

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-3-3

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 **35** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** Sections – **A, B, C, D** and **E**.
- (iii) In **Section A** – Questions no. **1** to **18** are multiple choice (MCQ) type questions, carrying **1** mark each.
- (iv) In **Section B** – Questions no. **19** to **25** very short answer (VSA) type questions, carrying **2** marks each.
- (v) In **Section C** – Questions no. **26** to **30** are short answer (SA) type questions, carrying **3** marks each.
- (vi) In **Section D** – Questions no. **31** and **32** are case-based questions carrying **4** marks each.
- (vii) In **Section E** – Questions no. **33** to **35** are long answer (LA) type questions carrying **5** marks each.
- (viii) There is no overall choice. However, an internal choice has been provided in 2 questions in Section B, 2 questions in Section C, 2 questions in Section D and 2 questions in Section E.
- (ix) Use of calculators is not allowed.

Section A (18 marks)

Questions no. 1 to 18 are Multiple Choice (MCQ) type Questions, carrying 1 mark each.

1. Kohlrausch gave the following relation for strong electrolyte: $\Lambda = \Lambda_0 - A\sqrt{C}$. Which of the following equality holds true? [1 mark]

- (A) $\Lambda = \Lambda_0$ as $C \rightarrow \sqrt{A}$
- (B) $\Lambda = \Lambda_0$ as $C \rightarrow 0$
- (C) $\Lambda = \Lambda_0$ as $C \rightarrow \infty$
- (D) $\Lambda = \Lambda_0$ as $C \rightarrow 1$

Correct Answer: (B) $\Lambda = \Lambda_0$ as $C \rightarrow 0$

Solution:

Concept:

- Molar conductivity Λ is related to concentration C by $\Lambda = \Lambda_0 - A\sqrt{C}$ for a strong electrolyte in dilute solution.
- Λ_0 is the limiting molar conductivity at infinite dilution; A is a positive constant for the given electrolyte, solvent and temperature.

Step 1: Apply the limiting condition For Λ to approach Λ_0 , the correction term $A\sqrt{C}$ must approach zero. Since $A \neq 0$, this requires $\sqrt{C} \rightarrow 0$, and hence $C \rightarrow 0$. This is infinite dilution, when interionic effects become negligible.

Step 2: Check the other options At $C \rightarrow 1$, the correction is A , not zero. At $C \rightarrow \sqrt{A}$, it is also nonzero for positive A . Taking $C \rightarrow \infty$ cannot make the correction vanish; moreover, the dilute-solution relation should not be extrapolated to such high concentrations.

Step 3: Conclusion $\Lambda \rightarrow \Lambda_0$ as $C \rightarrow 0$. Hence, the correct option is (B).

Quick Tip to Solve: Set the concentration-dependent correction term to zero to identify the infinite-dilution limit.

2. Which of the following belongs to the class of alkyl halides? [1 mark]

- (A) $\text{CH}_2 = \text{CH} - \text{Cl}$
- (B) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$
- (C) $\text{CH}_2 = \text{CH} - \text{CHCl} - \text{CH}_3$
- (D) $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{Cl}$

Correct Answer: (B) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$

Solution:

Concept:

- In a simple alkyl halide the halogen is bonded to a saturated sp^3 -hybridised carbon. Classification also distinguishes vinylic and unsaturation-adjacent halides.

Quick Tip to Solve: Locate the halogen-bearing carbon first, then check whether it is on or immediately beside a multiple bond.

- A vinylic halogen is bonded directly to a double-bond carbon; an allylic halogen is bonded to the saturated carbon immediately beside a double bond.

Step 1: Locate the carbon bonded to chlorine In option (B), $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$, chlorine is attached to the terminal saturated CH_2 carbon. This carbon is not directly adjacent to the double bond, so the compound belongs to the simple alkyl-halide class intended here.

Step 2: Distinguish the other structures Option (A), $\text{CH}_2 = \text{CH} - \text{Cl}$, is a vinylic halide because chlorine is on an sp^2 carbon. Option (C), $\text{CH}_2 = \text{CH} - \text{CHCl} - \text{CH}_3$, is allylic because its chlorine-bearing carbon lies immediately beside the double bond. Option (D), $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{Cl}$, is propargylic because its chlorine-bearing carbon is beside a triple bond; it is the analogous special unsaturation-adjacent class.

Step 3: Conclusion $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{Cl}$ is the simple alkyl halide. Hence, the correct option is (B).

Quick Tip to Solve: Locate the halogen-bearing carbon first, then check whether it is on or immediately beside a multiple bond.

3. An azeotropic mixture of two liquids has a boiling point higher than either of the two liquids when it: [1 mark]

- (A) shows large negative deviation from Raoult's law.
- (B) shows no deviation from Raoult's law.
- (C) shows large positive deviation from Raoult's law.
- (D) obeys Raoult's law.

Correct Answer: (A) shows large negative deviation from Raoult's law.

Solution:

Concept:

- An azeotrope boils at a constant temperature with the same composition in liquid and vapour phases.
- Large negative deviation from Raoult's law can form a maximum-boiling azeotrope; large positive deviation can form a minimum-boiling azeotrope.

Step 1: Relate attraction to vapour pressure For negative deviation, attractions between unlike molecules are stronger than the corresponding attractions in the pure liquids. Escape of molecules into the vapour becomes harder, so the total vapour pressure falls below the ideal Raoult-law value.

Step 2: Connect pressure and boiling point A liquid boils when its vapour pressure equals the external pressure. A mixture with a sufficiently low vapour pressure must be heated more to reach that pressure, producing a maximum-boiling azeotrope with a boiling point above those of both components. Large positive deviation gives the opposite behaviour. Options (B) and (D) describe ideal behaviour, which does not produce the stated azeotrope.

Step 3: Conclusion A large negative deviation produces the stated maximum-boiling azeotrope. Hence, the correct option is (A).

Quick Tip to Solve: Remember the chain: stronger unlike attractions, lower vapour pressure, higher boiling point.

4. For the conversion of propene into 1-propanol, which of the following reagents and conditions should be used? [1 mark]

- (A) Conc. H_2SO_4 ; H_2O and heat
- (B) B_2H_6 ; $\text{H}_2\text{O}_2/\text{OH}^-$
- (C) Dilute H_2SO_4
- (D) $\text{H}_2\text{O}/\text{H}^+$

Correct Answer: (B) B_2H_6 ; $\text{H}_2\text{O}_2/\text{OH}^-$

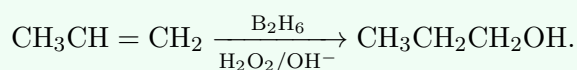
Solution:

Concept:

- Hydroboration followed by oxidation converts an alkene into an alcohol with anti-Markovnikov orientation.
- Boron attaches to the less substituted carbon during hydroboration; alkaline hydrogen peroxide replaces the carbon-boron bond by a carbon-oxygen bond.

Step 1: Choose the required orientation Propene is $\text{CH}_3\text{CH}=\text{CH}_2$. To obtain 1-propanol, the hydroxyl group must appear at the terminal carbon, giving $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$. This requires anti-Markovnikov hydration, which is achieved using diborane followed by $\text{H}_2\text{O}_2/\text{OH}^-$.

Step 2: Compare the acid-catalysed routes The conversion can be summarised as



Concentrated sulphuric acid followed by water and heat, dilute sulphuric acid, and $\text{H}_2\text{O}/\text{H}^+$ all give Markovnikov hydration under the stated conditions. Their principal alcohol product is 2-propanol, not the required 1-propanol.

Step 3: Conclusion Use B_2H_6 ; $\text{H}_2\text{O}_2/\text{OH}^-$. Hence, the correct option is (B).

Quick Tip to Solve: For a terminal alkene, use hydroboration-oxidation when the required alcohol has a terminal OH group.

5. Which of the following reagents would one choose to transform CH_3COCl into acetone? [1 mark]

- (A) $(\text{CH}_3)_2\text{Cd}$
- (B) CH_3MgBr
- (C) CH_3Cl
- (D) $(\text{CH}_3\text{O})_2\text{Mg}$

Correct Answer: (A) $(\text{CH}_3)_2\text{Cd}$

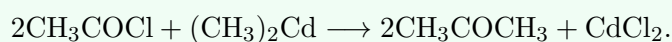
Solution:

Concept:

- Acid chlorides react with dialkylcadmium reagents to form ketones by replacement of chloride with an alkyl group.
- Dialkylcadmium is less reactive than a Grignard reagent and does not ordinarily add further to the ketone formed under these preparation conditions.

Step 1: Identify the group to be introduced Acetyl chloride is CH_3COCl , whereas acetone is CH_3COCH_3 . Therefore, chloride must be replaced with a methyl group while retaining the carbonyl group. Dimethylcadmium supplies the required methyl group.

Step 2: Write the reaction and reject the alternatives The balanced conversion is



Methylmagnesium bromide is too reactive for selective ketone preparation: it adds further to the initially formed acetone and gives a tertiary alcohol after hydrolysis. Methyl chloride does not supply a nucleophilic methyl group. Magnesium methoxide supplies methoxide rather than the methyl group needed to form acetone.

Step 3: Conclusion Choose $(\text{CH}_3)_2\text{Cd}$, dimethylcadmium. Hence, the correct option is (A).

Quick Tip to Solve: To stop an acid chloride at a ketone, choose dialkylcadmium rather than the more reactive Grignard reagent.

6. The reaction of ammonia with a large excess of methyl chloride will yield mainly: [1 mark]

- (A) methylamine
- (B) dimethylamine
- (C) tetramethylammonium chloride
- (D) trimethylamine

Correct Answer: (C) tetramethylammonium chloride

Solution:

Concept:

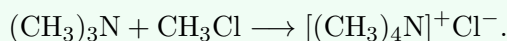
- Ammonia undergoes successive alkylation with an alkyl halide; its alkylamine products can themselves react further.

Quick Tip to Solve: Excess alkyl halide drives alkylation to a quaternary salt; excess ammonia instead favours a primary amine.

- With a large excess of methyl chloride, alkylation proceeds through primary, secondary and tertiary amines to a quaternary ammonium salt.

Step 1: Follow successive methylation Ammonia first forms methylamine, CH_3NH_2 . Further methylation gives dimethylamine, $(\text{CH}_3)_2\text{NH}$, followed by trimethylamine, $(\text{CH}_3)_3\text{N}$. These intermediates retain a nitrogen lone pair and can therefore undergo further reaction with methyl chloride.

Step 2: Identify the terminal product Trimethylamine reacts with another molecule of methyl chloride:



The large excess of methyl chloride favours this exhaustive methylation. Methylamine, dimethylamine and trimethylamine are intermediate products, so options (A), (B) and (D) do not represent the main final product under these conditions. The quaternary nitrogen has no lone pair for another such alkylation.

Step 3: Conclusion The main product is $[(\text{CH}_3)_4\text{N}]^+\text{Cl}^-$, tetramethylammonium chloride. Hence, the correct option is (C).

Quick Tip to Solve: Excess alkyl halide drives alkylation to a quaternary salt; excess ammonia instead favours a primary amine.

7. In the ring structure of glucose, the anomeric carbon is:

[1 mark]

- (A) C-2
- (B) C-3
- (C) C-4
- (D) C-1

Correct Answer: (D) C-1

Solution:

Concept:

- The anomeric carbon of a cyclic sugar is the carbon that was the carbonyl carbon in its open-chain form.
- Glucose is an aldose: its aldehyde carbon is C-1. Ring formation creates a hemiacetal and a new stereogenic centre at this carbon.

Step 1: Trace the aldehyde carbon during cyclisation In open-chain glucose the aldehyde group is at C-1. The hydroxyl group on C-5 reacts intramolecularly with this aldehyde group to form the six-membered glucopyranose ring. The original carbonyl carbon remains numbered C-1.

Step 2: Locate the new stereogenic centre After ring closure C-1 is bonded to the ring oxygen, a hydroxyl group, hydrogen and C-2. Two configurations at C-1 give the alpha and beta anomers, so C-1 is the anomeric carbon. C-2, C-3 and C-4 are already stereogenic carbons in the open chain; none is the carbonyl carbon that produces the anomeric centre.

Step 3: Conclusion The anomeric carbon in glucose is $\boxed{\text{C}-1}$. Hence, the correct option is (D).

Quick Tip to Solve: Trace the open-chain carbonyl carbon into the ring: it becomes the anomeric carbon, C-1 for glucose.

8. Deficiency of Vitamin B causes:

[1 mark]

- (A) rickets
- (B) muscular weakness
- (C) scurvy
- (D) beri-beri

Correct Answer: (D) beri-beri

Solution:

Concept:

- Vitamins are essential organic nutrients required in small amounts; their prolonged deficiency produces characteristic disorders.
- Vitamin B₁, or thiamine, belongs to the water-soluble vitamin B group. Its deficiency causes beri-beri.

Step 1: Identify the relevant vitamin The familiar deficiency disease associated with vitamin B in this question is beri-beri, specifically due to lack of thiamine, B₁. It affects normal nerve and muscle function.

Step 2: Distinguish the other deficiency diseases Rickets is associated with deficiency of vitamin D, while scurvy is caused by deficiency of vitamin C. Muscular weakness is not the specific named vitamin B deficiency disease sought here; it is commonly associated in the textbook deficiency table with vitamin E.

Step 3: Conclusion Deficiency of vitamin B₁ causes beri-beri. Hence, the correct option is (D).

Quick Tip to Solve: Link thiamine (vitamin B₁) directly with beri-beri; keep vitamin C–scurvy and vitamin D–rickets separate.

9. The cathode reaction during the charging of a lead storage battery leads to the:

[1 mark]

- (A) formation of PbSO₄
- (B) reduction of Pb²⁺ to Pb⁴⁺
- (C) formation of PbO₂ and Pb
- (D) deposition of Pb at the anode

Correct Answer: No exact cathode-only option; intended (C) lists overall charging products, PbO₂ and Pb.

Solution:

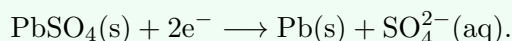
Concept:

- Reduction occurs at the cathode in both galvanic and electrolytic operation. Charging reverses the discharge reactions of a lead storage battery.
- During charging, PbSO₄ is reduced to Pb at the cathode, while PbO₂ is regenerated at the anode.

Step 1: Write the cathode half-reaction during charging The external supply drives reduction of

Quick Tip to Solve: For charging, first label the cathode as the reduction electrode: PbSO₄ gains electrons there to regenerate lead.

lead(II) sulphate at the negative plate:



Lead therefore forms at the cathode. The oxidation state decreases from +2 to 0, as required for reduction.

Step 2: Compare all the printed alternatives Formation of PbSO_4 describes discharge, not charging. A change from Pb^{2+} to Pb^{4+} is oxidation, not reduction. During charging, PbO_2 forms at the anode and Pb at the cathode, so option (C) gives the overall products rather than the cathode product alone. Lead is not deposited at the charging anode, ruling out (D).

Step 3: Conclusion The charging cathode forms Pb only. No printed option is strictly correct for the cathode reaction; option (C) is the intended overall-charging answer, with PbO_2 forming at the anode.

Quick Tip to Solve: For charging, first label the cathode as the reduction electrode: PbSO_4 gains electrons there to regenerate lead.

10. Which one of the following pairs will not form an ideal solution?

[1 mark]

- (A) Benzene and Toluene
- (B) Nitric acid and Water
- (C) Hexane and Heptane
- (D) Ethyl chloride and Ethyl bromide

Correct Answer: (B) Nitric acid and Water

Solution:

Concept:

- An ideal solution obeys Raoult's law over the entire composition range: $p_i = x_i p_i^\circ$, where x_i is the mole fraction of component i .
- For ideal mixing, unlike-molecule interactions resemble like-molecule interactions, and $\Delta H_{\text{mix}} = 0$, $\Delta V_{\text{mix}} = 0$.

Step 1: Identify the strongly interacting pair Nitric acid and water interact strongly on mixing, including hydration and ionisation of the acid. Their unlike-component interactions differ substantially from those in the pure liquids, so the mixture is non-ideal.

Step 2: Check the remaining pairs Benzene and toluene have similar aromatic structures and intermolecular interactions. Hexane and heptane are similar non-polar hydrocarbons. Ethyl chloride and ethyl bromide also have similar molecular structures. These are standard approximately ideal pairs, unlike nitric acid and water.

Step 3: Conclusion Nitric acid and water do not form an ideal solution. Hence, the correct option is (B).

Quick Tip to Solve: Look for unlike components that interact strongly: acid plus water is the exceptional pair among these structurally similar liquid pairs.

11. The half-life of a reaction is doubled when the initial concentration is doubled. The order of the reaction is: [1 mark]

- (A) 1
- (B) 2
- (C) 4
- (D) 0

Correct Answer: (D) 0

Solution:

Concept:

- The half-life $t_{1/2}$ is the time required for the reactant concentration to decrease from $[A]_0$ to $[A]_0/2$.
- For a zero-order reaction, $[A] = [A]_0 - kt$, so $t_{1/2} = [A]_0/(2k)$, where k is the rate constant.

Step 1: Use the observed proportionality The question states that doubling $[A]_0$ doubles $t_{1/2}$. Thus half-life is directly proportional to initial concentration. Substituting $[A] = [A]_0/2$ into the zero-order integrated equation gives

$$\frac{[A]_0}{2} = [A]_0 - kt_{1/2}, \quad t_{1/2} = \frac{[A]_0}{2k}.$$

Step 2: Exclude the other orders For first order, $t_{1/2} = \ln 2/k$, independent of $[A]_0$. For second order it varies as $[A]_0^{-1}$, so doubling concentration halves the half-life. For fourth order it varies as $[A]_0^{-3}$, so doubling concentration reduces it to one eighth. Only zero order gives the stated doubling.

Step 3: Conclusion The order of the reaction is 0. Hence, the correct option is (D).

Quick Tip to Solve: Remember the concentration dependence: zero-order half-life increases with $[A]_0$, first-order half-life stays constant, and second-order half-life decreases.

12. Which of the following ions has the maximum number of unpaired d-electrons?

[Atomic number: Fe = 26, V = 23, Ti = 22, Sc = 21]

[1 mark]

- (A) Fe^{3+}
- (B) V^{3+}
- (C) Ti^{3+}
- (D) Sc^{3+}

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

Solution:

Concept:

- To form transition-metal cations, remove 4s electrons before 3d electrons, using the given atomic numbers.
- Hund's rule places electrons singly in the five degenerate d orbitals before pairing. A d^5 free ion has five unpaired electrons.

Step 1: Obtain each ionic configuration The neutral configurations are Fe: $[\text{Ar}]3d^64s^2$, V: $[\text{Ar}]3d^34s^2$,

Quick Tip to Solve: Remove 4s electrons first; among these ions, the half-filled $3d^5$ configuration immediately identifies the maximum unpaired-electron count.

Ti: $[\text{Ar}]3d^24s^2$, and Sc: $[\text{Ar}]3d^14s^2$. Removing three electrons gives $\text{Fe}^{3+} : 3d^5$, $\text{V}^{3+} : 3d^2$, $\text{Ti}^{3+} : 3d^1$, and $\text{Sc}^{3+} : 3d^0$.

Step 2: Count the unpaired d-electrons For the free ions stated here, the unpaired d -electron counts are respectively 5, 2, 1, 0. The five electrons in Fe^{3+} occupy the five d orbitals singly, giving the largest count. No ligand field or low-spin complex is specified in this question.

Step 3: Conclusion Fe^{3+} has the maximum number, five, of unpaired d -electrons. Hence, the correct option is (A).

Quick Tip to Solve: Remove $4s$ electrons first; among these ions, the half-filled $3d^5$ configuration immediately identifies the maximum unpaired-electron count.

13. Which of the following is a polydentate ligand?

[1 mark]

- (A) NH_3
- (B) $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$
- (C) EDTA^{4-}
- (D) $\text{C}_2\text{O}_4^{2-}$

Correct Answer: (C) EDTA^{4-}

Solution:

Concept:

- Denticity is the number of donor atoms of one ligand that bind simultaneously to a metal centre.
- In the standard CBSE classification used here, ligands are classified separately as unidentate, didentate and polydentate; EDTA^{4-} is hexadentate.

Step 1: Count the donor sites in EDTA EDTA^{4-} , ethylenediaminetetraacetate, binds through two nitrogen atoms and four carboxylate oxygen atoms. Its total of six donor sites makes it a hexadentate ligand, the polydentate example required in this classification.

Step 2: Classify the other ligands Ammonia binds through one nitrogen donor atom and is unidentate. Ethane-1,2-diamine, $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$, binds through two nitrogen atoms and is didentate. Oxalate, $\text{C}_2\text{O}_4^{2-}$, also normally binds through two oxygen atoms and is didentate. Although the broad term multidentate can include didentate ligands, this MCQ uses the textbook categories separately.

Step 3: Conclusion EDTA^{4-} is the polydentate (hexadentate) ligand intended here. Hence, the correct option is (C).

Quick Tip to Solve: For the CBSE ligand-classification examples, match ammonia to one donor, en and oxalate to two, and EDTA to six.

14. Which of the following coordination compounds exhibits linkage isomerism?

[1 mark]

- (A) $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
(B) $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]\text{Cl}$
(C) $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$
(D) $[\text{Co}(\text{en})_3]\text{Cl}_3$

Correct Answer: (C) $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$

Solution:

Concept:

- Linkage isomerism occurs when an ambidentate ligand can coordinate through either of two different donor atoms.
- The nitrite ligand, NO_2^- , can bind through nitrogen (nitro) or through oxygen (nitrito).

Step 1: Identify the ambidentate ligand $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$ contains coordinated nitrite. The NO_2^- ligand may attach to cobalt through N as $\text{Co} - \text{NO}_2$, or through O as $\text{Co} - \text{ONO}$. The corresponding coordination entities have the same composition but different donor-atom linkages.

Step 2: Check the remaining complexes Coordinated ammonia binds through nitrogen and chloride through chlorine, so the first complex has no such alternative donor atom. Carbonato ligands bind through oxygen; changing between carbonate oxygen atoms does not create the N/O linkage alternatives of nitrite. Ethane-1,2-diamine binds through its nitrogen donors and does not supply an ambidentate N/O choice. The nitrate ions outside the brackets are counterions, not the coordinated nitrite ligand.

Step 3: Conclusion $[\text{Co}(\text{NH}_3)_5\text{NO}_2](\text{NO}_3)_2$ exhibits linkage isomerism. Hence, the correct option is (C).

Quick Tip to Solve: Inspect the ligands inside the brackets: coordinated NO_2^- gives the nitro-N versus nitrito-O linkage pair.

15. Assertion (A): Nucleophilic substitution of iodoethane is easier than chloroethane.

Reason (R): Bond energy of C - Cl bond is less than C - I bond.

Select the correct option:

[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:

- Nucleophilic substitution replaces a halogen atom by a nucleophile; cleavage of the carbon-halogen bond is necessary.
- A weaker carbon-halogen bond and a better leaving group favour substitution. The bond strength order is $\text{C}-\text{Cl} > \text{C}-\text{I}$.

Step 1: Evaluate the Assertion The Assertion is true. In iodoethane, the longer C–I bond is weaker than the C–Cl bond in chloroethane. Also, I^- is a better leaving group than Cl^- . Therefore iodoethane undergoes nucleophilic substitution more readily under comparable conditions.

Step 2: Evaluate the Reason The Reason is false: it reverses the bond-energy order. The carbon-chlorine bond has greater bond energy than the carbon-iodine bond, so it is more difficult to break.

Step 3: Choose the Assertion-Reason relationship Since A is true but R is false, the Reason cannot explain the Assertion. Options (A) and (B) both require a true Reason, while option (D) requires a false Assertion; none of those fits.

Step 4: Conclusion Iodoethane undergoes substitution more readily; A is true and R is false. Hence, the correct option is (C).

Quick Tip to Solve: For the same alkyl group, remember the leaving-group order $\text{I}^- > \text{Br}^- > \text{Cl}^-$; do not reverse the carbon-halogen bond-strength order.

16. Assertion (A): Order and molecularity of a reaction are always same.

Reason (R): Complex reactions involve a sequence of elementary reactions and the slowest step is rate determining. [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:

- Order is the sum of the powers of concentration terms in an experimentally determined rate law, such as $r = k[A]^m[B]^n$, whose order is $m + n$.
- Molecularity counts the reacting species in a single elementary step and is a positive integer; it is not assigned to an overall complex reaction.

Step 1: Evaluate the Assertion The Assertion is false. Order is measured experimentally and can be zero, fractional or integral, whereas molecularity is a positive integer for an elementary step. Thus the two are not always equal. Equality can occur for a simple elementary reaction, but this does not make the universal statement true.

Step 2: Evaluate the Reason The Reason is true. A complex reaction proceeds through several elementary steps, and the slowest step acts as the rate-determining step in the usual CBSE treatment. The observed rate law follows the mechanism and need not follow the stoichiometric coefficients of the overall reaction.

Step 3: Select the appropriate code Because A is false and R is true, option (D) applies. Options (A) and (B) incorrectly treat A as true, and option (C) incorrectly treats R as false.

Step 4: Conclusion Order and molecularity are not always the same; the Reason is true. Hence, the correct option is (D).

Quick Tip to Solve: First ask whether the reaction is elementary: molecularity belongs to an elementary step, while reaction order comes from the measured rate law.

17. Assertion (A): Zinc is not regarded as a transition element.

Reason (R): In zinc, 3d orbitals are completely filled in its ground state as well as in its oxidised state.

Select the correct option:

[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 transition element has an incompletely filled d subshell in its atom or in at least one of its commonly formed ions.
- Zinc has configuration $[\text{Ar}]3d^{10}4s^2$; its usual ion Zn^{2+} has configuration $[\text{Ar}]3d^{10}$.

Step 1: Evaluate the Assertion The Assertion is true. Although zinc belongs to the d block, it does not satisfy the definition of a transition element because its d subshell remains completely filled in the atom and in its normal oxidised state.

Step 2: Evaluate the Reason The Reason is true. Zinc loses the two outer 4s electrons on forming Zn^{2+} ; no 3d electron is removed. Thus both Zn and Zn^{2+} retain the completely filled $3d^{10}$ subshell.

Step 3: Check the explanatory connection The filled d subshell is precisely why zinc fails the transition-element criterion. Hence R directly explains A. Option (B) misses this direct connection, and (C) and (D) wrongly declare one statement false.

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

Quick Tip to Solve: Check the d-electron count in both the neutral atom and its usual ion; a filled d^{10} subshell in both excludes zinc from transition elements.

18. Assertion (A): Fe^{2+} acts as a reducing agent.

Reason (R): Fe^{3+} state is stable due to $3d^5$ configuration.

Select the correct option:

[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 reducing agent donates electrons and is itself oxidised; $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$.
- Fe^{2+} has $3d^6$, while Fe^{3+} has the relatively stable half-filled $3d^5$ configuration.

Step 1: Evaluate the Assertion The Assertion is true. Fe^{2+} can donate an electron to a suitable oxidising species and become Fe^{3+} . Because it causes the other species to gain electrons, Fe^{2+} acts as a reducing agent.

Step 2: Evaluate the Reason The Reason is true. The $3d^5$ configuration of Fe^{3+} is half-filled, giving additional stability. Conversion of $3d^6$ in Fe^{2+} to this half-filled state favours its oxidation when an appropriate oxidising agent is present.

Step 3: Check whether the Reason explains the Assertion The stability of the product Fe^{3+} explains the tendency of Fe^{2+} to lose an electron, so R explains A. Option (B) denies this connection, while (C) and (D) incorrectly reject a true statement.

Step 4: Conclusion Both A and R are true, and R correctly explains the reducing behaviour of Fe^{2+} . Hence, the correct option is (A).

Quick Tip to Solve: Write $\text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + e^-$: electron loss means the species is a reducing agent, and the resulting d^5 state explains the tendency.

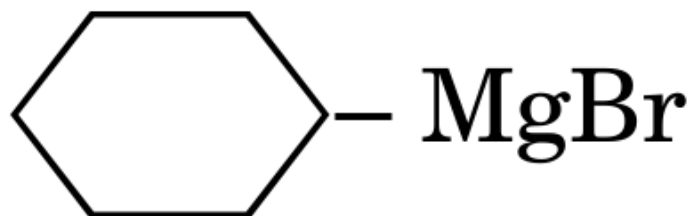
Section B (14 marks)

19. Give the structures and IUPAC name of the products expected from the following reactions:

(a) Reaction of methanal with the Grignard reagent shown below followed by hydrolysis.

(b) Reaction of phenol with $\text{Br}_2(\text{aq})$.

[2 marks]

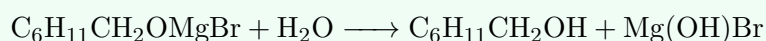
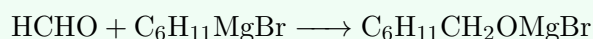


Solution:

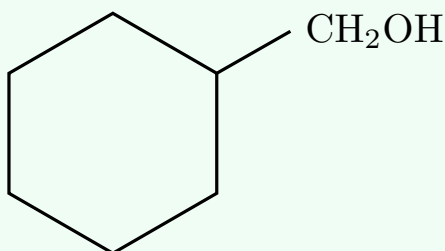
Concept:

- A Grignard reagent RMgBr adds its organic group R to methanal; hydrolysis of the alkoxide gives the primary alcohol RCH_2OH .
- The hydroxyl group activates phenol strongly at its ortho and para positions. Bromine water therefore gives substitution at positions 2, 4 and 6.

Step 1: Identify the Grignard product in part (a) The printed reagent has a saturated six-membered ring bonded to MgBr , so the organic group is cyclohexyl, C_6H_{11} . Addition to methanal forms the magnesium alkoxide, and hydrolysis protonates its oxygen:

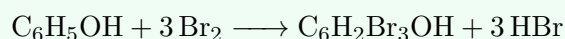


The product structure is a cyclohexane ring bearing a $-\text{CH}_2\text{OH}$ group, written $\text{C}_6\text{H}_{11}-\text{CH}_2-\text{OH}$. Its IUPAC name is **cyclohexylmethanol**. The carbon from methanal becomes the hydroxymethyl carbon; the ring remains saturated.



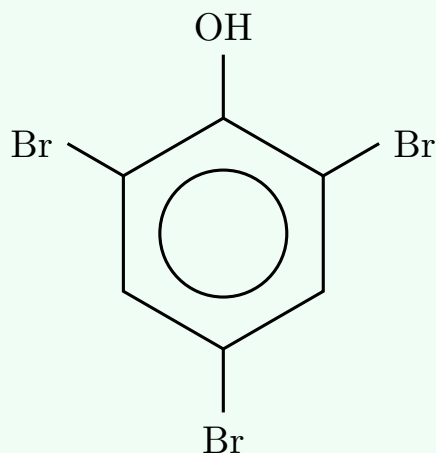
(a) Cyclohexylmethanol

Step 2: Identify the bromination product in part (b) In bromine water, phenol undergoes rapid substitution at both ortho positions and the para position:



Quick Tip to Solve: Methanal adds one $-\text{CH}_2\text{OH}$ carbon to the Grignard group; retain the saturated cyclohexyl ring. With bromine water, fill all three activated positions of phenol.

The product structure has -OH at carbon 1 of the benzene ring and -Br at carbons 2, 4 and 6. Its IUPAC name is **2,4,6-tribromophenol**; it separates as a white precipitate. Aqueous bromine gives this trisubstituted product rather than just a single bromophenol.



(b) 2,4,6-Tribromophenol

Step 3: Conclusion (a) $\text{C}_6\text{H}_{11}\text{-CH}_2\text{-OH}$: cyclohexylmethanol. (b) A phenol ring bearing bromine at positions 2, 4 and 6: 2,4,6-tribromophenol.

Quick Tip to Solve: Methanal adds one $\text{-CH}_2\text{OH}$ carbon to the Grignard group; retain the saturated cyclohexyl ring. With bromine water, fill all three activated positions of phenol.

20. The half-life of a first order reaction is 60 minutes. How long will it take to consume 90% of the reactant?

[Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 10 = 1$]

[2 marks]

Solution:

Concept:

- For a first-order reaction, $t = \frac{2.303}{k} \log \frac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0$, $[A]_t$ are initial and remaining concentrations.
- The half-life relation is $t_{1/2} = \frac{0.693}{k}$. Consuming 90% leaves 10% of the initial reactant.

Step 1: Find the rate constant from the half-life Use the given half-life $t_{1/2} = 60$ min. Then

$$k = \frac{0.693}{60} = 0.01155 \text{ min}^{-1}.$$

The time unit of the rate constant is consistent with the required time in minutes. For a first-order reaction, this half-life is independent of the starting concentration.

Step 2: Use the fraction of reactant remaining After 90% has been consumed, $[A]_t = 0.10[A]_0$, so

Quick Tip to Solve: Convert percentage consumed to fraction remaining first: 90% consumed means a concentration ratio of 10, so use $t = 60 \log(10)/\log(2)$.

$[A]_0/[A]_t = 10$. Substituting into the integrated law,

$$t = \frac{2.303}{0.01155} \log 10 \simeq 199.4 \text{ min.}$$

Equivalently, eliminate k using the supplied logarithms:

$$t = t_{1/2} \frac{\log 10}{\log 2} = 60 \frac{1}{0.3010} = 199.34 \text{ min.}$$

The small numerical difference comes from rounding 0.693 and 2.303; both give about 199 minutes. The supplied value of $\log 3$ is unnecessary.

Step 3: Conclusion The time required to consume 90% of the reactant is approximately 199.3 min, or about 3.32 h.

Quick Tip to Solve: Convert percentage consumed to fraction remaining first: 90% consumed means a concentration ratio of 10, so use $t = 60 \log(10)/\log(2)$.

21. Write the chemical equation involved in the following reactions:

(a) Carbylamine reaction

(b) Gabriel phthalimide synthesis

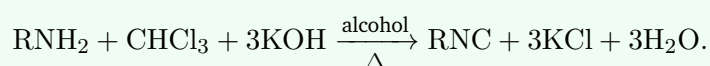
[2 marks]

Solution:

Concept:

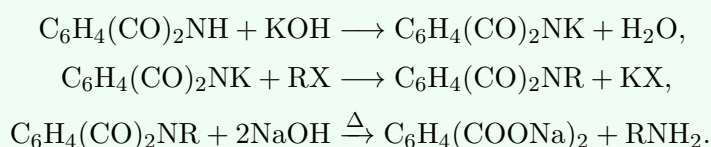
- Carbylamine reaction: a primary amine reacts with chloroform and alcoholic potassium hydroxide on heating to form an isocyanide. Both aliphatic and aromatic primary amines respond.
- Gabriel synthesis converts phthalimide into its potassium salt, then an alkyl derivative; hydrolysis releases a primary aliphatic amine. In the equations, R denotes an alkyl group and X a halogen.

Step 1: (a) Write the carbylamine equation On heating a primary amine with chloroform and alcoholic KOH, the reaction is



The product RNC is an isocyanide with an offensive smell. Secondary and tertiary amines do not give this reaction because the required primary amino group is absent.

Step 2: (b) Write the stages of Gabriel phthalimide synthesis Using $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ to represent phthalimide, the reaction sequence is



Alkaline hydrolysis of the N-alkylphthalimide yields the primary amine and disodium phthalate. The method gives primary aliphatic amines; aryl halides do not undergo the required nucleophilic

Quick Tip to Solve: For carbylamine remember three KOH molecules; for Gabriel write salt formation, alkylation and hydrolysis in that order.

substitution readily.

Step 3: Conclusion Carbylamine reaction forms RNC from RNH_2 , while Gabriel synthesis forms RNH_2 by alkylation and hydrolysis of phthalimide.

Quick Tip to Solve: For carbylamine remember three KOH molecules; for Gabriel write salt formation, alkylation and hydrolysis in that order.

22. What type of deviation from Raoult's law is shown by a mixture of ethanol and acetone? Give reason. [2 marks]

Solution:

Concept:

- Raoult's law for an ideal binary solution is $p_i = x_i p_i^\circ$, where p_i is the partial vapour pressure, x_i the liquid-phase mole fraction and p_i° the vapour pressure of pure component i .
- Positive deviation means the observed vapour pressure is greater than the ideal value. It occurs when interactions between unlike molecules are weaker overall than those in the pure liquids.

Step 1: Identify the deviation A mixture of ethanol and acetone shows **positive deviation** from Raoult's law. Thus its total vapour pressure exceeds the ideal value at the same temperature and composition:

$$p_{\text{observed}} > x_{\text{ethanol}} p_{\text{ethanol}}^\circ + x_{\text{acetone}} p_{\text{acetone}}^\circ$$

Step 2: Explain the molecular reason Pure ethanol molecules are associated by intermolecular hydrogen bonds between their hydroxyl groups. On adding acetone, its molecules enter between ethanol molecules and disrupt this hydrogen-bonded association. Although ethanol can interact with acetone, the unlike interactions are weaker overall than the interactions being replaced. Molecules are therefore held less strongly in the liquid and escape more readily into the vapour phase, increasing the vapour pressure.

Step 3: Conclusion Ethanol and acetone show positive deviation because acetone disrupts ethanol's hydrogen-bonded association, increasing the escaping tendency of molecules and the vapour pressure.

Quick Tip to Solve: Link disruption of ethanol hydrogen bonds to easier escape into vapour; easier escape means positive deviation.

23(a). (i) How are carbohydrates stored in animal body? Mention any one organ where they are present.

(ii) What is the basic structural difference between starch and cellulose? [2 marks]

Solution:

Concept:

- Glycogen is the storage polysaccharide of animals. It is a highly branched polymer of α -D-glucose and serves as a reserve source of glucose.

Quick Tip to Solve: Pair animal storage with glycogen; then remember starch is alpha glucose and cellulose is beta glucose.

- The configuration of glucose and the type of glycosidic linkage distinguish starch from cellulose: starch contains α -D-glucose, whereas cellulose contains β -D-glucose.

Step 1: (i) State the storage form and one organ Carbohydrates are stored in the animal body as **glycogen**. One organ in which glycogen is present is the **liver**; it is also stored in muscles. When the body requires glucose, glycogen can be broken down to supply it, which makes it a useful carbohydrate reserve.

Step 2: (ii) Compare starch and cellulose structurally Starch is a polymer of α -D-glucose. Its amylose component has mainly $\alpha(1 \rightarrow 4)$ glycosidic linkages, while amylopectin has $\alpha(1 \rightarrow 4)$ chains with $\alpha(1 \rightarrow 6)$ branch points. Cellulose is a linear polymer of β -D-glucose joined by $\beta(1 \rightarrow 4)$ glycosidic linkages. Thus the basic difference is the alpha versus beta configuration of the glucose units and their linkages, not a difference in the molecular formula of the constituent glucose.

Step 3: Conclusion (i) Animals store carbohydrates as glycogen, for example in the liver. (ii) Starch contains α -D-glucose units, while cellulose contains β -D-glucose units.

Quick Tip to Solve: Pair animal storage with glycogen; then remember starch is alpha glucose and cellulose is beta glucose.

OR

23(b). Differentiate between:

(i) Peptide linkage and Glycosidic linkage

(ii) Nucleoside and Nucleotide

[2 marks]

Solution:

Concept:

- A condensation reaction joins monomer units with elimination of water. The functional groups that combine determine whether the resulting bond is a peptide or glycosidic linkage.
- A nucleoside contains a nitrogenous base and a pentose sugar. Adding phosphate to a nucleoside produces a nucleotide, the repeating unit of a nucleic acid.

Step 1: (i) Differentiate the two linkages A **peptide linkage**, $-\text{CO} - \text{NH}-$, is an amide bond formed between the carboxyl group of one amino acid and the amino group of another, with elimination of water. It joins amino acids in peptides and proteins. A **glycosidic linkage** is the oxygen bridge, $\text{C} - \text{O} - \text{C}$, joining monosaccharide units through condensation of their hydroxyl groups, one involving an anomeric carbon. It joins sugar units in disaccharides and polysaccharides. Hence the monomers and the chemical groups forming the bonds differ.

Step 2: (ii) Differentiate nucleoside and nucleotide A **nucleoside** consists of a nitrogenous base attached to a pentose sugar, such as ribose or deoxyribose. It contains no phosphate group. A **nucleotide** consists of the same base-sugar combination together with a phosphate group, usually esterified to the sugar's 5' hydroxyl group. For example, adenosine is a nucleoside whereas adenosine monophosphate is a nucleotide.

Step 3: Conclusion (i) A peptide linkage joins amino acids through $-\text{CO} - \text{NH}-$; a glycosidic linkage

Quick Tip to Solve: Use the monomers to identify the linkage, and check for phosphate to distinguish a nucleotide from a nucleoside.

joins sugar units through oxygen. (ii) Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.

Quick Tip to Solve: Use the monomers to identify the linkage, and check for phosphate to distinguish a nucleotide from a nucleoside.

24(a). Define fuel cell and write its two advantages.

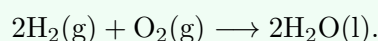
[2 marks]

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.
- The electrode reactions are oxidation of the fuel at the anode and reduction of the oxidant at the cathode; electrons flow through the external circuit.

Step 1: Define a fuel cell A fuel cell is an electrochemical cell in which a fuel and an oxidising agent are supplied continuously to the electrodes, and their redox reaction produces electrical energy directly. For example, in the hydrogen–oxygen fuel cell, hydrogen is the fuel and oxygen is the oxidant. Its overall reaction is



Step 2: State two advantages First, fuel cells have high efficiency because they convert chemical energy directly into electricity, avoiding the heat-to-mechanical-energy conversion of a conventional thermal power plant. Second, the hydrogen–oxygen fuel cell is environmentally clean: its reaction product is water, so its operation does not release smoke or polluting combustion gases.

Step 3: Conclusion A fuel cell produces electricity directly from continuously supplied reactants. Its advantages are high energy-conversion efficiency and, for the hydrogen–oxygen cell, clean operation with water as the product.

Quick Tip to Solve: For the clean-operation advantage, name the hydrogen–oxygen fuel cell and its water product explicitly.

OR

24(b). Using E° values of X and Y given below, predict which is better for coating the surface of Iron to prevent corrosion and why?

Given: $E^\circ_{\text{X}^{2+}/\text{X}} = -2.36 \text{ V}$, $E^\circ_{\text{Y}^{2+}/\text{Y}} = -0.14 \text{ V}$, $E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ V}$

[2 marks]

Solution:

Concept:

- A more negative standard reduction potential indicates a greater tendency for the metal to be oxidised and act as a sacrificial anode.

Quick Tip to Solve: Compare each coating potential with iron: the more negative coating protects exposed iron sacrificially.

- In sacrificial protection, the coating metal oxidises preferentially while iron remains the protected cathode, even if the coating is scratched.

Step 1: Compare the coating metals with iron The standard reduction potentials are

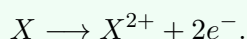
$$E_{X^{2+}/X}^{\circ} = -2.36 \text{ V},$$

$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.44 \text{ V},$$

$$E_{Y^{2+}/Y}^{\circ} = -0.14 \text{ V}.$$

Since the potential of X is more negative than that of iron, X is more readily oxidised. Y has a more positive reduction potential than iron, so iron is more readily oxidised than Y.

Step 2: Explain protection at a damaged coating X acts as the sacrificial anode and undergoes



The electrons protect iron from oxidation. This protection continues even where the coating is scratched and iron is exposed. A coating of Y can provide a physical barrier while intact, but at a scratch iron becomes the anode relative to Y and corrodes. Thus X provides the more reliable electrochemical protection.

Step 3: Conclusion X is better for coating iron because it has a more negative standard reduction potential and oxidises preferentially as a sacrificial anode.

Quick Tip to Solve: Compare each coating potential with iron: the more negative coating protects exposed iron sacrificially.

25. Give reasons:

(a) Formic acid is a stronger acid than acetic acid.

(b) Alpha (α)-Hydrogens of aldehydes and ketones are acidic.

[2 marks]

Solution:

Concept:

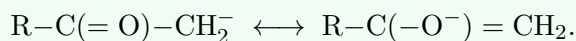
- Acid strength depends on the stability of the conjugate base: a more stable conjugate base favours loss of H^{+} .
- The methyl group has an electron-releasing $+I$ effect, whereas the carbonyl group withdraws electron density and stabilises an adjacent carbanion by resonance.

Step 1: (a) Compare formic acid and acetic acid Acetic acid has a methyl group attached to the carboxyl group. Its electron-releasing $+I$ effect increases electron density on the carboxylate group and destabilises the negatively charged acetate ion relative to the formate ion. Formic acid has hydrogen in place of the methyl group, so it lacks this destabilising alkyl-group effect. Consequently, formic acid loses a proton more readily and is the stronger acid.

Step 2: (b) Explain the acidity of alpha-hydrogens An alpha-hydrogen is attached to the carbon next to the carbonyl group. The electron-withdrawing effect of the carbonyl group facilitates removal

Quick Tip to Solve: For acidity comparisons, identify the conjugate base and explain how induction or resonance affects its stability.

of this hydrogen as H^+ . The resulting conjugate base is an enolate ion whose negative charge is delocalised between the alpha-carbon and oxygen. For a general aldehyde or ketone, its resonance forms are



Here R may be H or an alkyl group. This resonance stabilisation makes alpha-hydrogens acidic.

Step 3: Conclusion (a) Formic acid is stronger because it lacks the electron-releasing methyl group of acetic acid. (b) Alpha-hydrogens are acidic because the conjugate enolate ion is stabilised by resonance and the carbonyl group withdraws electron density.

Quick Tip to Solve: For acidity comparisons, identify the conjugate base and explain how induction or resonance affects its stability.

Section C (15 marks)

26. The rate of a reaction doubles when temperature changes from 27°C to 37°C . Calculate energy of activation for the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(Given: $\log 2 = 0.3010$, $\log 3 = 0.4771$, $\log 4 = 0.6021$)

[3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, R is the gas constant and T is absolute temperature.
- For unchanged reactant concentrations, the rate ratio equals the rate-constant ratio. Assuming the pre-exponential factor A is unchanged over the temperature interval,

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

Step 1: Convert temperatures and write the rate ratio The temperatures must be expressed in kelvin:

$$T_1 = 27 + 273 = 300 \text{ K}, \quad T_2 = 37 + 273 = 310 \text{ K}.$$

The rate doubles for the same reactant concentrations, so $k_2/k_1 = 2$. We use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and the supplied value $\log 2 = 0.3010$.

Step 2: Rearrange the two-temperature Arrhenius equation Substituting the known quantities gives

$$0.3010 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{300} - \frac{1}{310} \right).$$

The reciprocal-temperature difference is

$$\frac{1}{300} - \frac{1}{310} = \frac{310 - 300}{300 \times 310} = \frac{10}{93000} \text{ K}^{-1}.$$

Quick Tip to Solve: Convert both temperatures to kelvin first; combine the reciprocal difference as $(T_2 - T_1)/(T_1 T_2)$ to avoid subtraction errors.

Hence

$$E_a = \frac{2.303 \times 8.314 \times 0.3010 \times 93000}{10}.$$

Step 3: Calculate and check the units The numerical value is

$$E_a = 5.36 \times 10^4 \text{ J mol}^{-1} = 53.6 \text{ kJ mol}^{-1}.$$

The kelvin factor from the reciprocal-temperature difference cancels the K^{-1} in R, leaving energy per mole. Since both $\log 2$ and $1/T_1 - 1/T_2$ are positive, the calculated activation energy is positive, as expected for a reaction whose rate increases with temperature.

Step 4: Conclusion The energy of activation is $E_a \approx 53.6 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Convert both temperatures to kelvin first; combine the reciprocal difference as $(T_2 - T_1)/(T_1 T_2)$ to avoid subtraction errors.

27. Write the structure of product when D-Glucose reacts with the following: (any three)

(a) HI

(b) Conc. HNO_3

(c) Br_2 water

(d) HCN

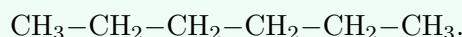
[3 marks]

Solution:

Concept:

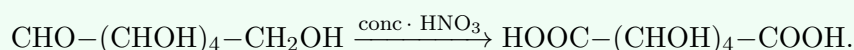
- Open-chain D-glucose has the condensed structure $\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH}$: an aldehyde end, four secondary alcohol groups and one primary alcohol end.
- Strong reduction removes oxygen, oxidation changes susceptible terminal groups to COOH , and HCN adds across the aldehyde carbonyl group.

Step 1: (a) Reduction with HI On prolonged heating with HI, all oxygen-containing groups are reduced, while the unbranched chain of six carbon atoms is retained. The product is n-hexane, whose structure is



This reaction provides evidence that the six carbon atoms of glucose form a straight chain; the product is not a cyclic hydrocarbon.

Step 2: (b) Oxidation with concentrated nitric acid Concentrated HNO_3 oxidises both the aldehyde group at C1 and the primary alcohol group at C6 to carboxyl groups. The four intervening secondary alcohol groups remain in the product:

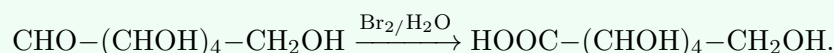


The product is saccharic acid (D-glucaric acid), a dicarboxylic acid.

Step 3: (c) Mild oxidation with bromine water Bromine water selectively oxidises the aldehyde group

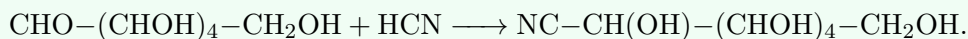
Quick Tip to Solve: Compare the two ends of glucose: bromine water oxidises only CHO, whereas concentrated nitric acid oxidises both CHO and CH_2OH .

to a carboxyl group; the terminal primary alcohol group is unchanged. Thus gluconic acid is formed:



Its single carboxyl group distinguishes it from the nitric-acid oxidation product.

Step 4: (d) Addition of HCN Cyanide attacks the aldehyde carbonyl carbon, and protonation of oxygen produces a cyanohydrin. The former aldehyde carbon now bears H, OH and CN:



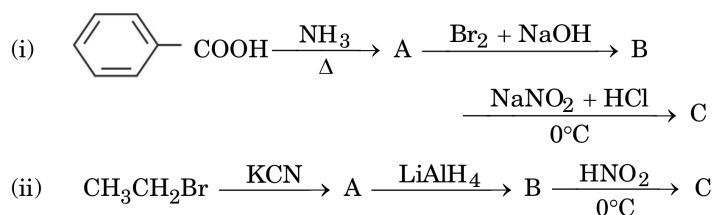
Addition creates a new stereogenic centre, so the cyanohydrin can occur as two diastereomers; the condensed structure states the connectivity of the product.

Step 5: Conclusion The products are (a) $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$, (b) $\text{HOOC}(\text{CHOH})_4\text{COOH}$, (c) $\text{HOOC}(\text{CHOH})_4\text{CH}_2\text{OH}$, and (d) $\text{NC}-\text{CH}(\text{OH})-(\text{CHOH})_4-\text{CH}_2\text{OH}$. Any three answer the question.

Quick Tip to Solve: Compare the two ends of glucose: bromine water oxidises only CHO, whereas concentrated nitric acid oxidises both CHO and CH_2OH .

28(a). Write the structures of A, B and C in the following reactions:

[3 marks]



Solution:

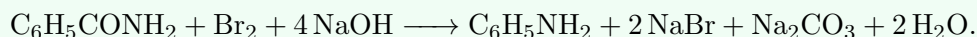
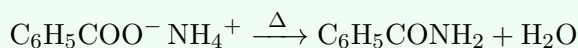
Concept:

- Heating an ammonium carboxylate gives an amide. Hofmann bromamide degradation gives a primary amine with one fewer carbon atom.
- Aromatic primary amines form diazonium salts with NaNO_2/HCl at low temperature. Aliphatic primary amines instead give alcohols with nitrous acid and evolve nitrogen.
- KCN introduces the carbon of a nitrile group; LiAlH_4 reduces $-\text{C}\equiv\text{N}$ to $-\text{CH}_2\text{NH}_2$ without loss of carbon.

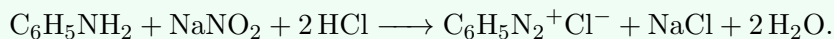
Step 1: (i) Identify the amide, amine and diazonium salt Benzoic acid initially forms ammonium benzoate with ammonia. Heating removes water and gives benzamide, so A is $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}_2$. Bromine and aqueous NaOH then cause Hofmann degradation: the carbonyl carbon is removed and B

Quick Tip to Solve: Track carbon count: Hofmann degradation removes one carbon; KCN adds one, and nitrile reduction retains that added carbon.

is aniline, $\text{C}_6\text{H}_5-\text{NH}_2$.



Finally, NaNO_2/HCl generates nitrous acid in situ. At 0°C , diazotisation gives C, benzenediazonium chloride, with structure $\text{C}_6\text{H}_5-\text{N}\equiv\text{N}^+ \text{Cl}^-$:

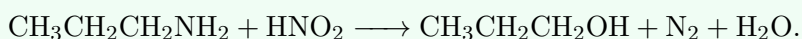


Include the chloride counter-ion in C.

Step 2: (ii) Identify the nitrile, aliphatic amine and alcohol KCN replaces bromide through the cyanide carbon, adding one carbon. A is propanenitrile, $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{N}$. Reduction converts the nitrile carbon into CH_2NH_2 ; B is propan-1-amine, $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$.



Unlike the aromatic salt in (i), the aliphatic diazonium intermediate is unstable even when cold. It loses nitrogen and gives C, propan-1-ol:



Step 3: Conclusion (i) A = $\text{C}_6\text{H}_5\text{CONH}_2$, B = $\text{C}_6\text{H}_5\text{NH}_2$, C = $\text{C}_6\text{H}_5-\text{N}\equiv\text{N}^+ \text{Cl}^-$. (ii) A = $\text{CH}_3\text{CH}_2\text{CN}$, B = $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$, C = $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$.

Quick Tip to Solve: Track carbon count: Hofmann degradation removes one carbon; KCN adds one, and nitrile reduction retains that added carbon.

OR

28(b). How will you convert the following:

(i) Aniline to p-bromoaniline

(ii) Ethanoic acid to methanamine

(iii) Butanenitrile to 1-aminobutane

[3 marks]

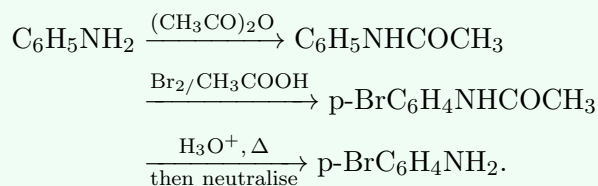
Solution:

Concept:

- Acetylation protects aniline against excessive bromination. The acetamido group directs ortho/para; hydrolysis restores the amino group.
- Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the amide carbonyl carbon. Nitrile reduction converts RCN into RCH_2NH_2 , retaining all carbon atoms.

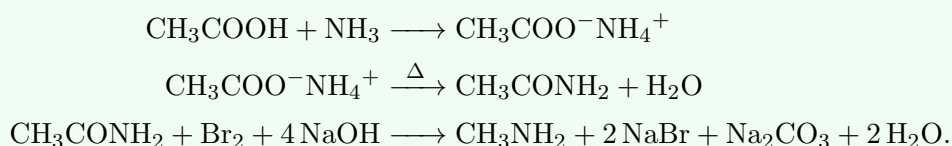
Quick Tip to Solve: Protect aniline before bromination; choose Hofmann degradation to shorten a chain, but nitrile reduction to retain its length.

Step 1: (i) Aniline to p-bromoaniline Treat aniline with acetic anhydride to form acetanilide, then brominate with Br₂ in glacial acetic acid. The less hindered para position gives the major product. Isolate p-bromoacetanilide; hydrolyse it with aqueous acid and heat, then neutralise.



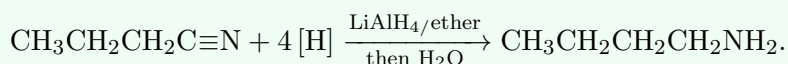
Direct bromine water gives 2,4,6-tribromoaniline; protection is essential for selective monobromination.

Step 2: (ii) Ethanoic acid to methanamine Treat ethanoic acid with ammonia to form ammonium ethanoate. Heating this salt produces ethanamide. Then use Br₂/NaOH for Hofmann bromamide degradation:



Loss of the carbonyl carbon gives the one-carbon amine, methanamine, CH₃NH₂. Amide reduction would retain two carbons and give the wrong amine.

Step 3: (iii) Butanenitrile to 1-aminobutane Reduce butanenitrile with LiAlH₄ in dry ether, followed by aqueous work-up. The nitrile carbon becomes the terminal carbon of the amino-containing chain:



The product is butan-1-amine (1-aminobutane); the nitrile carbon is retained in its four-carbon chain.

Step 4: Conclusion Use (i) acetylation, para bromination and hydrolysis; (ii) amide formation followed by Br₂/NaOH; and (iii) LiAlH₄ reduction followed by aqueous work-up to obtain the three required amines.

Quick Tip to Solve: Protect aniline before bromination; choose Hofmann degradation to shorten a chain, but nitrile reduction to retain its length.

29. 0.3 g of acetic acid ($M = 60 \text{ g mol}^{-1}$) dissolved in 30 g of benzene shows a depression in freezing point equal to 0.45°C . Calculate the percentage association of acid if it forms a dimer in the solution. (Given: K_f for benzene = $5.12 \text{ K kg mol}^{-1}$) [3 marks]

Solution:

Concept:

- Freezing-point depression obeys $\Delta T_f = iK_fm$, where i is the van't Hoff factor, K_f is the molal depression constant and m is the molality calculated using the unassociated acid.

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; first convert the solvent mass from grams to kilograms.

- Association reduces the number of dissolved particles. For dimer formation, $2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2$, the relation is $i = 1 - \alpha/2$, where α is the fraction of acid molecules associated.

Step 1: Calculate the initial molality The amount of acetic acid and the mass of solvent in kilograms are

$$n = \frac{0.3}{60} = 0.005 \text{ mol}, \quad w_{\text{benzene}} = 0.030 \text{ kg}.$$

Therefore, before allowing for association,

$$m = \frac{0.005}{0.030} = \frac{1}{6} \text{ mol kg}^{-1}.$$

The solvent mass, rather than the total solution mass, is used to calculate molality.

Step 2: Find the observed particle factor If no association occurred, the depression would be

$$K_f m = 5.12 \times \frac{1}{6} = 0.85333 \text{ K}.$$

Since the observed depression is only 0.45 K,

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.45}{0.85333} = 0.52734375.$$

A temperature interval of 0.45°C equals 0.45 K. The value below unity is consistent with association.

Step 3: Determine the fraction associated Start with one mole of acid molecules. If the fraction associated is α , there are $1 - \alpha$ moles of monomer and $\alpha/2$ moles of dimer. Thus the total number of moles of particles is

$$i = (1 - \alpha) + \frac{\alpha}{2} = 1 - \frac{\alpha}{2}.$$

Substituting the measured factor gives

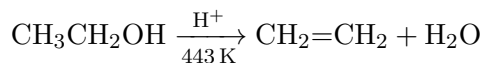
$$\alpha = 2(1 - i) = 2(1 - 0.52734375) = 0.9453125.$$

Multiplication by 100 converts this fraction into the required percentage.

Step 4: Conclusion The percentage association of acetic acid is 94.53% (approximately 94.5%).

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; first convert the solvent mass from grams to kilograms.

30. (a) Write the mechanism of the following reaction:



(b) Write the equation of the reaction for the preparation of phenol from cumene.

[3 marks]

Solution:

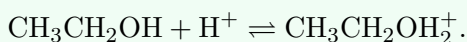
Concept:

- Acid-catalysed dehydration of ethanol at 443 K eliminates water and forms ethene. Protonation converts the poor leaving group $-\text{OH}$ into the good leaving group H_2O .

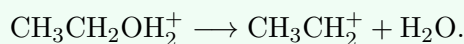
Quick Tip to Solve: Check the reaction direction and temperature: ethanol at 443 K undergoes dehydration. Cumene gives both phenol and acetone.

- Cumene is isopropylbenzene. Air oxidation gives cumene hydroperoxide, which undergoes acid-catalysed cleavage to phenol and acetone.

Step 1: (a) Protonation of ethanol The oxygen atom of ethanol uses a lone pair to accept a proton from the acid. The resulting protonated alcohol is an oxonium ion:



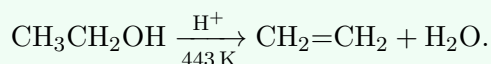
Step 2: (a) Loss of water and formation of ethene In the standard stepwise representation of acid-catalysed dehydration, the protonated alcohol loses water in the slow step:



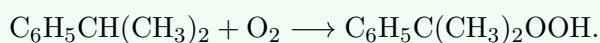
The carbocation then loses a proton from the adjacent carbon. The electrons of that carbon-hydrogen bond form the carbon-carbon double bond:



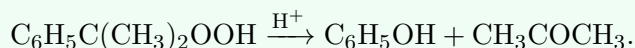
The acid catalyst is regenerated. These steps give the overall reaction



Step 3: (b) Oxidation and cleavage of cumene Cumene is first oxidised by oxygen from air to form cumene hydroperoxide:



On treatment with dilute acid, the hydroperoxide cleaves to phenol and acetone:



Step 4: Conclusion (a) Protonation, loss of water and loss of a proton convert ethanol into ethene at 443 K. (b) Cumene oxidation followed by acid cleavage of its hydroperoxide gives phenol and acetone.

Quick Tip to Solve: Check the reaction direction and temperature: ethanol at 443 K undergoes dehydration. Cumene gives both phenol and acetone.

Section D (8 marks)

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

31(i). Read the following case and answer the questions that follow.

The polarity of C - X bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reaction with metal atoms to form organometallic compounds. Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of -OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution of arenes. Nucleophilic substitution reactions are categorised into S_N1 and S_N2 on the basis of their kinetic properties. Chirality has a profound role in understanding the S_N1 and S_N2 mechanism.

Answer the following questions:

What happens when bromobenzene is treated with Mg in the presence of dry ether?

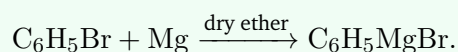
[1 mark]

Solution:

Concept:

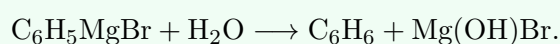
- Magnesium reacts with an organic halide in anhydrous ether to form an organomagnesium halide, called a Grignard reagent.
- For bromobenzene, magnesium is inserted into the carbon-bromine bond and the phenyl group remains attached to magnesium.

Step 1: Write the product-forming equation Bromobenzene reacts with magnesium in dry ether as follows:



The product is phenylmagnesium bromide, an aryl Grignard reagent. Magnesium becomes bonded to both the phenyl group and bromine.

Step 2: Explain why dry ether is required Ether provides the solvent medium for forming the Grignard reagent, while exclusion of moisture prevents its destruction. Water would protonate the phenyl group and give benzene:



Therefore, benzene is not the product under the stated dry conditions.

Step 3: Conclusion Bromobenzene forms $\boxed{\text{C}_6\text{H}_5\text{MgBr}}$, phenylmagnesium bromide, in the presence of magnesium and dry ether.

Quick Tip to Solve: With Mg and dry ether, insert Mg between the organic group and halogen to write the Grignard reagent.

31(ii). Which compound in each of the following pairs will react faster in S_N1 reaction with OH^- ?

(1) $CH_2=CH-CH_2-Cl$ or $CH_3-CH_2-CH_2-Cl$

(2) $(CH_3)_3C-Cl$ or CH_3Cl

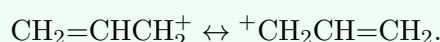
[1 mark]

Solution:

Concept:

- The slow step of an S_N1 reaction is ionisation to form a carbocation. Greater carbocation stability makes this step faster.
- Resonance stabilises an allylic carbocation, while hyperconjugation and the electron-releasing effect of alkyl groups stabilise a tertiary carbocation.

Step 1: Compare allyl chloride and propyl chloride $CH_2=CHCH_2Cl$ reacts faster. Its ionisation produces the resonance-stabilised allyl carbocation:



Propyl chloride, $CH_3CH_2CH_2Cl$, would form an unstable primary carbocation with no such resonance stabilisation.

Step 2: Compare tert-butyl chloride and methyl chloride $(CH_3)_3CCl$ reacts faster because it forms a tertiary carbocation, $(CH_3)_3C^+$, stabilised by its three methyl groups. Methyl chloride would require formation of CH_3^+ , which has no alkyl groups to provide this stabilisation. The incoming OH^- attacks after ionisation; its approach does not determine the relative S_N1 rates.

Step 3: Conclusion The faster compounds are (1) $CH_2=CHCH_2Cl$ and (2) $(CH_3)_3CCl$.

Quick Tip to Solve: For S_N1 , compare the carbocations formed after chloride leaves; resonance and tertiary substitution favour faster ionisation.

31(iii). Write the equations for the preparation of 1-iodobutane from

(1) 1-chlorobutane

(2) but-1-ene.

[2 marks]

Solution:

Concept:

- Finkelstein reaction replaces chlorine or bromine in a primary haloalkane by iodine using sodium iodide in dry acetone; precipitation of the sodium halide drives the reaction.
- The peroxide effect gives anti-Markovnikov addition of HBr to an alkene, placing bromine on the terminal carbon. This effect does not apply to HI .

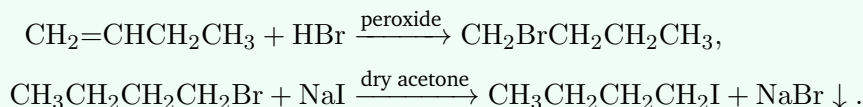
Step 1: (1) Start with 1-chlorobutane Treat 1-chlorobutane with sodium iodide in dry acetone. Iodide substitutes the terminal chlorine without changing the four-carbon chain:



Quick Tip to Solve: To put iodine on the terminal carbon of an alkene, first use HBr /peroxide, then exchange Br for I ; do not use HI /peroxide.

Sodium chloride is insoluble in acetone, so its precipitation favours formation of the iodide.

Step 2: (2) Start with but-1-ene First add HBr in the presence of an organic peroxide. Anti-Markovnikov addition produces 1-bromobutane. Then replace bromine by iodine by the Finkelstein reaction:



Direct addition of HI to but-1-ene would favour 2-iodobutane by Markovnikov addition, so the bromide intermediate is essential for the terminal iodide.

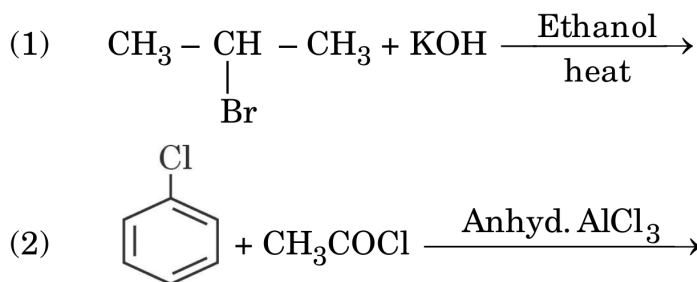
Step 3: Conclusion 1-Chlorobutane gives 1-iodobutane with NaI in dry acetone. But-1-ene gives it through peroxide-assisted HBr addition followed by NaI in dry acetone.

Quick Tip to Solve: To put iodine on the terminal carbon of an alkene, first use HBr/peroxide, then exchange Br for I; do not use HI/peroxide.

OR

31(iii). Write the structure of the major products in each of the following reactions:

[2 marks]

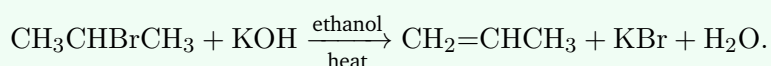


Solution:

Concept:

- Heating an alkyl halide with ethanolic KOH favours dehydrohalogenation: loss of a beta-hydrogen and the halogen forms a carbon-carbon double bond.
- Chlorine deactivates an aromatic ring but directs electrophilic substitution to the ortho and para positions through resonance. In acylation, the less crowded para product predominates.

Step 1: (1) Eliminate HBr from 2-bromopropane In $\text{CH}_3\text{CHBrCH}_3$, either terminal methyl group provides an equivalent beta-hydrogen. Heating with ethanolic KOH removes a beta-hydrogen and bromine from adjacent carbons, forming propene:



Both possible directions of elimination give the same alkene because the starting molecule is symmetric. Aqueous KOH, in contrast, would favour substitution to propan-2-ol.

Step 2: (2) Acylate chlorobenzene Anhydrous AlCl_3 activates acetyl chloride to supply the acyl

Quick Tip to Solve: Read ethanol and heat as elimination conditions; for chlorobenzene acylation, place the acetyl group para to chlorine for the major product.

electrophile. Chlorine directs the incoming -COCH_3 group to the ortho and para positions; the para position has less steric crowding. Thus the major product is para-chloroacetophenone, with chlorine and acetyl groups opposite one another on the ring:



The minor ortho isomer has these groups adjacent, whereas the requested major structure has them at positions 1 and 4.

Step 3: Conclusion (1) Propene: $\text{CH}_2=\text{CHCH}_3$.

(2) Para-chloroacetophenone: $\text{p-ClC}_6\text{H}_4\text{COCH}_3$.

Quick Tip to Solve: Read ethanol and heat as elimination conditions; for chlorobenzene acylation, place the acetyl group para to chlorine for the major product.

32(i). Read the following case and answer the questions that follow.

Coordination compounds are widely present in the minerals, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems and medicine. Alfred Werner's theory postulated the use of two types of linkages (primary and secondary), by a metal atom/ion in a coordination compound. He predicted the geometrical shapes of a large number of coordination entities using the property of isomerism. The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to describe the optical properties of these compounds. The Crystal Field Theory (CFT) explains the effect of different crystal fields (provided by the ligands taken as point charges) on the degeneracy of d-orbital energies of the central metal atom/ion.

Answer the following questions:

When a coordination compound $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ is mixed with AgNO_3 solution, 2 moles of AgCl are precipitated per mole of the compound. Write the structural formula of the complex and secondary valency for Nickel ion.

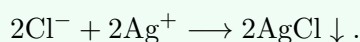
[1 mark]

Solution:

Concept:

- Chloride ions outside the coordination sphere ionise in water and precipitate with Ag^+ as AgCl .
- Werner secondary valency is the coordination number: the number of donor atoms directly bound to the central metal ion.

Step 1: Locate the chloride ions Two moles of AgCl per mole of compound show that both chloride ions are ionisable counter-ions outside the coordination sphere:



Neither chloride therefore occupies a ligand position on nickel.

Step 2: Place the water ligands in the coordination sphere The six neutral water molecules coordinate to Ni^{2+} , giving $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. Two external chloride ions balance its charge, so the compound is

Quick Tip to Solve: Use the amount of AgCl to count chloride counter-ions; then count the water donor atoms inside the brackets for secondary valency.

$[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$. Each water supplies one oxygen donor atom, giving six metal-ligand linkages.

Step 3: Conclusion Structural formula: $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$. Secondary valency of nickel: 6 .

Quick Tip to Solve: Use the amount of AgCl to count chloride counter-ions; then count the water donor atoms inside the brackets for secondary valency.

32(ii). Write the IUPAC name of the ionisation isomer of $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$.

[1 mark]

Solution:

Concept:

- Ionisation isomers exchange a coordinated anionic ligand with an anion outside the coordination sphere, so their solutions release different anions.
- In naming a complex cation, name its ligands alphabetically, then the metal with its oxidation state; name the counter-ion last.

Step 1: Exchange sulfate and chloride The given compound has sulfate coordinated to cobalt and chloride as its counter-ion. Exchanging these gives the ionisation isomer $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, with chloride coordinated and sulfate outside the brackets. The ammonia ligands remain unchanged.

Step 2: Determine oxidation state and name The complex cation must have charge $+2$ to balance SO_4^{2-} . Since ammonia is neutral and coordinated chloride has charge -1 , $x - 1 = +2$, giving cobalt oxidation state $+3$. Five ammonia ligands are named pentaammine and chloride is named chlorido; ammine precedes chlorido alphabetically.

Step 3: Conclusion The ionisation isomer is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$, named pentaamminechlorido-cobalt(III) sulfate.

Quick Tip to Solve: Swap the anion inside the brackets with the counter-ion first, then calculate the metal oxidation state before naming the isomer.

32(iii). Using Valence Bond Theory, predict the geometry and magnetic nature of:

(1) $[\text{Ni}(\text{CO})_4]$

(2) $[\text{Fe}(\text{CN})_6]^{3-}$

[Atomic number: $\text{Ni} = 28$, $\text{Fe} = 26$]

[2 marks]

Solution:

Concept:

- VBT assigns geometry from the hybrid orbitals used for metal-ligand bonds: sp^3 gives tetrahedral geometry, while d^2sp^3 gives octahedral geometry.
- A complex with all electrons paired is diamagnetic. Any unpaired electron makes it paramagnetic; strong-field ligands can cause pairing of metal d electrons.

Step 1: (1) Analyse tetracarbonylnickel(0) CO is neutral, so nickel has oxidation state zero in

Quick Tip to Solve: Find oxidation state before counting d electrons: neutral Ni with CO becomes paired d10, while Fe(III) with cyanide is low-spin d5 and still has one unpaired electron.

$[\text{Ni}(\text{CO})_4]$. Free nickel has configuration $[\text{Ar}]3d^84s^2$. Under the influence of CO, the two $4s$ electrons enter the $3d$ subshell, giving the paired $3d^{10}$ arrangement. The vacant $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals to accept lone pairs from four CO ligands. These point towards the vertices of a tetrahedron. All metal electrons are paired, so the complex is diamagnetic.

Step 2: (2) Analyse hexacyanidoferrate(III) For $[\text{Fe}(\text{CN})_6]^{3-}$, let the iron oxidation state be x . Then $x + 6(-1) = -3$, so $x = +3$. Thus Fe^{3+} has configuration $[\text{Ar}]3d^5$. The strong-field cyanide ligands pair the five $3d$ electrons into three orbitals as 2, 2, 1, leaving two inner $3d$ orbitals vacant. These two orbitals, one $4s$ and three $4p$ orbitals form six d^2sp^3 hybrids. The resulting inner-orbital complex is octahedral. One electron remains unpaired, so it is paramagnetic even though it is low spin.

Step 3: Conclusion $[\text{Ni}(\text{CO})_4]$: sp^3 , tetrahedral and diamagnetic. $[\text{Fe}(\text{CN})_6]^{3-}$: d^2sp^3 , octahedral and paramagnetic with one unpaired electron.

Quick Tip to Solve: Find oxidation state before counting d electrons: neutral Ni with CO becomes paired d^{10} , while Fe(III) with cyanide is low-spin d^5 and still has one unpaired electron.

OR

32(iii). Give reasons:

(1) Low spin tetrahedral complexes are not formed.

(2) $[\text{Co}(\text{NH}_3)_6]^{3+}$ is an inner orbital complex whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is an outer orbital complex.

[Atomic number: Co = 27, Ni = 28]

[2 marks]

Solution:

Concept:

- The tetrahedral crystal-field splitting is small: $\Delta_t = \frac{4}{9}\Delta_o$ for the same metal ion and ligands. Electrons pair only when the splitting exceeds the pairing energy P .
- In valence bond theory, an inner orbital octahedral complex uses two vacant $(n-1)d$ orbitals and has d^2sp^3 hybridisation. An outer orbital octahedral complex uses nd orbitals and has sp^3d^2 hybridisation.

Step 1: (1) Explain the absence of low spin tetrahedral complexes In tetrahedral complexes, the splitting Δ_t is generally smaller than the electron-pairing energy P . It therefore costs less energy for electrons to occupy the higher set of orbitals singly than to pair in the lower set. Thus tetrahedral complexes remain high spin; the small splitting does not cause the pairing needed for a low spin arrangement.

Step 2: (2) Compare the available orbitals in the two metal ions Neutral cobalt is $[\text{Ar}]3d^74s^2$, so Co^{3+} is $[\text{Ar}]3d^6$. In $[\text{Co}(\text{NH}_3)_6]^{3+}$, ammonia causes pairing of the six $3d$ electrons into three orbitals, leaving two $3d$ orbitals vacant. These join one $4s$ and three $4p$ orbitals to form d^2sp^3 hybrids. Nickel is $[\text{Ar}]3d^84s^2$, so Ni^{2+} is $[\text{Ar}]3d^8$. Eight electrons cannot be accommodated in only three $3d$ orbitals, whose total capacity is six; hence two vacant $3d$ orbitals cannot be obtained even by pairing. The complex instead uses $4s$, three $4p$ and two $4d$ orbitals for sp^3d^2 hybridisation.

Step 3: Conclusion Low spin tetrahedral complexes are not formed because $\Delta_t < P$. $[\text{Co}(\text{NH}_3)_6]^{3+}$

Quick Tip to Solve: Count the metal-ion d electrons first: a d^8 ion cannot leave two of its five $3d$ orbitals vacant.

uses inner $3d$ orbitals ($d^2 sp^3$), whereas $[\text{Ni}(\text{NH}_3)_6]^{2+}$ uses outer $4d$ orbitals ($sp^3 d^2$).

Quick Tip to Solve: Count the metal-ion d electrons first: a d8 ion cannot leave two of its five 3d orbitals vacant.

Section E (15 marks)

33(a). (i) An organic compound (X) having molecular formula $\text{C}_5\text{H}_{10}\text{O}$ can show various properties depending on its structures. Draw each of the structures if it

- (1) gives positive iodoform test.
- (2) shows Cannizzaro's reaction.
- (3) reduces Tollens' reagent and has a chiral carbon.

(ii) Write the reaction involved in the following:

- (1) Wolff-Kishner reduction
- (2) Hell-Volhard-Zelinsky reaction

[5 marks]

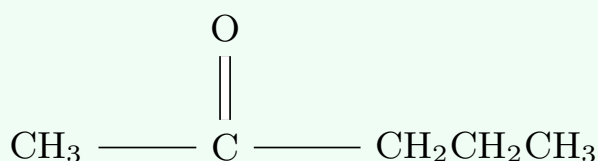
Solution:

Concept:

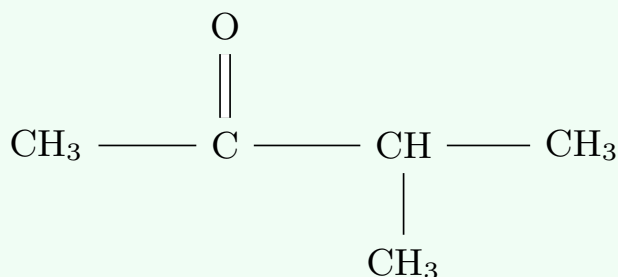
- A positive iodoform test identifies the methyl ketone group $\text{CH}_3\text{CO}-$, which produces yellow CHI_3 with iodine and alkali.
- Cannizzaro disproportionation occurs in aldehydes without an α -hydrogen. Tollens' reagent is reduced by aldehydes, and a chiral tetrahedral carbon is bonded to four different groups.
- Wolff-Kishner reduction converts a carbonyl group to a methylene group. The Hell-Volhard-Zelinsky (HVZ) reaction replaces an α -hydrogen of a carboxylic acid by halogen.

Step 1: (i)(1) Identify the structures giving the iodoform test For $\text{C}_5\text{H}_{10}\text{O}$, a methyl ketone has the form $\text{CH}_3\text{COC}_3\text{H}_7$. The propyl group may be straight chain or branched, giving pentan-2-one and 3-methylbutan-2-one, respectively. Both structures shown below contain $\text{CH}_3\text{CO}-$. Each forms yellow iodoform in I_2/NaOH . Pentan-3-one lacks a methyl group directly bonded to the carbonyl carbon, so it does not give this test.

Quick Tip to Solve: For $\text{C}_5\text{H}_{10}\text{O}$, use the test to choose the functional group first, then check the alpha carbon and all four groups at a proposed chiral centre.



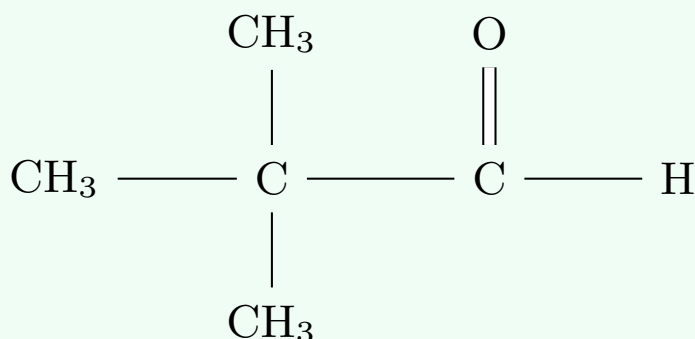
Pentan-2-one



3-Methylbutan-2-one

The two methyl ketones that give a positive iodoform test.

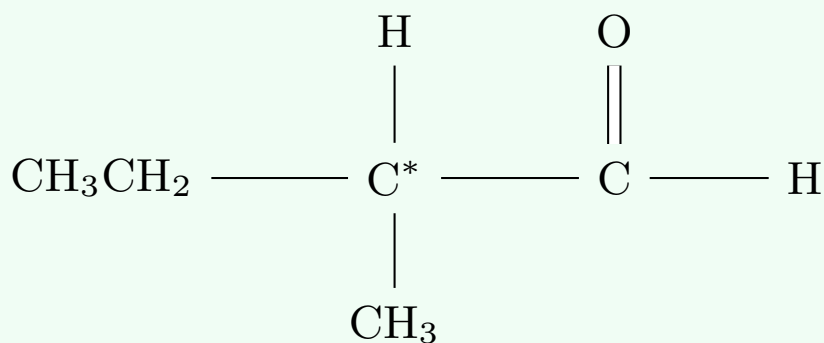
Step 2: (i)(2) Identify the aldehyde without an alpha hydrogen The required structure is 2,2-dimethylpropanal, $(\text{CH}_3)_3\text{CCHO}$. Its carbon next to $-\text{CHO}$ is bonded to three methyl groups and the aldehyde carbon; it carries no hydrogen. It therefore undergoes Cannizzaro reaction with concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol. Its five carbon atoms and ten hydrogen atoms agree with the stated formula.



2,2-Dimethylpropanal: the alpha carbon has no hydrogen.

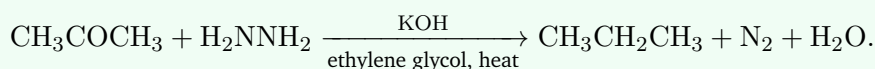
Step 3: (i)(3) Identify the chiral aldehyde The structure is 2-methylbutanal, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$. The aldehyde group reduces Tollens' reagent to metallic silver. The starred carbon in the drawing has four distinct substituents: $-\text{H}$, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$ and $-\text{CHO}$; hence it is chiral. The terminal aldehyde carbon itself is trigonal planar and is not the chiral centre.

Quick Tip to Solve: For $\text{C}_5\text{H}_{10}\text{O}$, use the test to choose the functional group first, then check the alpha carbon and all four groups at a proposed chiral centre.



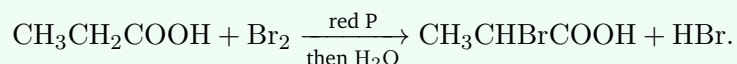
2-Methylbutanal: the starred carbon is chiral.

Step 4: (ii)(1) Write the Wolff–Kishner reduction The aldehyde or ketone first reacts with hydrazine to form a hydrazone. Heating the hydrazone with potassium hydroxide in a high boiling solvent such as ethylene glycol replaces the carbonyl oxygen by two hydrogen atoms, liberating nitrogen. A ketone example is



Thus propanone is reduced to propane; the carbon skeleton remains unchanged.

Step 5: (ii)(2) Write the Hell–Volhard–Zelinsky reaction A carboxylic acid containing an α -hydrogen reacts with bromine in the presence of red phosphorus, followed by hydrolysis, to give an α -bromocarboxylic acid. For example,



Propanoic acid gives 2-bromopropanoic acid. Bromination occurs at the carbon adjacent to the carboxyl group; an acid lacking an α -hydrogen does not undergo this reaction.

Step 6: Conclusion The required structures are pentan-2-one or 3-methylbutan-2-one for the iodoform test, 2,2-dimethylpropanal for Cannizzaro reaction, and 2-methylbutanal for the chiral Tollens-positive compound. Wolff–Kishner reduction gives an alkane from a carbonyl compound, while HVZ gives an α -halocarboxylic acid.

Quick Tip to Solve: For $\text{C}_5\text{H}_{10}\text{O}$, use the test to choose the functional group first, then check the alpha carbon and all four groups at a proposed chiral centre.

33(b). (i) How can you convert each of the following compounds to Benzoic acid?

- (1) Acetophenone
- (2) Ethylbenzene
- (3) Bromobenzene

(ii) Arrange the following compounds in increasing order of their property as indicated:

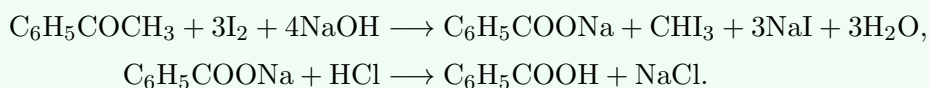
- (1) $\text{O}_2\text{N}-\text{CH}_2-\text{COOH}$, $\text{F}-\text{CH}_2-\text{COOH}$, $\text{CN}-\text{CH}_2\text{COOH}$ (Acidic character)
- (2) Ethanal, Propanal, Butanone, Propanone (Reactivity in nucleophilic addition reactions) [5 marks]

Solution:

Concept:

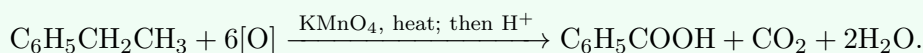
- A methyl ketone, RCOCH_3 , undergoes the haloform reaction with iodine and alkali to form RCOO^- ; acidification gives the corresponding carboxylic acid.
- An alkylbenzene having a benzylic hydrogen is oxidised by hot alkaline KMnO_4 to a benzoate salt. A phenylmagnesium halide reacts with CO_2 , followed by acidic hydrolysis, to give benzoic acid.
- Electron-withdrawing groups stabilise a carboxylate ion through the negative inductive effect, increasing acidity. For these substituents, the withdrawing effect increases as $\text{F} < \text{CN} < \text{NO}_2$.
- Nucleophilic addition is favoured by a more electrophilic and less crowded carbonyl carbon. Alkyl groups reduce its electrophilicity by their positive inductive effect and hinder the approaching nucleophile.

Step 1: (i)(1) Convert acetophenone by the haloform reaction Treat acetophenone with I_2/NaOH . Its methyl ketone group gives sodium benzoate and a yellow precipitate of iodoform. Acidify the benzoate with dilute hydrochloric acid:



The carbonyl carbon remains in the benzoic acid, while the methyl carbon leaves as iodoform.

Step 2: (i)(2) Oxidise the side chain of ethylbenzene Heat ethylbenzene with alkaline potassium permanganate and then acidify. The benzylic carbon becomes the carboxyl carbon; the remaining side-chain carbon is oxidised further. An overall oxidation equation, written using oxygen equivalents, is

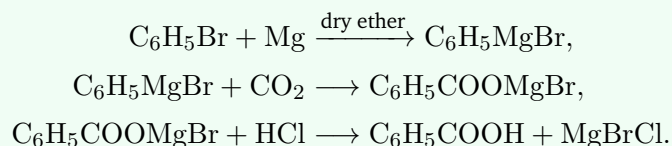


In the alkaline reaction mixture the organic product is initially a benzoate salt, so the acidification step is essential to isolate benzoic acid.

Step 3: (i)(3) Carboxylate the Grignard reagent from bromobenzene React bromobenzene with magnesium in dry ether to form phenylmagnesium bromide. Add carbon dioxide (dry ice), then carry

Quick Tip to Solve: For benzoic acid conversions, identify methyl ketone, benzylic side chain or aryl halide first; these point to haloform, oxidation or Grignard carboxylation respectively.

out acidic hydrolysis:



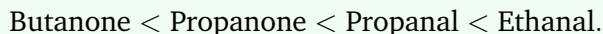
Dry conditions prevent water from destroying the Grignard reagent. Carbon dioxide supplies the additional carbon of the carboxyl group.

Step 4: (ii)(1) Compare acidic character Each compound has the substituent on the carbon adjacent to COOH, so the negative inductive effect acts over the same distance. Greater electron withdrawal stabilises the negative charge in the conjugate carboxylate ion and makes loss of H^+ easier. The nitro group withdraws most strongly, followed by cyano and then fluoro. Thus the increasing acidic character is



Here NCCH_2COOH denotes the printed cyanoacetic acid, $\text{CN}-\text{CH}_2\text{COOH}$, with the cyano carbon bonded to CH_2 .

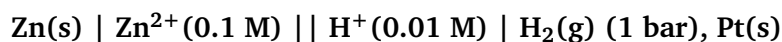
Step 5: (ii)(2) Compare nucleophilic addition reactivity Aldehydes have one alkyl group and one hydrogen attached to the carbonyl carbon, whereas ketones have two alkyl groups. Consequently, aldehydes are less crowded and their carbonyl carbons are more electrophilic, so they react faster than these ketones. Within each pair, an ethyl group causes greater steric hindrance and electron donation than a methyl group: butanone is less reactive than propanone, and propanal is less reactive than ethanal. Therefore the increasing order is



Step 6: Conclusion Benzoic acid is obtained from acetophenone by I_2/NaOH followed by acidification, from ethylbenzene by hot alkaline KMnO_4 followed by acidification, and from bromobenzene through $\text{Mg}/\text{dry ether}$, CO_2 , then acidic hydrolysis. The increasing orders are $\text{FCH}_2\text{COOH} < \text{NCCH}_2\text{COOH} < \text{O}_2\text{NCH}_2\text{COOH}$ for acidity and butanone < propanone < propanal < ethanal for nucleophilic addition.

Quick Tip to Solve: For benzoic acid conversions, identify methyl ketone, benzylic side chain or aryl halide first; these point to haloform, oxidation or Grignard carboxylation respectively.

34. (a) Calculate the emf of the following cell at 25°C:



[Given: $E_{\text{Zn}^{2+}/\text{Zn}}^\circ = -0.76 \text{ V}$, $E_{\text{H}^+/\text{H}_2}^\circ = 0.00 \text{ V}$, $\log 10 = 1$]

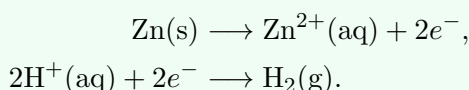
(b) State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? [5 marks]

Solution:

Concept:

- The cell emf is the cathode reduction potential minus the anode reduction potential: $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$. Zinc is oxidised and hydrogen ions are reduced in the cell as written.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{n} \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- Kohlrausch's law describes the independent contributions of ions to limiting molar conductivity. Conductivity κ measures conduction by the ions in a unit volume, whereas molar conductivity Λ_m measures conduction associated with one mole of electrolyte.

Step 1: (a) Write the cell reaction and standard emf At the zinc electrode (anode), oxidation occurs; at the hydrogen electrode (cathode), reduction occurs:



Adding the half-reactions gives $\text{Zn(s)} + 2\text{H}^+(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$, so $n = 2$. Using the supplied standard reduction potentials,

$$E_{\text{cell}}^\circ = 0.00 - (-0.76) = 0.76 \text{ V}.$$

Step 2: (a) Substitute the nonstandard conditions The reaction quotient contains the square of the hydrogen-ion concentration because two hydrogen ions appear in the balanced reaction. Taking concentrations relative to 1 M and gas pressure relative to 1 bar,

$$Q = \frac{[\text{Zn}^{2+}](p_{\text{H}_2}/p^\circ)}{[\text{H}^+]^2} = \frac{0.1 \times 1}{(0.01)^2} = 10^3.$$

Hence $\log Q = 3 \log 10 = 3$, and the Nernst equation gives

$$\begin{aligned}E_{\text{cell}} &= 0.76 - \frac{0.0591}{2} \times 3 \\ &= 0.76 - 0.08865 \text{ V}.\end{aligned}$$

The hydrogen ions are dilute, making their reduction potential lower than its standard value; this accounts for the decrease from the standard cell emf.

Step 3: (b) State Kohlrausch's law At infinite dilution, each ion contributes independently to the limiting molar conductivity of an electrolyte, irrespective of the nature of the other ion with which it

Quick Tip to Solve: Balance the cell reaction before forming Q : the coefficient 2 on H^+ makes its concentration squared, while $n = 2$ sets the Nernst denominator.

is associated. Thus,

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ,$$

where λ_+° and λ_-° are the limiting ionic molar conductivities and ν_+ , ν_- are the numbers of cations and anions in one formula unit. For example, $\Lambda_m^\circ(\text{ZnCl}_2) = \lambda_{\text{Zn}^{2+}}^\circ + 2\lambda_{\text{Cl}^-}^\circ$.

Step 4: (b) Explain the effect of dilution on conductivity Dilution adds solvent and lowers the number of ions per unit volume of solution. Consequently, a given volume contains fewer charge carriers, so its conductivity κ decreases. This must be distinguished from molar conductivity: dilution reduces interionic interactions and can increase ionisation, so Λ_m increases towards its limiting value even though κ decreases.

Step 5: Conclusion (a) The cell emf at 25°C is $0.67135 \text{ V} \approx 0.671 \text{ V}$. (b) At infinite dilution, limiting molar conductivity is the sum of independent ionic contributions. Conductivity decreases on dilution because there are fewer ions per unit volume.

Quick Tip to Solve: Balance the cell reaction before forming Q: the coefficient 2 on H⁺ makes its concentration squared, while n = 2 sets the Nernst denominator.

35(a). (i) Account for the following:

(1) Transition metals form complex compounds.

(2) The $E_{\text{Mn}^{2+}/\text{Mn}}^\circ$ value for manganese is highly negative whereas $E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^\circ$ is highly positive.

(3) Cu⁺ ion is unstable in aqueous solution.

(ii) Write the equations involved in the preparation of KMnO₄ from Pyrolusite ore (MnO₂). [5 marks]

Solution:

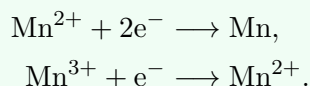
Concept:

- Complex formation involves donation of a ligand's lone pair to a metal ion. Small ionic size, high charge density and suitable vacant orbitals favour coordination.
- A standard reduction potential measures the tendency of the oxidised species to accept electrons. A particularly stable product favours reduction, whereas a particularly stable reactant resists it.
- Manganese(II) has the stable half-filled configuration [Ar]3d⁵. Hydration energy also affects the relative stability of metal ions in aqueous solution.
- In preparing permanganate, manganese is first oxidised from +4 in MnO₂ to +6 in manganate, and then to +7 in permanganate.

Step 1: (i)(1) Explain complex formation Transition-metal ions are generally small and possess a relatively high ionic charge, giving them high charge density. They attract electron pairs donated by ligands strongly. They also have suitable vacant orbitals that can accept these electron pairs to form coordinate bonds. Thus, several ligands can coordinate around a central transition-metal ion, producing a complex compound; for example, [Fe(CN)₆]⁴⁻. The ligand acts as a Lewis base and the central metal ion as a Lewis acid.

Quick Tip to Solve: For manganese potentials, write the reduction half-reaction and locate the stable 3d⁵ ion; for ore conversion, track manganese as +4 → +6 → +7.

Step 2: (i)(2) Explain the two manganese potentials The relevant reduction processes are



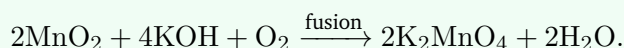
The Mn^{2+} ion has the especially stable half-filled $3d^5$ configuration. Its reduction to manganese metal is therefore difficult, so $E^{\circ}_{\text{Mn}^{2+}/\text{Mn}}$ is highly negative. Conversely, Mn^{3+} , which has a $3d^4$ configuration, readily gains an electron to form stable $3d^5$ Mn^{2+} . Hence $E^{\circ}_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is highly positive: Mn^{3+} is readily reduced and acts as an oxidising agent.

Step 3: (i)(3) Explain the instability of copper(I) In aqueous solution, Cu^{+} undergoes disproportionation:



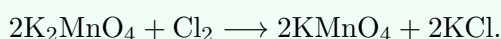
One copper(I) ion is oxidised to copper(II), while the other is reduced to copper metal. Although oxidation of Cu^{+} requires the second ionisation energy, the much more negative hydration enthalpy of Cu^{2+} provides sufficient stabilisation to compensate for this energy requirement. Consequently, hydrated Cu^{2+} is favoured and Cu^{+} is unstable in water.

Step 4: (ii) Convert pyrolusite into potassium manganate Fuse pyrolusite, MnO_2 , with potassium hydroxide in the presence of air or another oxidising agent. Oxygen oxidises manganese from +4 to +6, forming green potassium manganate:



The equation conserves manganese, potassium, oxygen and hydrogen; the green product contains the manganate ion MnO_4^{2-} .

Step 5: (ii) Oxidise manganate to permanganate Oxidise the manganate solution with chlorine to obtain purple potassium permanganate:



Each manganate ion loses one electron as manganese changes from +6 to +7, while one chlorine molecule gains two electrons to form two chloride ions. Thus two manganate units are required per chlorine molecule. Industrially, manganate can also be oxidised electrolytically; its anode reaction is $\text{MnO}_4^{2-} \longrightarrow \text{MnO}_4^{-} + \text{e}^{-}$.

Step 6: Conclusion Transition-metal ions form complexes because of their small size, high charge density and suitable vacant orbitals. Stable $3d^5$ Mn^{2+} explains both manganese potentials. Aqueous Cu^{+} disproportionates because hydration strongly stabilises Cu^{2+} . Pyrolusite is converted first into green K_2MnO_4 by alkaline oxidative fusion and then into purple KMnO_4 by oxidation.

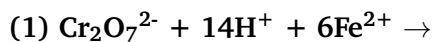
Quick Tip to Solve: For manganese potentials, write the reduction half-reaction and locate the stable $3d^5$ ion; for ore conversion, track manganese as $+4 \rightarrow +6 \rightarrow +7$.

35(b). (i) Identify the following:

(1) Transition metal of 3d series that exhibits only one oxidation state.

(2) Transition metal of 3d series that acts as a strong reducing agent in +2 oxidation state in aqueous solution.

(ii) Complete and balance the following equations:



(iii) What is Misch metal? Write its one use.

[5 marks]

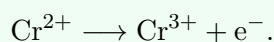
Solution:

Concept:

- Electronic configuration controls the stability of oxidation states. A species that is readily oxidised acts as a reducing agent because it donates electrons to another species.
 - In acidic solution, dichromate is reduced from chromium(VI) to chromium(III), while Fe^{2+} is oxidised to Fe^{3+} . Half-reactions must conserve both atoms and electric charge.
 - Heating potassium permanganate gives potassium manganate, manganese dioxide and oxygen.
- Misch metal is an alloy containing mainly lanthanoid metals and iron.

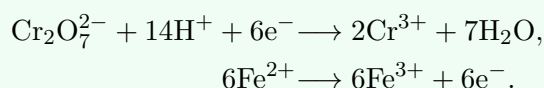
Step 1: (i)(1) Identify the metal with one oxidation state The metal is scandium, Sc, which exhibits the +3 oxidation state in its compounds. Its electronic configuration is $[\text{Ar}] 3d^1 4s^2$. Loss of the two 4s electrons and the one 3d electron gives Sc^{3+} with the stable $[\text{Ar}]$ configuration. Zinc is not the required answer: although it commonly exhibits +2, zinc is not a transition element because both its atom and its common ion have completely filled d subshells.

Step 2: (i)(2) Identify the strong reducing agent The metal is chromium, Cr. In aqueous solution, Cr^{2+} , having a $3d^4$ configuration, is readily oxidised to Cr^{3+} , having a relatively stable $3d^3$ configuration:

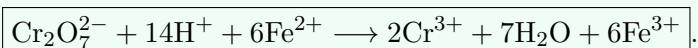


The released electron reduces another species, so chromium in its +2 oxidation state is a strong reducing agent. In an octahedral aqueous complex, the d^3 configuration has three electrons in the lower-energy t_{2g} orbitals, contributing to the stability of chromium(III).

Step 3: (ii)(1) Balance the dichromate reaction The reduction and oxidation half-reactions are



Adding them cancels the six electrons and gives

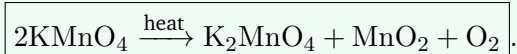


Each of the two chromium atoms gains three electrons, and each iron(II) ion loses one electron. The

Quick Tip to Solve: For acidic dichromate, remember that two chromium(VI) atoms accept six electrons in total, so six iron(II) ions are needed. For heated permanganate, start with two formula units to conserve potassium.

equation contains two chromium atoms, seven oxygen atoms, fourteen hydrogen atoms and six iron atoms on either side. The total charge on each side is +24, confirming charge balance.

Step 4: (ii)(2) Complete the thermal decomposition On heating, potassium permanganate decomposes as follows:



The products are potassium manganate, manganese dioxide and oxygen gas. Two potassium atoms and two manganese atoms are conserved. The eight oxygen atoms on the left equal the four in manganate, two in manganese dioxide and two in oxygen on the right. Thus, the coefficient of potassium permanganate must be two.

Step 5: (iii) Define Misch metal and give a use Misch metal is an alloy containing approximately 95% lanthanoid metals and 5% iron, with traces of sulphur, carbon, calcium and aluminium. One use is in magnesium-based alloys for making bullets and shells. Its lanthanoid-rich composition distinguishes it from an alloy consisting of a single pure rare-earth metal.

Step 6: Conclusion (i) The metals are (1) scandium and (2) chromium. (ii) The balanced equations are $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}$ and $2\text{KMnO}_4 \xrightarrow{\text{heat}} \text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$. (iii) Misch metal contains about 95% lanthanoids and 5% iron with traces of other elements; it is used in magnesium-based alloys for bullets and shells.

Quick Tip to Solve: For acidic dichromate, remember that two chromium(VI) atoms accept six electrons in total, so six iron(II) ions are needed. For heated permanganate, start with two formula units to conserve potassium.