chain, hydroboration targets the alkene, and Tollens reagent targets the aldehyde.

33(b)(ii). Carry out the following conversions:

(I) Benzaldehyde to Benzophenone

(II) Benzaldehyde to 3-phenyl propanol [2 marks]

Solution:

Concept:

- Grignard addition builds a carbon-carbon bond; aldol condensation extends a carbonyl chain, and complete reduction gives an alcohol.
- A secondary alcohol is oxidised to a ketone; catalytic hydrogenation of an unsaturated aldehyde reduces both its alkene and carbonyl groups.

Step 1: (I): Build benzophenone through a secondary alcohol Add phenylmagnesium bromide to benzaldehyde in dry ether, then hydrolyse with dilute acid. This forms diphenylmethanol, which is oxidised with acidified dichromate to benzophenone:

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

$$(C_6H_5)_2CHOMgBr \xrightarrow{H_3O^+} (C_6H_5)_2CHOH \xrightarrow{K_2Cr_2O_7/H^+} (C_6H_5)_2CO.$$

The Grignard reagent supplies the second phenyl group, and oxidation changes the secondary alcohol into the ketone.

Step 2: (II): Extend the chain and reduce to 3-phenylpropan-1-ol Carry out crossed aldol condensation with ethanal in dilute alkali, followed by heating. Benzaldehyde has no alpha hydrogen and acts as the electrophile; ethanal supplies the two-carbon fragment.

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

The product is cinnamaldehyde. Complete hydrogenation with excess H_2 over nickel reduces both the carbon-carbon double bond and the aldehyde group:

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

Quick Tip to Solve: Count carbons before choosing reagents: phenylmagnesium bromide adds a phenyl group, while ethanal adds two chain carbons in the crossed aldol condensation.

The product contains three chain carbons and a terminal hydroxyl group, as required.

Step 3: Conclusion (I) Benzaldehyde $\xrightarrow{C_6H_5MgBr,\ \text{then}\ H_3O^+}$ diphenylmethanol $\xrightarrow{K_2Cr_2O_7/H^+}$ benzophenone. (II) Benzaldehyde $\xrightarrow{CH_3CHO,\ \text{dil. NaOH, heat}}$ cinnamaldehyde $\xrightarrow{2\,H_2/Ni}$ 3-phenylpropan-1-ol.

Quick Tip to Solve: Count carbons before choosing reagents: phenylmagnesium bromide adds a phenyl group, while ethanal adds two chain carbons in the crossed aldol condensation.