

CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-3-2

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **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. $18 \times 1 = 18$

1. Which of the following has the highest melting point?

[1 mark]

- (A) o-Dichlorobenzene
- (B) m-Dichlorobenzene
- (C) p-Dichlorobenzene
- (D) All have the same melting point

Correct Answer: (C) p-Dichlorobenzene

Solution:

Concept:

- The melting point of a molecular solid depends on the stability of its crystal lattice and the efficiency of molecular packing.
- Greater molecular symmetry can favour closer packing; the position of substituents therefore affects the melting points of isomers.

Step 1: Compare the symmetry of the isomers In the para isomer, the two identical chlorine substituents occupy opposite positions on the benzene ring. This arrangement is more symmetrical than the adjacent positions in the ortho isomer or the separated, non-opposite positions in the meta isomer.

Step 2: Relate symmetry to crystal packing The more symmetrical para molecules fit efficiently into the crystal lattice. Their better packing makes the solid more stable, so more thermal energy is needed to melt it. The ortho and meta isomers pack less efficiently; sharing a molecular formula does not make their crystal structures or melting points identical. Thus options (A), (B) and (D) do not satisfy the comparison.

Step 3: Conclusion p-Dichlorobenzene has the highest melting point. Hence, the correct option is (C).

Quick Tip to Solve: For the dichlorobenzene isomers, compare symmetry and crystal packing: the para arrangement packs best.

2. Sodium phenoxide when heated with CO₂ under pressure, followed by acidification, yields:

[1 mark]

- (A) Sodium benzoate
- (B) Salicylic acid
- (C) Salicylaldehyde
- (D) Benzoic acid

Correct Answer: (B) Salicylic acid

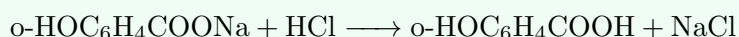
Solution:

Concept:

- Kolbe's reaction introduces a carboxyl group into sodium phenoxide by reaction with CO₂ under pressure on heating.
- Acidification converts the resulting sodium carboxylate into the corresponding carboxylic acid.

Step 1: Identify the carboxylation product The electron-rich phenoxide ring reacts with CO₂, predominantly at the ortho position relative to the oxygen substituent. The sodium salt formed is sodium salicylate, which retains the phenolic hydroxyl group and has a neighbouring carboxylate group.

Step 2: Apply the acidification step Acidification protonates the carboxylate group to yield 2-hydroxybenzoic acid, commonly called salicylic acid:



Sodium benzoate and benzoic acid lack the retained phenolic hydroxyl group. Salicylaldehyde contains an aldehyde group and is associated with the Reimer-Tiemann reaction, not this carboxylation.

Step 3: Conclusion The product is salicylic acid. Hence, the correct option is (B).

Quick Tip to Solve: Recognise sodium phenoxide plus carbon dioxide, then acidification, as Kolbe's route to salicylic acid.

3. A compound (A) with molecular formula $C_5H_{10}O$, forms a phenyl hydrazone and gives negative Tollens' and iodoform tests. The compound on reduction gives n-pentane. The compound (A) is:

[1 mark]

- (A) Pentan-3-one
- (B) Pentanal
- (C) Pentanol
- (D) Pentan-2-one

Correct Answer: (A) Pentan-3-one

Solution:

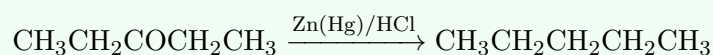
Concept:

- Aldehydes and ketones form phenylhydrazones through their carbonyl group. Ordinary alcohols do not give this reaction.
- An aliphatic aldehyde gives Tollens' test, while a methyl ketone containing CH_3CO^- gives the iodoform test.

Step 1: Use the carbonyl and Tollens' tests Phenylhydrazone formation identifies a carbonyl compound. Pentanol has no carbonyl group and its formula is $C_5H_{12}O$, so (C) is excluded. Pentanal would give a positive Tollens' test; hence the negative result excludes (B) and points to a ketone.

Step 2: Distinguish the two ketones Pentan-2-one, $CH_3COCH_2CH_2CH_3$, has the methyl ketone group and gives the iodoform test, so (D) is excluded. Pentan-3-one, $CH_3CH_2COCH_2CH_3$, lacks that group and gives a negative iodoform test. Both have five carbons, but only the latter satisfies all the tests.

Step 3: Check the reduction clue Complete reduction of the carbonyl group of pentan-3-one to a methylene group preserves its straight five-carbon skeleton:



This is consistent with the stated formation of n-pentane.

Step 4: Conclusion Compound (A) is pentan-3-one. Hence, the correct option is (A).

Quick Tip to Solve: Negative Tollens' and iodoform tests select a non-methyl ketone; compare the groups on both sides of the carbonyl.

4. Benzene diazonium chloride on hydrolysis gives:

[1 mark]

- (A) Phenol
- (B) Chlorobenzene
- (C) Benzene
- (D) Aniline

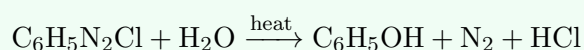
Correct Answer: (A) Phenol

Solution:

Concept:

- Arenediazonium salts undergo substitution reactions in which the diazonium group is replaced, with evolution of nitrogen gas.
- On warming with water, benzenediazonium chloride undergoes hydrolysis, replacing the diazonium group by a hydroxyl group.

Step 1: Write the hydrolysis reaction Water supplies the hydroxyl group that becomes attached to the aromatic carbon originally bonded to the diazonium group. Nitrogen is liberated during the reaction:



Step 2: Distinguish hydrolysis from other substitutions Chlorobenzene would require a chlorination substitution, commonly using cuprous chloride in hydrochloric acid. Benzene results from replacement by hydrogen, for example with hypophosphorous acid. Aniline is the amine used to prepare this diazonium salt by diazotisation, and is not the hydrolysis product. Thus (B), (C) and (D) describe different chemistry.

Step 3: Conclusion Hydrolysis gives phenol, $\text{C}_6\text{H}_5\text{OH}$. Hence, the correct option is (A).

Quick Tip to Solve: With an aryl diazonium salt, warm water replaces the diazonium group by hydroxyl and releases nitrogen.

5. Helical structure of proteins is stabilized by:

[1 mark]

- (A) ionic bond
- (B) covalent bond
- (C) hydrogen bond
- (D) Van der Waals forces

Correct Answer: (C) hydrogen bond

Solution:

Concept:

- The α -helix is a secondary structure of proteins, produced by regular coiling of the polypeptide backbone.
- Hydrogen bonds form between the carbonyl oxygen and the hydrogen attached to nitrogen in

Quick Tip to Solve: Separate peptide-chain formation from helix formation: peptide bonds join residues; hydrogen bonds stabilise the helix.

peptide groups.

Step 1: Identify the bonds holding the helix In an α -helix, backbone peptide groups form intrachain hydrogen bonds: a carbonyl group at residue i hydrogen-bonds with the N–H group at residue $i + 4$. These regularly repeated attractions hold successive turns in place and stabilise the coiled shape.

Step 2: Compare the other interactions Covalent peptide bonds link the amino acids and establish the primary structure, but are not the specific interactions stabilising the helical folding. Ionic attractions and van der Waals forces can contribute to protein stability generally, yet neither is the characteristic repeated backbone interaction responsible for the α -helix. This excludes (A), (B) and (D).

Step 3: Conclusion The helical structure is stabilised by hydrogen bonds. Hence, the correct option is (C).

Quick Tip to Solve: Separate peptide-chain formation from helix formation: peptide bonds join residues; hydrogen bonds stabilise the helix.

6. A vitamin which plays a vital role in the clotting of blood is:

[1 mark]

- (A) Vitamin A
- (B) Vitamin K
- (C) Vitamin D
- (D) Vitamin B

Correct Answer: (B) Vitamin K

Solution:

Concept:

- Vitamins are required in small quantities for specific physiological functions; different vitamins cannot be substituted for one another.
- Vitamin K is a fat-soluble vitamin essential for the normal formation of functional blood-clotting proteins, including prothrombin.

Step 1: Associate the function with its vitamin Normal blood coagulation depends on several clotting factors. Vitamin K supports the formation of functional clotting factors in the liver; its deficiency can delay clotting and cause excessive bleeding. This connects the function stated in the question directly to vitamin K.

Step 2: Eliminate the other choices Vitamin A is associated chiefly with vision and healthy epithelial tissues. Vitamin D supports calcium and phosphate balance and healthy bones. The B-group vitamins mainly serve roles in metabolic reactions, often as parts of coenzymes. None of these is the vitamin specifically identified with the clotting function asked here.

Step 3: Conclusion Vitamin K plays a vital role in blood clotting. Hence, the correct option is (B).

Quick Tip to Solve: Link vitamin K with clotting, vitamin A with vision and vitamin D with calcium and bones to eliminate these distractors.

7. The rate of reaction $A + B \rightarrow \text{Products}$, is given by the equation $r = k[A][B]$. If B is taken in large excess, the order of reaction would be:

[1 mark]

- (A) 2
- (B) 0
- (C) 1
- (D) Cannot be predicted

Correct Answer: (C) 1

Solution:

Concept:

- For the rate law $r = k[A][B]$, the sum of the concentration exponents is two: the full rate law is first order in each reactant.
- A reactant in large excess has an approximately constant concentration during the reaction, so its concentration can be absorbed into an observed rate constant.

Step 1: Treat the excess concentration as constant Since B is in large excess, the fraction of B consumed while A reacts is very small. Thus $[B] \approx [B]_0$, where $[B]_0$ is its initial concentration. Define the observed rate constant $k_{\text{obs}} = k[B]_0$.

Step 2: Read the effective order from the rate law Substituting the nearly constant concentration gives

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

The observed rate now varies with the first power of the changing concentration of A. The reaction therefore behaves as pseudo-first-order. Option (A) gives the overall order of the original unrestricted rate law; (B) is excluded because the rate still depends on A, and (D) is excluded because the given rate law determines the behaviour.

Step 3: Conclusion With B in large excess, the effective order is 1 (pseudo-first-order). Hence, the correct option is (C).

Quick Tip to Solve: Absorb the concentration of the reactant in large excess into the rate constant, then count only the remaining variable powers.

8. 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 constant temperature with the same composition in liquid and vapour phases.
- A maximum-boiling azeotrope is produced by a sufficiently large negative deviation from Raoult's law; stronger unlike-molecule attractions lower the escaping tendency.

Step 1: Relate vapour pressure to boiling point A liquid boils when its vapour pressure equals the external pressure. Strong attractions between unlike molecules lower the mixture's vapour pressure below the ideal value, so a higher temperature is needed to reach the external pressure.

Step 2: Compare the possible deviations Large negative deviation can therefore give a boiling point above those of both pure liquids. Large positive deviation raises vapour pressure and produces a minimum-boiling azeotrope instead. Showing no deviation and obeying Raoult's law both describe ideal behaviour, which does not produce the stated maximum-boiling azeotrope.

Step 3: Conclusion The mixture shows a large negative deviation from Raoult's law. Hence, the correct option is (A).

Quick Tip to Solve: Link lower vapour pressure to higher boiling point: maximum-boiling azeotropes require large negative deviation.

9. 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:

- For a strong electrolyte at low concentration, $\Lambda = \Lambda_0 - A\sqrt{C}$, where Λ is molar conductivity, C is concentration and A is a positive constant.
- The limiting molar conductivity Λ_0 is approached at infinite dilution, which means concentration tends to zero.

Quick Tip to Solve: For a limiting molar conductivity question, make the concentration-dependent term vanish by taking concentration to zero.

Step 1: Set the conductivity correction to zero Equality with the limiting value requires the concentration correction to vanish:

$$\Lambda_0 - \Lambda = A\sqrt{C} \rightarrow 0.$$

For fixed positive A , this occurs as $C \rightarrow 0$.

Step 2: Test the other concentration limits If $C \rightarrow \sqrt{A}$, the correction tends to $A\sqrt{\sqrt{A}}$, not zero. If $C \rightarrow 1$, it tends to A . Increasing concentration towards infinity is the opposite of infinite dilution and is also outside the dilute-solution range of this relation; it cannot give the limiting conductivity.

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

Quick Tip to Solve: For a limiting molar conductivity question, make the concentration-dependent term vanish by taking concentration to zero.

10. Isotonic solutions have:

[1 mark]

- (A) same osmotic pressure
- (B) same boiling point
- (C) same melting point
- (D) same vapour pressure

Correct Answer: (A) same osmotic pressure

Solution:

Concept:

- Isotonic solutions are solutions with equal osmotic pressures at the same temperature.
- For a dilute solution, $\pi = iCRT$, where i is the van't Hoff factor, C is molarity, R is the gas constant and T is absolute temperature.

Step 1: Apply the definition of isotonic solutions For two isotonic solutions at a common temperature, $\pi_1 = \pi_2$. Thus there is no net osmotic flow of solvent when the solutions are separated by a suitable semipermeable membrane. In the dilute limit this also means $i_1C_1 = i_2C_2$.

Step 2: Distinguish the other properties Isotonicity compares osmotic pressure directly. It does not, by definition, require equal boiling points, melting points or vapour pressures. Those properties also depend on the solvent and the relevant concentration scale, so they cannot replace equality of osmotic pressure as the general criterion.

Step 3: Conclusion Isotonic solutions have the same osmotic pressure at the same temperature. Hence, the correct option is (A).

Quick Tip to Solve: Translate isotonic directly into equal osmotic pressure; use $i_1C_1 = i_2C_2$ only when both solutions have the same temperature.

11. KMnO_4 acts as an oxidising agent in alkaline medium. When alkaline KMnO_4 is treated with KI, iodide ion is oxidised to:

[1 mark]

- (A) I_2
- (B) IO^-
- (C) IO_3^-
- (D) IO_4^-

Correct Answer: (C) IO_3^-

Solution:

Concept:

- Alkaline permanganate oxidises iodide, I^- , to iodate, IO_3^- .
- Oxidation increases oxidation number: iodine changes from -1 in iodide to $+5$ in iodate and loses six electrons.

Step 1: Write the oxidation in alkaline medium The balanced oxidation half-reaction is



Both atoms and charge balance. This identifies the oxygen-containing product formed when iodide is oxidised by alkaline permanganate.

Step 2: Check the listed iodine species Iodine has oxidation numbers 0, $+1$, $+5$ and $+7$ in I_2 , IO^- , IO_3^- and IO_4^- , respectively. The stated alkaline permanganate reaction gives iodate, the $+5$ species; it does not stop at iodine or hypoiodite, and periodate is not the product of this reaction.

Step 3: Conclusion Iodide is oxidised to iodate, IO_3^- . Hence, the correct option is (C).

Quick Tip to Solve: Remember the medium-specific product: alkaline permanganate converts iodide into iodate, where iodine is in oxidation state $+5$.

12. Which of the following transition metals does not show variable oxidation state?

[1 mark]

- (A) Ti
- (B) Cr
- (C) Cu
- (D) Sc

Correct Answer: (D) Sc

Solution:

Concept:

- Variable oxidation states in transition metals arise because their outer ns and $(n-1)d$ electrons can participate in bonding.
- Scandium has electronic configuration $[\text{Ar}] 3d^1 4s^2$ and shows the characteristic oxidation state $+3$ in its ordinary compounds.

Quick Tip to Solve: Use scandium's $3d^1 4s^2$ configuration: loss of all three outer electrons gives its characteristic $+3$ state.

Step 1: Examine scandium Removing the two $4s$ electrons and the one $3d$ electron gives Sc^{3+} with the stable $[\text{Ar}]$ configuration. Further removal would involve the inner closed shell, and scandium consequently does not show variable oxidation states in the usual chemistry considered here.

Step 2: Check the remaining metals Titanium shows oxidation states such as +2, +3, +4; chromium shows +2, +3, +6; and copper commonly shows +1, +2. Thus each of options (A), (B) and (C) has more than one familiar oxidation state, unlike scandium.

Step 3: Conclusion Scandium, Sc, does not show variable oxidation state in its ordinary compounds. Hence, the correct option is (D).

Quick Tip to Solve: Use scandium's $3d^1 4s^2$ configuration: loss of all three outer electrons gives its characteristic +3 state.

13. Which of the following complexes is a 'chelate' complex?

[1 mark]

- (A) $[\text{Co}(\text{NH}_3)_6]^{3+}$
- (B) $[\text{Co}(\text{en})_3]^{3+}$
- (C) $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
- (D) $[\text{CoF}_6]^{3-}$

Correct Answer: (B) $[\text{Co}(\text{en})_3]^{3+}$

Solution:

Concept:

- A chelate forms when a ligand binds to the same metal through two or more donor atoms, forming a ring that includes the metal.
- Ethylenediamine, abbreviated en, is $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, a bidentate ligand with two nitrogen donor atoms.

Step 1: Identify the ring-forming ligand In $[\text{Co}(\text{en})_3]^{3+}$, each en molecule coordinates to cobalt through both nitrogen atoms. The connecting carbon chain completes a five-membered ring with the cobalt ion. Three en ligands therefore form three chelate rings around the central metal.

Step 2: Check the other ligand sets Ammonia, chloride and fluoride are monodentate ligands in the listed complexes. Consequently, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ and $[\text{CoF}_6]^{3-}$ contain no ligand attached through two donor atoms to make a ring. Having several separate monodentate ligands does not produce chelation.

Step 3: Conclusion The chelate complex is $[\text{Co}(\text{en})_3]^{3+}$. Hence, the correct option is (B).

Quick Tip to Solve: Look for a single ligand with multiple donor atoms: en binds through two nitrogen atoms and makes a ring with the metal.

14. Optical isomerism is not shown by the complex:

[1 mark]

- (A) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (trans form)
(B) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (cis form)
(C) $[\text{Cr}(\text{ox})_3]^{3-}$
(D) $[\text{Cr}(\text{en})_3]^{3+}$

Correct Answer: (A) $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (trans form)

Solution:

Concept:

- Optical isomers are non-superimposable mirror-image forms of a chiral complex.
- For octahedral complexes with bidentate ligands such as en or oxalate (ox), the arrangement of the chelate rings determines whether the complex is chiral.

Step 1: Examine the trans arrangement In trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, the two chloride ligands occupy opposite positions. The coordination arrangement possesses symmetry that makes the mirror image superimposable, so the trans form is optically inactive.

Step 2: Compare the other three complexes The cis form of $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ has two non-superimposable mirror-image arrangements. The tris-chelate complexes $[\text{Cr}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{en})_3]^{3+}$ likewise have right-handed and left-handed arrangements of their three chelate rings, called Δ and Λ forms. Thus options (B), (C) and (D) all show optical isomerism.

Step 3: Conclusion Optical isomerism is not shown by trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. Hence, the correct option is (A).

Quick Tip to Solve: For octahedral $[\text{M}(\text{en})_2\text{X}_2]$, distinguish cis from trans: the cis arrangement is optically active, while the trans arrangement is not.

15. 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.

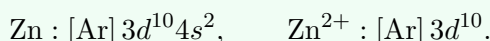
Correct Answer: (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

Solution:**Concept:**

- A transition element has an incompletely filled d subshell in its atom or in at least one of its usual oxidation states.
- In forming Zn^{2+} , the two outermost 4s electrons are lost before the 3d electrons.

Step 1: Judge Assertion (A) Zinc does not satisfy the defining requirement of a partly filled d subshell in its atom or its usual ion. It is therefore not regarded as a transition element, even though it lies in the d block. Assertion (A) is true.

Step 2: Judge Reason (R) The electronic configurations are



The 3d subshell is completely filled in both the ground-state atom and the usual oxidised state. Reason (R) is true.

Step 3: Test the explanatory link The filled d subshell is precisely why zinc fails the transition-element criterion. Thus the reason explains the assertion; the option saying both are true but unrelated is incorrect. Options that call either statement false are also excluded.

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

Quick Tip to Solve: For zinc, write both the atom and the common ion: a d^{10} configuration in each excludes transition character.

16. 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 the halogen in an alkyl halide; ease of carbon-halogen bond cleavage and leaving-group ability affect its rate.
- The C-I bond is weaker than C-Cl, and I^- is a better leaving group than Cl^- .

Step 1: Judge Assertion (A) For the same ethyl group and comparable reaction conditions, iodoethane

Quick Tip to Solve: For the same alkyl group, remember the substitution trend $\text{R-I} > \text{R-Br} > \text{R-Cl}$; weaker bonds favour halide departure.

undergoes nucleophilic substitution more readily than chloroethane. Iodide departs more easily, so Assertion (A) is true.

Step 2: Judge Reason (R) The printed reason reverses the bond-energy order. Iodine is larger than chlorine, making the carbon-iodine bond longer and weaker. Therefore

$$D(\text{C-I}) < D(\text{C-Cl}),$$

where D denotes bond dissociation energy. Reason (R) is false.

Step 3: Test the explanatory link A false reason cannot explain the true assertion. The options stating that both statements are true must be rejected, as must the option stating that the assertion is false. The required code is the one for true A and false R.

Step 4: Conclusion Assertion is true, but Reason is false. Hence, the correct option is (C).

Quick Tip to Solve: For the same alkyl group, remember the substitution trend $\text{R-I} > \text{R-Br} > \text{R-Cl}$; weaker bonds favour halide departure.

17. Assertion (A): Electrolysis of aqueous solution of NaCl gives chlorine gas at anode instead of oxygen gas.

Reason (R): Formation of oxygen gas at anode requires overpotential.

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:

- At the anode, oxidation occurs. Chloride ions can lose electrons to form chlorine: $2\text{Cl}^- \longrightarrow \text{Cl}_2 + 2\text{e}^-$.
- Overpotential is the additional electrode potential required beyond the thermodynamic value to drive an electrode process at an appreciable rate.

Step 1: Judge Assertion (A) In the usual electrolysis of aqueous sodium chloride considered here, chlorine is liberated at the anode. Chloride oxidation competes with oxidation of water, and chloride is discharged under these conditions. Thus Assertion (A) is true.

Step 2: Judge Reason (R) Oxygen evolution from water requires an appreciable overpotential. Consequently, standard electrode potentials alone do not determine which product is actually evolved

Quick Tip to Solve: When electrolysis products differ from a prediction using standard potentials, check overpotential as well as ion concentration.

at a practical rate. The additional potential required for oxygen formation makes Reason (R) true.

Step 3: Test the explanatory link The oxygen-evolution overpotential allows chloride oxidation and chlorine formation to occur preferentially in the stated electrolysis. It directly explains why the thermodynamically expected oxygen is not the observed anode product here. The option denying the explanatory link, and those declaring either statement false, are excluded.

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

Quick Tip to Solve: When electrolysis products differ from a prediction using standard potentials, check overpotential as well as ion concentration.

18. 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:

- The order of a reaction is the sum of concentration exponents in its experimentally determined rate law.
- Molecularity counts the reacting species participating in a single elementary step; it is not assigned to an overall complex reaction.

Step 1: Judge Assertion (A) Order and molecularity are not always equal. Order may be zero, fractional or integral, whereas molecularity of an elementary step is a positive integer. Their equality for a simple elementary reaction cannot be extended to every reaction. Therefore Assertion (A) is false.

Step 2: Judge Reason (R) A complex reaction proceeds through a sequence of elementary steps. In the usual rate-determining-step treatment, the slowest step controls the overall rate, while preceding equilibria may relate intermediate concentrations to reactant concentrations. Reason (R) correctly describes this picture and is true.

Step 3: Test the explanatory link Since A is false and R is true, neither of the options in which both statements are true applies. The option with a true assertion and a false reason is also ruled out. Select the code that explicitly states false A and true R.

Step 4: Conclusion Assertion is false, but Reason is true. Hence, the correct option is (D).

Quick Tip to Solve: The word "always" is the trap: determine order from the rate law and molecularity only from an elementary step.

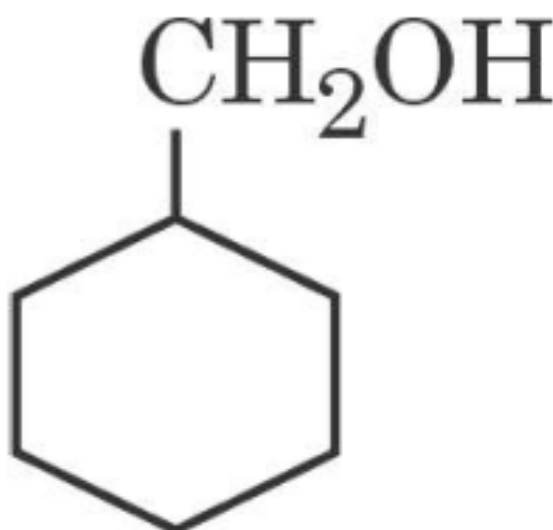
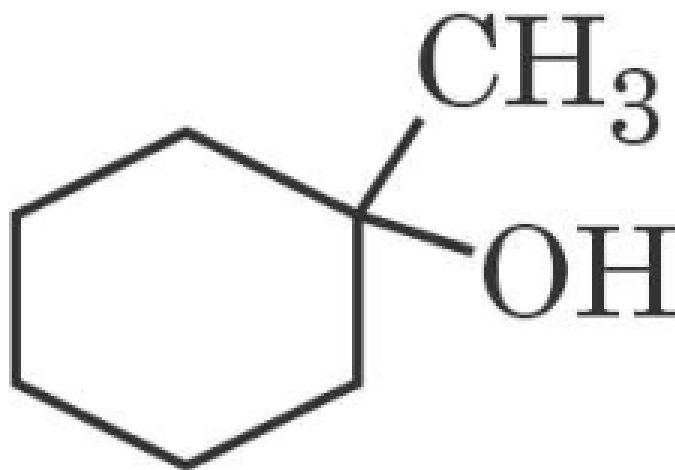
Section B (14 marks)

19. Show how you will synthesise:

(a) from a suitable alkene.

(b) from methanal using a suitable Grignard reagent.

[2 marks]



Solution:

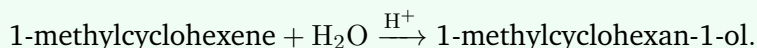
Concept:

- Acid-catalysed hydration adds water across an alkene double bond according to Markovnikov's rule: the hydroxyl group goes to the more substituted carbon.
- A Grignard reagent RMgX adds to methanal and, after acidic hydrolysis, gives the primary alcohol RCH_2OH . The carbon of methanal becomes the CH_2OH carbon.

Step 1: (a) **Choose the alkene and hydrate it** The first pictured alcohol is 1-methylcyclohexan-1-ol. Choose 1-methylcyclohexene, whose double bond includes the carbon bearing the methyl group.

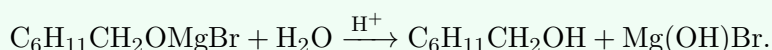
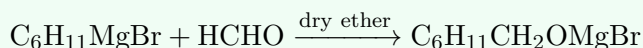
Quick Tip to Solve: For a methanal route, remove CH_2OH from the target: the remaining group is R in the required RMgX .

Hydrate it using water in the presence of dilute sulphuric acid:



Protonation gives the more stable tertiary carbocation at carbon 1; water attacks this carbon and deprotonation regenerates the acid. The hydroxyl and methyl groups therefore occupy the same ring carbon, as required.

Step 2: (b) Select the Grignard reagent and hydrolyse The second pictured alcohol is cyclohexylmethanol, $\text{C}_6\text{H}_{11}\text{CH}_2\text{OH}$. Its cyclohexyl group must come from cyclohexylmagnesium bromide, $\text{C}_6\text{H}_{11}\text{MgBr}$. First react it with methanal in dry ether, then perform acidic hydrolysis:



Dry conditions are essential during addition because water would destroy the Grignard reagent before it reacts with methanal.

Step 3: Conclusion (a) Hydrate 1-methylcyclohexene with $\text{H}_2\text{O}/\text{H}^+$. (b) Add cyclohexylmagnesium bromide to methanal in dry ether, followed by acidic hydrolysis, to obtain cyclohexylmethanol.

Quick Tip to Solve: For a methanal route, remove CH_2OH from the target: the remaining group is R in the required RMgX .

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

(a) Carbylamine reaction

(b) Gabriel phthalimide synthesis

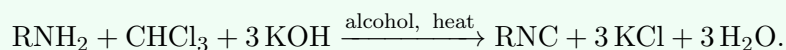
[2 marks]

Solution:

Concept:

- The carbylamine reaction converts a primary amine into an isocyanide on heating with chloroform and alcoholic potassium hydroxide.
- Gabriel phthalimide synthesis prepares primary aliphatic amines by alkylation of potassium phthalimide, followed by hydrolysis; R denotes an alkyl group and X a halogen.

Step 1: (a) Write the carbylamine equation For a primary amine RNH_2 , the balanced equation is



Here RNC is an isocyanide with an offensive smell. The reaction is given by both aliphatic and aromatic primary amines, but not by secondary or tertiary amines. The product is an isocyanide, not the nitrile RCN.

Step 2: (b) Write the Gabriel synthesis sequence First convert phthalimide into its potassium salt,

Quick Tip to Solve: Keep the nitrogen linkage straight: carbylamine forms $\text{R}-\text{NC}$, whereas Gabriel synthesis releases $\text{R}-\text{NH}_2$.

then allow it to react with an alkyl halide:



The two carbonyl groups shown in these condensed formulae belong to the cyclic phthalimide group. Alkaline hydrolysis of the N-alkyl derivative releases the primary amine:



The alkylation proceeds by nucleophilic substitution. Aryl halides do not undergo this substitution readily, so this method does not prepare primary aromatic amines.

Step 3: Conclusion Carbylamine formation gives RNC from a primary amine. Gabriel synthesis gives RNH_2 through potassium phthalimide, its N-alkyl derivative, and hydrolysis.

Quick Tip to Solve: Keep the nitrogen linkage straight: carbylamine forms $\text{R}-\text{NC}$, whereas Gabriel synthesis releases $\text{R}-\text{NH}_2$.

21(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:

- Animals store excess glucose as glycogen, a highly branched polysaccharide that can be hydrolysed to release glucose when required.
- The configuration of the glucose units and their glycosidic linkages determines the structure of a polysaccharide.

Step 1: Identify the storage carbohydrate and its location (i) Carbohydrates are stored in the animal body in the form of **glycogen**. One organ containing glycogen is the **liver**. Glycogen is also stored in skeletal muscles; its branched structure provides many sites from which glucose units can be released.

Step 2: Compare the glucose units and linkages (ii) Starch is a polymer of α -D-glucose, whereas cellulose is a polymer of β -D-glucose. In starch, amylose has $\alpha(1 \rightarrow 4)$ linkages, while amylopectin also has $\alpha(1 \rightarrow 6)$ branch linkages. Cellulose has $\beta(1 \rightarrow 4)$ linkages and forms straight, unbranched chains. Thus, the basic difference is the alpha versus beta configuration of the glucose residues and their linkages, not the identity of the monosaccharide as glucose.

Step 3: Conclusion (i) Glycogen is the carbohydrate reserve in animals; the liver is one storage organ. (ii) Starch contains α -D-glucose units, while cellulose contains β -D-glucose units.

Quick Tip to Solve: Pair animal storage with glycogen, and distinguish starch from cellulose by remembering alpha linkages versus beta linkages.

21(b). Differentiate between:

(i) Peptide linkage and Glycosidic linkage

(ii) Nucleoside and Nucleotide

[2 marks]

Solution:

Concept:

- Condensation joins smaller biomolecules with elimination of water; the nature of the connecting group distinguishes peptide and glycosidic linkages.
- A nucleoside contains a nitrogenous base and a pentose sugar. Adding a phosphate group gives a nucleotide, the building unit of nucleic acids.

Step 1: Differentiate the two linkages (i) 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 loss of water. It joins amino acid residues in proteins. A **glycosidic linkage**, $\text{C}-\text{O}-\text{C}$, joins monosaccharide residues through an oxygen atom, involving the anomeric carbon of a sugar. It is formed by condensation of hydroxyl groups and occurs in disaccharides and polysaccharides.

Step 2: Differentiate their components (ii) A **nucleoside** consists of a nitrogenous base attached to a pentose sugar by an N-glycosidic bond; it has no phosphate group. A **nucleotide** consists of the same base-sugar unit together with a phosphate group esterified to the sugar. For example, adenosine is a nucleoside, whereas adenosine monophosphate is a nucleotide.

Step 3: Conclusion Peptide bonds join amino acids, whereas glycosidic bonds join sugar residues. A nucleoside is base plus sugar; a nucleotide is base plus sugar plus phosphate.

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

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

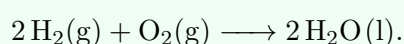
[2 marks]

Solution:

Concept:

- A galvanic cell converts the chemical energy of a spontaneous redox reaction directly into electrical energy by separating oxidation and reduction at two electrodes.
- A fuel cell continues to operate while fuel and oxidant are supplied continuously to its electrodes and the reaction products are removed.

Step 1: Define a fuel cell A **fuel cell** is a galvanic cell in which the chemical energy of the combustion reaction of a continuously supplied fuel and oxidant is converted directly into electrical energy. For example, a hydrogen-oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant, with the overall reaction



The reactants are supplied from outside the cell rather than being limited to an initial quantity stored

Quick Tip to Solve: Include continuous fuel supply in the definition, and use the hydrogen-oxygen cell to explain why water is a clean product.

within it.

Step 2: State two advantages 1. **High efficiency:** Direct conversion of chemical energy into electrical energy gives fuel cells higher energy-conversion efficiency than conventional methods that first produce heat and then mechanical work.

2. **Clean operation:** A hydrogen–oxygen fuel cell produces water as its reaction product, so it does not emit smoke or carbon dioxide during operation. This environmental advantage refers specifically to the cell's operation with hydrogen and oxygen.

Step 3: Conclusion A fuel cell generates electricity directly from a continuously supplied fuel and oxidant. Two advantages are high efficiency and clean operation, as illustrated by the hydrogen–oxygen cell.

Quick Tip to Solve: Include continuous fuel supply in the definition, and use the hydrogen–oxygen cell to explain why water is a clean product.

OR

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

[2 marks]

Solution:

Concept:

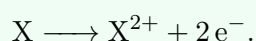
- A more negative standard reduction potential indicates a greater tendency of the metal to undergo oxidation when coupled to a metal with a higher reduction potential.
- A sacrificial coating protects iron by oxidising preferentially, making iron the cathode. The protection can continue even when a small scratch exposes the iron surface.

Step 1: Compare the reduction potentials The given values are ordered as

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

Thus, metal X is more readily oxidised than iron, whereas metal Y is less readily oxidised than iron. A coating should supply electrons by its own oxidation to protect exposed iron from becoming the anode.

Step 2: Explain sacrificial protection For X coupled to iron, X acts as the sacrificial anode:



Iron acts as the cathode and is protected from oxidation. By contrast, if a coating of Y is scratched in the presence of an electrolyte, iron becomes the anode of the iron–Y couple and undergoes corrosion. Although an intact Y coating can form a physical barrier, it does not provide sacrificial protection at a scratch.

Step 3: Conclusion X is the better coating metal because its more negative reduction potential

Quick Tip to Solve: For sacrificial protection, select the coating with a reduction potential more negative than that of iron, not the more noble metal.

makes it oxidise preferentially and protect iron sacrificially.

Quick Tip to Solve: For sacrificial protection, select the coating with a reduction potential more negative than that of iron, not the more noble metal.

23. On mixing liquid X and liquid Y, volume of the resulting solution decreases. What type of deviation from Raoult's law is shown by the resulting solution? What change in temperature would you observe after mixing liquids X and Y? [2 marks]

Solution:

Concept:

- Raoult's law for an ideal liquid mixture is $p_i = x_i p_i^\circ$, where x_i is the mole fraction and p_i° is the pure liquid vapour pressure.
- Stronger unlike-molecule attractions favour contraction on mixing and reduce the escaping tendency of the liquid molecules. Such mixing is exothermic, with $\Delta H_{\text{mix}} < 0$.

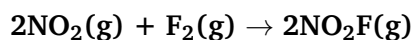
Step 1: Relate contraction to molecular attraction The decrease in volume indicates that the molecules pack more closely after mixing: attractions between X and Y molecules are stronger than those in the separate liquids. Consequently, molecules escape into the vapour phase less readily. The partial vapour pressures, and hence the total vapour pressure, lie below the ideal values predicted by Raoult's law.

Step 2: Identify the thermal effect of mixing Formation of stronger X–Y attractions releases more energy than is required to disrupt the original attractions. The mixing therefore releases heat. This heat warms the mixture, so an increase in temperature is observed immediately after mixing.

Step 3: Conclusion The solution shows **negative deviation from Raoult's law**, and its **temperature increases** on mixing because the process is exothermic.

Quick Tip to Solve: Link contraction to stronger X–Y attractions: lower vapour pressure means negative deviation, while heat release means a temperature rise.

24. The following data were obtained for the reaction:



Determine the overall order of reaction.

[2 marks]

Experiment No.	$[\text{NO}_2]/\text{M}$	$[\text{F}_2]/\text{M}$	Initial rate M min^{-1}
1	0.2	0.05	6×10^{-3}
2	0.4	0.05	1.2×10^{-2}
3	0.8	0.10	4.8×10^{-2}

Solution:

Concept:

- The experimental rate law is $r = k[\text{NO}_2]^m[\text{F}_2]^n$, where k is the rate constant, m, n are the partial orders, and r is the initial rate.
- Compare experiments at the same temperature to cancel k . The overall reaction order is $m + n$; it is not obtained by simply adding stoichiometric coefficients.

Step 1: Compare experiments 1 and 2 The concentration of F_2 remains 0.05 M, while that of NO_2 doubles from 0.2 to 0.4 M. The rate also doubles:

$$\frac{r_2}{r_1} = \frac{1.2 \times 10^{-2}}{6 \times 10^{-3}} = 2 = \left(\frac{0.4}{0.2}\right)^m = 2^m.$$

Therefore $m = 1$: the reaction is first order with respect to NO_2 .

Step 2: Compare experiments 2 and 3 Here both reactant concentrations double, and the rate increases fourfold. Account for the already established first-order dependence on NO_2 :

$$\frac{r_3}{r_2} = \frac{4.8 \times 10^{-2}}{1.2 \times 10^{-2}} = 4 = \left(\frac{0.8}{0.4}\right)^1 \left(\frac{0.10}{0.05}\right)^n = 2 \times 2^n.$$

Thus $2^n = 2$, giving $n = 1$. The rate law is $r = k[\text{NO}_2][\text{F}_2]$.

Step 3: Conclusion The overall order is $m + n = 1 + 1 = 2$. The reaction is first order in each reactant and second order overall.

Quick Tip to Solve: First use experiments 1 and 2 to isolate the order in NO_2 ; then divide the fourfold rate change in experiments 2 and 3 by the known twofold NO_2 effect.

25. Give reasons for the following:

(a) Carboxylic carbon is less electrophilic than Carbonyl carbon of aldehydes and ketones.

(b) Propanal is more reactive than Propanone towards addition of HCN.

[2 marks]

Solution:

Concept:

- A nucleophile attacks an electron-deficient carbon atom; electron donation to that carbon reduces its electrophilicity and slows nucleophilic addition.
- Both electronic effects and steric hindrance control carbonyl reactivity. Alkyl groups donate electron density through their $+I$ effect and also hinder approach to the carbonyl carbon.

Step 1: Explain the effect of the hydroxyl group in a carboxylic acid In RCOOH , a lone pair on the hydroxyl oxygen is delocalised towards the carbonyl group by resonance. This electron donation reduces the partial positive charge on the carboxylic carbon. Aldehydes and ketones do not have this additional adjacent oxygen donating its lone pair. Hence the carboxylic carbon is less electron deficient and less electrophilic than their carbonyl carbon.

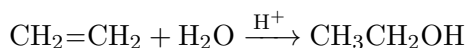
Step 2: Compare propanal and propanone during cyanide attack Addition of HCN involves attack by the nucleophile CN^- at the carbonyl carbon, followed by protonation. Propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, has one alkyl group and one hydrogen attached to this carbon. Propanone, CH_3COCH_3 , has two electron-donating alkyl groups, which lower its carbonyl carbon's electrophilicity more strongly. These two alkyl groups also make nucleophilic approach more hindered than in the aldehyde, where one substituent is the much smaller hydrogen atom.

Step 3: Conclusion (a) Resonance donation from the hydroxyl oxygen lowers the electrophilicity of carboxylic carbon. (b) Propanal adds HCN more readily because its carbonyl carbon is more electrophilic and less sterically hindered than that of propanone.

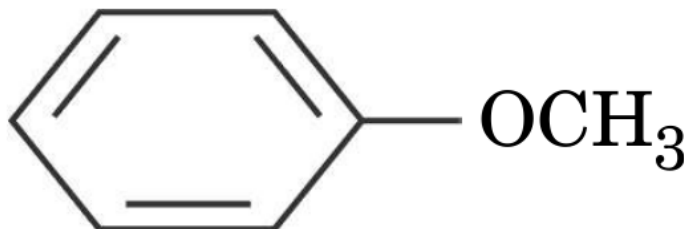
Quick Tip to Solve: For carbonyl addition, check electron donation first and crowding second: replacing an aldehydic H with an alkyl group reduces reactivity in both ways.

Section C (15 marks)

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



(b) Write the structures of the products obtained by heating the following compound with conc. HI. [3 marks]



Solution:

Concept:

- Acid-catalysed hydration is electrophilic addition of water to an alkene through protonation, nucleophilic attack by water, and deprotonation. The acid catalyst is regenerated.
- In an aryl methyl ether, iodide attacks the methyl carbon after oxygen protonation. The aryl-oxygen bond has partial double-bond character and cannot undergo the usual S_N2 displacement at the ring carbon.

Step 1: Protonate ethene in part (a) The electron-rich double bond attacks a proton supplied by hydronium. A carbon-hydrogen bond forms and the other carbon becomes the carbocation centre:



In electron-pair terms, the alkene π electrons move towards H, while the hydronium O-H bond electrons return to oxygen. Ethene is symmetrical, so either carbon gives the same ethyl carbocation.

Step 2: Add water to the carbocation A lone pair on the oxygen of a water molecule attacks the positively charged carbon. This forms a carbon-oxygen bond and gives protonated ethanol:



Step 3: Remove a proton and regenerate the catalyst Another water molecule removes a proton from the oxonium ion. The O-H bond electrons remain on the alcohol oxygen, producing neutral ethanol and regenerating hydronium:

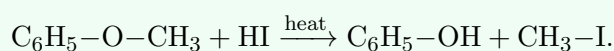


Combining these stages gives the acid-catalysed conversion of ethene and water into ethanol.

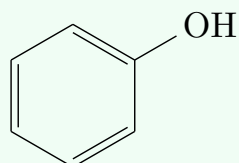
Step 4: Cleave anisole in part (b) Concentrated HI first protonates the ether oxygen. The iodide ion

Quick Tip to Solve: Track the charges during hydration: carbocation, oxonium ion, then neutral alcohol. For anisole with HI, cleave O-CH₃ and retain the oxygen on the ring.

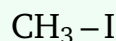
then attacks the unhindered methyl carbon by S_N2 displacement, breaking the methyl-oxygen bond. The oxygen remains attached to the aromatic ring:



Thus the products are phenol and iodomethane. Phenol does not undergo replacement of its aryl-oxygen bond by iodide under these conditions.



Phenol



Iodomethane

Structures of phenol and iodomethane

Step 5: Conclusion (a) Protonation of ethene, water attack and deprotonation form ethanol, $\text{CH}_3\text{CH}_2\text{OH}$. (b) Heating anisole with concentrated HI gives **phenol**, $\text{C}_6\text{H}_5\text{OH}$, and **iodomethane**, CH_3I .

Quick Tip to Solve: Track the charges during hydration: carbocation, oxonium ion, then neutral alcohol. For anisole with HI, cleave $\text{O}-\text{CH}_3$ and retain the oxygen on the ring.

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

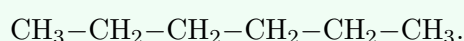
[3 marks]

Solution:

Concept:

- The open-chain structure of D-glucose is $\text{CHO}-(\text{CHOH})_4-\text{CH}_2\text{OH}$. Its terminal aldehyde, primary alcohol and four secondary alcohol groups determine its reactions.
- Prolonged heating with HI reduces the oxygen-containing groups. Mild oxidation affects the aldehyde, whereas concentrated HNO_3 oxidises both terminal groups.
- HCN adds across the carbonyl group to form a cyanohydrin, introducing a new carbon atom through the cyanide group.

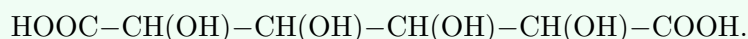
Step 1: Identify the product with HI (a) On prolonged heating with HI, the oxygen-containing groups are reduced without changing the straight chain of six carbon atoms. The product structure is



Quick Tip to Solve: Track the two ends of glucose: bromine water oxidises only the aldehyde end, concentrated nitric acid oxidises both ends, and HCN adds one carbon at the aldehyde end.

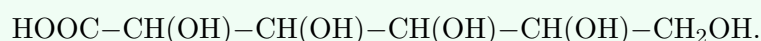
This is n-hexane; its formation establishes that the six carbon atoms of glucose are linked in an unbranched chain.

Step 2: Oxidise both ends with concentrated nitric acid (b) Concentrated HNO_3 oxidises the aldehyde group and the terminal primary alcohol group to carboxylic acid groups. The four intervening secondary alcohol groups remain in the product structure:



The product is saccharic acid, also called D-glucaric acid.

Step 3: Oxidise only the aldehyde with bromine water (c) Bromine water is a mild oxidising agent. It converts $-\text{CHO}$ into $-\text{COOH}$, leaving the terminal $-\text{CH}_2\text{OH}$ group unchanged. The product is gluconic acid:



Step 4: Add hydrogen cyanide to the aldehyde group (d) Addition of HCN changes the aldehyde carbon into a carbon bearing both hydroxyl and cyanide groups. The cyanohydrin has the condensed structure



The original four stereocentres retain their configurations, while a new stereocentre is formed at the former carbonyl carbon. Thus the reaction can give two cyanohydrins differing at this new centre.

Step 5: Conclusion The products are (a) n-hexane, (b) saccharic acid, (c) gluconic acid and (d) glucose cyanohydrin, with structures shown above. Any three of these reactions satisfy the question.

Quick Tip to Solve: Track the two ends of glucose: bromine water oxidises only the aldehyde end, concentrated nitric acid oxidises both ends, and HCN adds one carbon at the aldehyde end.

28. 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 k is the rate constant, A the frequency factor, E_a the activation energy and T the absolute temperature.
- For the same reactant concentrations, the reaction rate is proportional to k . Taking the ratio at two temperatures eliminates A , treated as constant over this small interval.

Step 1: Express the temperatures in kelvin The Arrhenius equation uses absolute temperatures, so convert both Celsius values before taking their reciprocals:

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

Quick Tip to Solve: Convert both temperatures to kelvin first; then replace the reciprocal difference by $(T_2 - T_1)/(T_1 T_2)$ to avoid a subtraction error.

Because the rate doubles under otherwise identical conditions, $k_2/k_1 = 2$. The gas constant is $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, which gives the activation energy in joules per mole.

Step 2: Apply the two-temperature Arrhenius equation Subtracting the logarithmic equations at the two temperatures gives

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

The temperature factor is

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

Both the logarithm of the rate ratio and this reciprocal-temperature difference are positive, as required for a positive activation energy.

Step 3: Substitute and evaluate the energy Rearrange to isolate E_a and use the given common logarithm $\log 2 = 0.3010$:

$$\begin{aligned} E_a &= \frac{2.303R \log 2}{(1/300) - (1/310)} \\ &= \frac{2.303 \times 8.314 \times 0.3010 \times 93000}{10} \\ &\approx 5.36 \times 10^4 \text{ J mol}^{-1}. \end{aligned}$$

Divide the value in joules per mole by 1000 to express it in kilojoules per mole. The given values of $\log 3$ and $\log 4$ are unnecessary because the rate ratio is two.

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; then replace the reciprocal difference by $(T_2 - T_1)/(T_1 T_2)$ to avoid a subtraction error.

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:

- Depression in freezing point is $\Delta T_f = iK_f m$, where i is the van't Hoff factor, K_f the cryoscopic constant and m the molality calculated before association.
- Acetic acid associates in benzene: $2 \text{ CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2$. Dimerisation reduces the number of solute particles, so $i < 1$.
- If α is the fraction of the original acid molecules that associate into dimers, particle counting gives $i = 1 - \alpha/2$.

Step 1: Calculate the initial molality Find the initial amount of acid and convert the solvent mass to kilograms:

$$n = \frac{0.3}{60} = 0.005 \text{ mol}, \quad w_{\text{benzene}} = \frac{30}{1000} = 0.030 \text{ kg}.$$

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; $1 - i$ is the fractional loss of particles, not the fraction of acid molecules associated.

Hence the molality based on the normal molar mass is

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

Step 2: Find the van't Hoff factor Without association, the expected freezing-point depression would be

$$(\Delta T_f)_{\text{normal}} = K_f m = 5.12 \times \frac{1}{6} = 0.85333 \text{ K}.$$

A temperature difference of 0.45°C is also 0.45 K . Thus

$$i = \frac{(\Delta T_f)_{\text{observed}}}{(\Delta T_f)_{\text{normal}}} = \frac{0.45}{5.12/6} = 0.52734375.$$

Step 3: Convert the particle reduction into association From one mole of acid, $1 - \alpha$ mole remains unassociated and $\alpha/2$ mole of dimers forms. Counting these particles gives

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

Solving for the association fraction gives

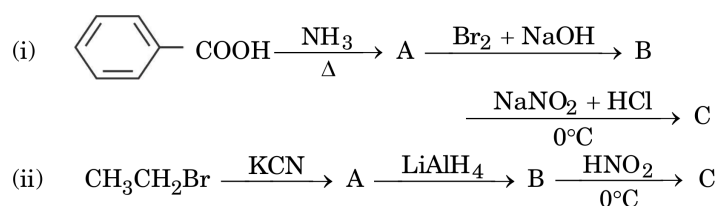
$$\begin{aligned}\alpha &= 2(1 - i) = 2(1 - 0.52734375) \\ &= 0.9453125, \\ \alpha \times 100 &= 94.53125\%.\end{aligned}$$

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

Quick Tip to Solve: For dimerisation use $\alpha = 2(1 - i)$; $1 - i$ is the fractional loss of particles, not the fraction of acid molecules associated.

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

[3 marks]



Solution:

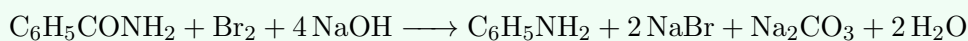
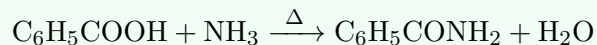
Concept:

- Heating a carboxylic acid with ammonia forms its amide. Hofmann bromamide degradation converts RCONH_2 into RNH_2 , removing the carbonyl carbon.
- Cyanide substitution adds one carbon to an alkyl chain; reduction of RCN gives RCH_2NH_2 without removing a carbon.

Quick Tip to Solve: Track carbon atoms: KCN adds one, nitrile reduction retains it, and Hofmann degradation removes the amide carbonyl carbon.

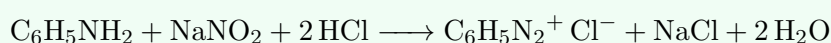
- At 0°C, a primary aromatic amine forms a diazonium salt with nitrous acid, whereas a primary aliphatic amine gives an alcohol with evolution of nitrogen.

Step 1: Identify the amide and amine in sequence (i) Benzoic acid first forms ammonium benzoate with ammonia; heating removes water and gives benzamide. Bromine and sodium hydroxide then cause Hofmann degradation:



Thus A is benzamide, $\text{C}_6\text{H}_5-\text{C}(=\text{O})-\text{NH}_2$, and B is aniline, $\text{C}_6\text{H}_5-\text{NH}_2$. The phenyl group is retained, but the amide carbonyl carbon is lost.

Step 2: Diazotise aniline in sequence (i) Sodium nitrite and hydrochloric acid generate nitrous acid in situ. In the cold, aniline gives benzenediazonium chloride:



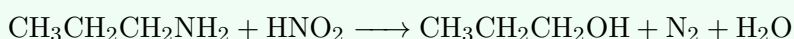
C therefore has the structure $\text{C}_6\text{H}_5-\text{N}\equiv\text{N}^+ \text{Cl}^-$. The low temperature retains the diazonium salt; heating with water would instead lead to phenol.

Step 3: Follow the carbon chain in sequence (ii) Potassium cyanide replaces bromide through its carbon end, giving propanenitrile rather than an isocyanide. Lithium aluminium hydride reduces the nitrile group to a primary amino group:



Hence A is $\text{CH}_3\text{CH}_2-\text{C}\equiv\text{N}$ and B is $\text{CH}_3\text{CH}_2\text{CH}_2-\text{NH}_2$; both have three carbon atoms.

Step 4: React the aliphatic amine with nitrous acid Propan-1-amine forms an unstable aliphatic diazonium intermediate, which loses nitrogen and gives propan-1-ol:



This contrasts with the cold aromatic diazonium salt in sequence (i).

Step 5: 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 atoms: KCN adds one, nitrile reduction retains it, and Hofmann degradation removes the amide carbonyl carbon.

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

(i) Aniline to p-bromoaniline

(ii) Ethanoic acid to methanamine

(iii) Butanenitrile to 1-aminobutane

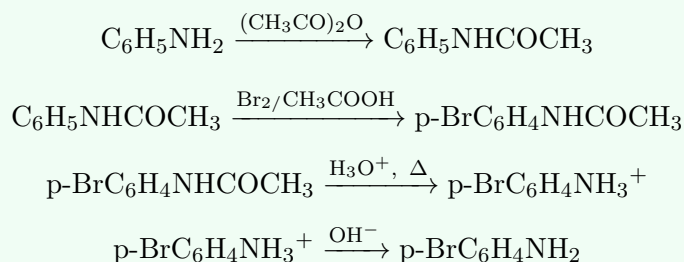
[3 marks]

Solution:

Concept:

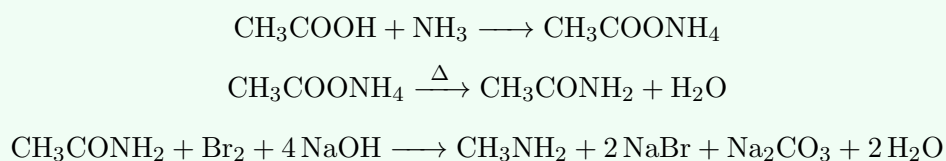
- Protect the strongly activating amino group of aniline by acetylation before bromination, then hydrolyse the protecting group.
- Hofmann bromamide degradation converts an amide into a primary amine with one carbon atom fewer. Nitrile reduction retains the nitrile carbon as $-\text{CH}_2\text{NH}_2$.

Step 1: Convert aniline into p-bromoaniline Acetylate aniline with acetic anhydride to form acetanilide. The protected group is still ortho/para directing, but its activating effect is reduced. Bromination in acetic acid gives predominantly the para product; hydrolyse the isolated para derivative and liberate the free amine:



Direct bromination of aniline with bromine water would give 2,4,6-tribromoaniline, so the protection step is essential for selective monobromination.

Step 2: Convert ethanoic acid into methanamine Treat ethanoic acid with ammonia and heat the resulting ammonium ethanoate to obtain ethanamide. Then use bromine and aqueous sodium hydroxide:



The carbonyl carbon leaves during Hofmann degradation, reducing the two-carbon starting material to one-carbon methanamine.

Step 3: Reduce butanenitrile to 1-aminobutane Reduce butanenitrile with lithium aluminium hydride in dry ether, followed by hydrolysis. The nitrile carbon becomes the terminal amino-bearing carbon:



All four carbon atoms are retained. The product is butan-1-amine, also called 1-aminobutane.

Step 4: Conclusion (i) Acetylation, para bromination and deprotection give p-bromoaniline.

Quick Tip to Solve: Protect aniline before monobromination; use Hofmann degradation to remove one carbon and nitrile reduction to retain the chain length.

- (ii) Amide formation followed by Hofmann degradation gives CH_3NH_2 .
(iii) Reduction of butanenitrile with LiAlH_4 , followed by hydrolysis, gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$.

Quick Tip to Solve: Protect aniline before monobromination; use Hofmann degradation to remove one carbon and nitrile reduction to retain the chain length.

Section D (8 marks)

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

31. 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:

[4 marks]

31(i). 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.

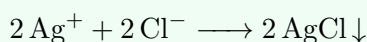
[1 mark]

Solution:

Concept:

- Only ionisable chloride ions outside the coordination sphere give an immediate precipitate of AgCl with AgNO_3 .
- Werner's secondary valency is the coordination number: the number of donor atoms directly bonded to the metal ion.

Step 1: Place the chloride ions outside the coordination sphere One mole of the compound gives two moles of AgCl , so both chloride ions are ionisable counter-ions:



Neither chloride ion is coordinated to nickel. The coordination entity therefore carries a charge of +2.

Step 2: Assign the water ligands and count donor atoms The six water molecules coordinate to Ni^{2+} , each through one oxygen donor atom. The complex cation is $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, balanced by two external chloride ions. Its coordination number is six, whereas nickel's oxidation state and primary valency are two.

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

Quick Tip to Solve: Use the moles of AgCl to count external chlorides; count coordinated water donors separately to obtain the secondary valency.

31(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 differ by exchange of an anionic ligand inside the coordination sphere with a counter-ion outside it.
- Name ligands alphabetically before the metal; state the metal's oxidation number in Roman numerals and then name the counter-ion.

Step 1: Exchange the coordinated and external anions In $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$, sulfate is coordinated and chloride is outside the sphere. Exchanging these ions gives the ionisation isomer $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$. Both compounds have the same overall composition, but liberate different counter-ions in solution.

Step 2: Determine the oxidation number and construct the name The external sulfate ion has charge -2 , so the complex ion has charge $+2$. Ammonia is neutral and the chlorido ligand has charge -1 . If cobalt's oxidation number is x ,

$$x + 5(0) - 1 = +2 \Rightarrow x = +3.$$

The ligands are named ammine and chlorido, in that alphabetical order; the multiplier penta does not affect alphabetisation. Since the complex ion is cationic, the metal name remains cobalt.

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: First swap sulfate and chloride across the brackets, then calculate cobalt's charge; naming the original complex would answer a different question.

31(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: Ni = 28, Fe = 26]

[2 marks]

Solution:

Concept:

- In valence bond theory, vacant metal orbitals hybridise to accept ligand lone pairs. Four sp^3 orbitals give tetrahedral geometry; six d^2sp^3 orbitals give octahedral geometry.
- A complex with unpaired electrons is paramagnetic; one with all electrons paired is diamagnetic. First determine the metal oxidation state and its d -electron count.

Step 1: Analyse nickel tetracarbonyl In $[\text{Ni}(\text{CO})_4]$, the neutral CO ligands leave nickel in oxidation state zero. Free nickel is $[\text{Ar}]3d^84s^2$. In the presence of the strong-field CO ligands, the electrons pair to give a filled $3d^{10}$ set, leaving the $4s$ orbital empty. One $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals for ligand donation. This gives a tetrahedral arrangement, with no unpaired electrons.

Step 2: Analyse hexacyanidoferrate(III) Let the iron oxidation state be x . Then $x + 6(-1) = -3$, so

Quick Tip to Solve: Strong-field does not always mean diamagnetic: the odd d^5 electron count of Fe^{3+} leaves one electron unpaired even after pairing.

$x = +3$. Thus Fe^{3+} is $[\text{Ar}]3d^5$. Strong-field CN^- causes pairing in the $3d$ orbitals: the five electrons occupy three orbitals as two pairs and one single electron. The two vacant $3d$ orbitals, one $4s$ and three $4p$ orbitals undergo d^2sp^3 hybridisation. The complex is octahedral and retains one unpaired electron.

Step 3: Conclusion (1) $[\text{Ni}(\text{CO})_4]$: sp^3 , tetrahedral and diamagnetic. (2) $[\text{Fe}(\text{CN})_6]^{3-}$: d^2sp^3 , octahedral and paramagnetic, with one unpaired electron.

Quick Tip to Solve: Strong-field does not always mean diamagnetic: the odd d^5 electron count of Fe^{3+} leaves one electron unpaired even after pairing.

OR

31(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:

- Spin depends on the competition between crystal-field splitting and pairing energy P . Electrons pair in lower orbitals only when the energy saved exceeds the pairing cost.
- An inner orbital octahedral complex uses two inner $3d$ orbitals in d^2sp^3 hybridisation; an outer orbital complex uses two $4d$ orbitals in sp^3d^2 hybridisation.

Step 1: Compare tetrahedral splitting with pairing energy Tetrahedral crystal-field splitting Δ_t is small: for the same metal and ligands, $\Delta_t \approx \frac{4}{9}\Delta_o$, where Δ_o is octahedral splitting. Ordinarily $\Delta_t < P$, so promoting an electron to a higher tetrahedral level costs less energy than pairing it in a lower level. Electrons therefore remain unpaired as far as possible, producing high-spin rather than low-spin tetrahedral complexes.

Step 2: Compare the vacant orbitals of cobalt and nickel In $[\text{Co}(\text{NH}_3)_6]^{3+}$, Co^{3+} is $3d^6$. With NH_3 and the high charge of cobalt(III), its six $3d$ electrons pair in three orbitals, leaving two $3d$ orbitals vacant. These participate in d^2sp^3 hybridisation, making the complex inner orbital.

In $[\text{Ni}(\text{NH}_3)_6]^{2+}$, Ni^{2+} is $3d^8$. Even with maximum pairing, eight electrons require at least four $3d$ orbitals; two vacant $3d$ orbitals cannot be provided. The complex uses $4s$, three $4p$ and two $4d$ orbitals, giving outer orbital sp^3d^2 hybridisation.

Step 3: Conclusion Small tetrahedral splitting does not favour pairing. The cobalt(III) complex can supply two empty inner $3d$ orbitals, whereas the nickel(II) complex must use outer $4d$ orbitals.

Quick Tip to Solve: For an octahedral complex, ask whether two inner d orbitals can be empty: a d^8 ion cannot provide them even after maximum pairing.

32. 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:

[4 marks]

32(i). What happens when bromobenzene is treated with Mg in the presence of dry ether? [1 mark]

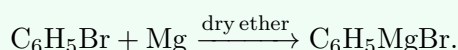
Solution:

Concept:

- Aryl halides react with magnesium in anhydrous ether to form organomagnesium halides, called Grignard reagents.
- Magnesium inserts into the carbon-halogen bond. Moisture must be excluded because water decomposes the organomagnesium product.

Step 1: Identify the organomagnesium compound Bromobenzene supplies the phenyl group, C_6H_5 . In dry ether, magnesium enters between this group and bromine, so the product is phenylmagnesium bromide.

Step 2: Write the reaction under dry conditions The reaction is



Ether provides the anhydrous medium needed to prepare the Grignard reagent; the product contains a carbon-magnesium bond.

Step 3: Conclusion Bromobenzene forms phenylmagnesium bromide, C_6H_5MgBr , a Grignard reagent.

Quick Tip to Solve: In a Grignard preparation, insert Mg between the organic group and its halogen, and always specify dry ether.

32(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:

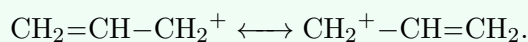
Concept:

- The slow step of an S_N1 reaction is carbon-halogen bond ionisation to form a carbocation. Greater carbocation stability gives faster ionisation.
- Resonance stabilises allylic carbocations, while hyperconjugation and the electron-releasing inductive effect stabilise tertiary alkyl carbocations.

Step 1: Compare allyl chloride with propyl chloride $CH_2=CH-CH_2Cl$ gives a resonance-stabilised

Quick Tip to Solve: For S_N1 , remove the halide mentally and compare carbocations; do not use the steric-hindrance order for S_N2 .

allylic carbocation:



In contrast, $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ would form a primary propyl carbocation without resonance stabilisation. Allyl chloride therefore reacts faster.

Step 2: Compare tert-butyl chloride with methyl chloride $(\text{CH}_3)_3\text{CCl}$ gives a tertiary carbocation stabilised by three methyl groups through hyperconjugation and the $+I$ effect. CH_3Cl would have to form the highly unstable methyl carbocation. Hence tert-butyl chloride reacts faster by the $\text{S}_{\text{N}}1$ mechanism.

Step 3: Conclusion The faster compounds are (1) $\text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ and (2) $(\text{CH}_3)_3\text{CCl}$.

Quick Tip to Solve: For $\text{S}_{\text{N}}1$, remove the halide mentally and compare carbocations; do not use the steric-hindrance order for $\text{S}_{\text{N}}2$.

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

(1) 1-chlorobutane

(2) but-1-ene.

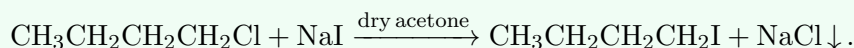
[2 marks]

Solution:

Concept:

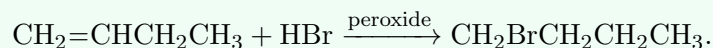
- The Finkelstein reaction replaces chloride or bromide in a primary haloalkane by iodide using NaI in dry acetone. Precipitation of NaCl or NaBr drives the reaction forward.
- In the presence of peroxide, HBr adds to an unsymmetrical alkene in the anti-Markovnikov direction. This peroxide effect applies to HBr , not to HI .

Step 1: Prepare the iodide from 1-chlorobutane Treat 1-chlorobutane with sodium iodide in dry acetone:

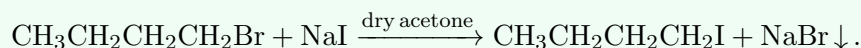


Iodide displaces chloride by nucleophilic substitution at the primary carbon. Sodium chloride precipitates because it is poorly soluble in acetone.

Step 2: Convert but-1-ene through 1-bromobutane First add HBr in the presence of peroxide to place bromine on the terminal carbon:



Then apply the Finkelstein reaction to the resulting 1-bromobutane:



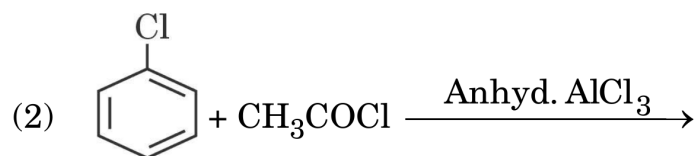
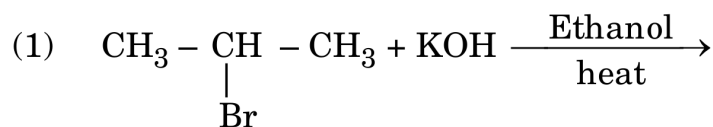
Direct addition of HI to but-1-ene would mainly give 2-iodobutane; peroxide cannot reverse the orientation of HI addition.

Step 3: Conclusion Use NaI in dry acetone for 1-chlorobutane. For but-1-ene, use HBr /peroxide first, followed by NaI in dry acetone, to obtain 1-iodobutane.

Quick Tip to Solve: To obtain a terminal iodide from a terminal alkene, first make the terminal bromide with HBr /peroxide, then exchange bromide for iodide.

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

[2 marks]

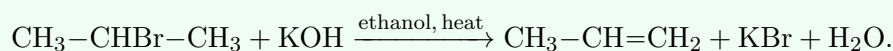


Solution:

Concept:

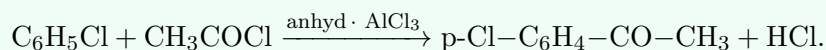
- On heating with alcoholic KOH, a haloalkane undergoes beta-elimination: a hydrogen atom from a carbon adjacent to the halogen-bearing carbon and the halogen are removed, forming a carbon-carbon double bond.
- Friedel-Crafts acylation introduces an acyl group into an aromatic ring using an acyl chloride and anhydrous AlCl_3 . Chlorine is deactivating but ortho/para-directing; the less crowded para product predominates.

Step 1: Eliminate hydrogen bromide from 2-bromopropane In $\text{CH}_3 - \text{CHBr} - \text{CH}_3$, the two methyl groups are equivalent. Removal of a beta-hydrogen from either methyl group together with bromine from the middle carbon therefore gives the same alkene:



The required product structure is $\text{CH}_3 - \text{CH} = \text{CH}_2$, propene. The hot alcoholic conditions favour elimination; aqueous alkali would favour substitution instead.

Step 2: Introduce the acetyl group into chlorobenzene Anhydrous AlCl_3 activates ethanoyl chloride, CH_3COCl , to generate the acylating electrophile. Chlorine directs electrophilic substitution to the ortho and para positions. The para position has less steric crowding between chlorine and the incoming acetyl group, so the major product is para-chloroacetophenone:



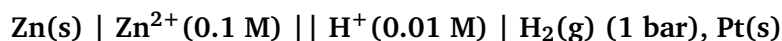
In this condensed structure, Cl and $-\text{COCH}_3$ occupy positions 1 and 4 on the benzene ring; the ortho isomer is the minor product.

Step 3: Conclusion The major products are (1) propene, $\text{CH}_3 - \text{CH} = \text{CH}_2$, and (2) para-chloroacetophenone, $\text{p-Cl-C}_6\text{H}_4\text{-CO-CH}_3$, with the two substituents para to each other.

Quick Tip to Solve: Read the solvent first: hot alcoholic alkali gives an alkene. In chlorobenzene acylation, keep chlorine on the ring and place the acetyl group mainly para to it.

Section E (15 marks)

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



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

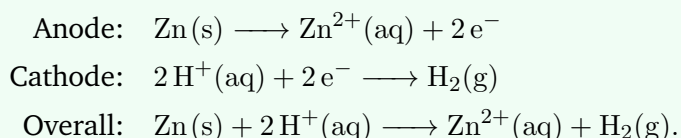
(b) State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? [5 marks]

Solution:

Concept:

- A galvanic cell oxidises the anode species and reduces the cathode species. Using reduction potentials, its standard emf is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$.
- At 25°C, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the dimensionless reaction quotient. Pure solids have unit activity.
- Limiting molar conductivity is the sum of independent ionic contributions. Conductivity κ , unlike molar conductivity Λ_m , depends on the number of mobile ions per unit volume.

Step 1: Write the electrode reactions and standard cell emf For part (a), zinc is the left-hand electrode and is oxidised, while hydrogen ions are reduced at the platinum electrode. Platinum is an inert conductor.



Thus $n = 2$. The given values are reduction potentials, so

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

Step 2: Form the reaction quotient and apply the Nernst equation Taking ionic activities as their concentrations relative to 1 mol L⁻¹, and hydrogen pressure relative to 1 bar,

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

Here the bracketed concentrations represent their numerical values in mol L⁻¹. The hydrogen-ion concentration is squared because its coefficient in the balanced reaction is two. Since $\log 10^3 = 3$,

$$\begin{aligned} E_{\text{cell}} &= 0.76 - \frac{0.0591}{2} \log 10^3 \\ &= 0.76 - 0.08865 \\ &= 0.67135 \text{ V} \approx 0.671 \text{ V}. \end{aligned}$$

The reaction quotient exceeds unity, so the calculated emf is lower than the standard emf, as expected.

Step 3: State Kohlrausch's law For part (b), Kohlrausch's law states that at infinite dilution each ion contributes a definite amount to the molar conductivity of an electrolyte, independently of the nature

Quick Tip to Solve: Balance the cell reaction before writing the Nernst quotient: the coefficient 2 on hydrogen ions becomes a square. Distinguish conductivity per solution volume from molar conductivity per mole.

of the other ion present. Consequently,

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

where λ_+° and λ_-° are the limiting ionic molar conductivities, and ν_+ and ν_- are the numbers of cations and anions supplied by one formula unit of the electrolyte.

Step 4: Explain the decrease in conductivity on dilution Adding solvent increases the volume and reduces the number of ions per unit volume. A given volume of the diluted solution therefore has fewer charge carriers, so its conductivity κ decreases. This remains the relevant effect even though ionic mobility increases and a weak electrolyte ionises more on dilution. Molar conductivity increases on dilution because it refers to the conducting contribution of one mole of electrolyte; conductivity refers to the conducting ability of the solution in a fixed geometry.

Step 5: Conclusion (a) The cell emf is 0.671 V at 25°C . (b) At infinite dilution, the limiting molar conductivity is the sum of the independent ionic contributions. Conductivity decreases on dilution because the number of ions per unit volume decreases.

Quick Tip to Solve: Balance the cell reaction before writing the Nernst quotient: the coefficient 2 on hydrogen ions becomes a square. Distinguish conductivity per solution volume from molar conductivity per mole.

34(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 KMnO_4 from Pyrolusite ore (MnO_2). [5 marks]

Solution:

Concept:

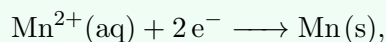
- Transition-metal ions form coordinate bonds by accepting lone pairs from ligands; their small size, high charge density and available orbitals favour complex formation.
- A standard reduction potential measures the tendency of the written species to accept electrons. The stability of the half-filled $3d^5$ configuration helps explain the manganese potentials.
- The stability of an ion in water depends on hydration as well as ionisation energies. Disproportionation is simultaneous oxidation and reduction of the same species.
- Preparation of KMnO_4 involves successive oxidation of manganese from +4 in MnO_2 , to +6 in manganate, and then to +7 in permanganate.

Step 1: Explain complex formation in part (i)(1) Transition-metal ions generally have small ionic radii and appreciable positive charge, producing high charge density. They also have vacant orbitals of suitable energy to accept electron pairs donated by ligands such as H_2O , NH_3 and CN^- . The resulting coordinate bonds stabilise complex ions. For example, water coordinates to Cu^{2+} to form $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

Step 2: Relate both manganese potentials to the stable configuration For part (i)(2), Mn^{2+} has the

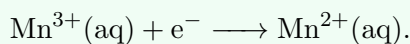
Quick Tip to Solve: For the manganese potentials, write each reduction half-reaction and locate the stable $3d^5$ ion on the reactant or product side. For the preparation, track manganese through +4, +6, then +7.

particularly stable half-filled configuration $[\text{Ar}]3d^5$. In the reduction



this stable aqueous ion is consumed. Its reduction to the metal is therefore comparatively unfavourable, giving a highly negative $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$.

In contrast, Mn^{3+} has configuration $[\text{Ar}]3d^4$. It readily accepts an electron to attain the stable half-filled configuration:



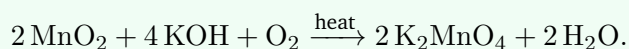
Formation of stable Mn^{2+} favours this reduction, so $E^\circ_{\text{Mn}^{3+}/\text{Mn}^{2+}}$ is highly positive. Thus the same stability explains the opposite signs for the two different reduction processes.

Step 3: Explain the aqueous instability of copper(I) In part (i)(3), the much more negative hydration enthalpy of Cu^{2+} , relative to Cu^+ , compensates for the energy needed to remove the second electron. Consequently, Cu^{2+} is strongly stabilised in aqueous solution and Cu^+ undergoes disproportionation:



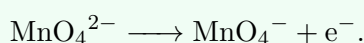
One copper(I) ion loses an electron while another gains it. The filled $3d^{10}$ configuration of Cu^+ alone therefore does not ensure its stability in water; hydration must also be considered.

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

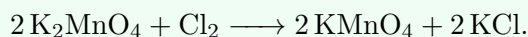


This equation conserves both manganese atoms and all oxygen, potassium and hydrogen atoms.

Step 5: Oxidise manganate to permanganate Extract the manganate with water. Oxidation of manganate ions gives purple permanganate ions. Commercially, this is achieved by electrolytic oxidation in alkaline solution; the anode reaction is



Alternatively, chlorine oxidises potassium manganate according to the balanced equation



Each manganese atom loses one electron as its oxidation state increases from +6 to +7; one chlorine molecule accepts the two electrons. Concentration of the resulting solution yields KMnO_4 crystals.

Step 6: Conclusion High charge density and suitable accepting orbitals explain complex formation. The stable $3d^5$ configuration of Mn^{2+} explains both manganese potentials, while strong hydration of Cu^{2+} drives aqueous Cu^+ disproportionation. Pyrolusite is converted successively into green K_2MnO_4 and purple KMnO_4 by oxidation.

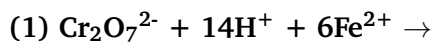
Quick Tip to Solve: For the manganese potentials, write each reduction half-reaction and locate the stable $3d^5$ ion on the reactant or product side. For the preparation, track manganese through +4, +6, then +7.

34(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]

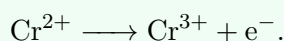
Solution:

Concept:

- The stability of a transition-metal ion depends on its electronic configuration. Scandium commonly forms the +3 state, whereas Cr^{2+} readily loses an electron to form Cr^{3+} .
 - In balancing a redox equation, conserve both atoms and total charge. In acidic medium, dichromate gains six electrons while each Fe^{2+} loses one electron.
 - Heating potassium permanganate forms potassium manganate, manganese dioxide and oxygen.
- Misch metal is an alloy rich in lanthanoid metals.

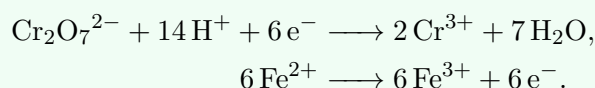
Step 1: (i)(1) Identify the metal with one usual oxidation state The metal is **scandium (Sc)**. Its atomic electronic configuration is $[\text{Ar}] 3d^1 4s^2$. Loss of its two 4s electrons and one 3d electron gives Sc^{3+} , with the stable noble-gas configuration $[\text{Ar}]$. Thus scandium exhibits only the +3 oxidation state in its usual compounds. Zinc is not the required answer because it is not classified as a transition metal: its atom and common ion have a completely filled d subshell.

Step 2: (i)(2) Identify the reducing agent The metal is **chromium (Cr)**. In aqueous solution, Cr^{2+} is a strong reducing agent because it is readily oxidised:

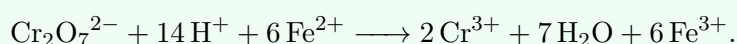


Its configuration changes from $3d^4$ to the more stable $3d^3$ configuration of Cr^{3+} . The electron it supplies reduces another species, so chromium in the +2 state acts as the reducing agent.

Step 3: (ii)(1) Balance the dichromate reaction Dichromate oxidises iron(II) to iron(III), while chromium(VI) is reduced to chromium(III). The half-reactions are



Adding them cancels the six electrons and gives



There are two chromium atoms, seven oxygen atoms, fourteen hydrogen atoms and six iron atoms on each side. The total charge is +24 on both sides, confirming the balance.

Quick Tip to Solve: For dichromate, match its six-electron gain with six iron(II) ions, then check charge. For heated permanganate, remember the three products: manganate, manganese dioxide and oxygen.

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



Potassium manganate, K_2MnO_4 , contains manganese in the +6 state; manganese dioxide, MnO_2 , contains it in the +4 state. The equation conserves two potassium atoms, two manganese atoms and eight oxygen atoms.

Step 5: (iii) State the composition and a use of Misch metal Misch metal is an alloy containing about 95% lanthanoid metals and about 5% iron, together with traces of sulfur, carbon, calcium and aluminium. It is used in making **lighter flints**: its ability to produce sparks on striking makes it useful for ignition.

Step 6: Conclusion (i) The metals are **scandium** and **chromium**, respectively. (ii) Acidified dichromate gives $2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}$; heating 2KMnO_4 gives $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$. (iii) Misch metal is the lanthanoid-iron alloy used in lighter flints.

Quick Tip to Solve: For dichromate, match its six-electron gain with six iron(II) ions, then check charge. For heated permanganate, remember the three products: manganate, manganese dioxide and oxygen.

35(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 methyl ketone contains the group $\text{CH}_3\text{CO}-$ and gives a yellow precipitate of CHI_3 with iodine and alkali.
- Aldehydes without an α -hydrogen undergo Cannizzaro disproportionation in concentrated alkali. Aldehydes reduce Tollens' reagent to metallic silver.
- A chiral carbon is a tetrahedral carbon attached to four different groups. Wolff-Kishner reduction converts a carbonyl group into a methylene group; the Hell-Volhard-Zelinsky reaction halogenates the α -carbon of a carboxylic acid having an α -hydrogen.

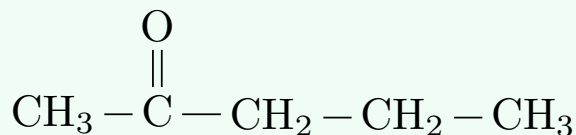
Step 1: (i)(1) Identify the methyl ketone structures For $\text{C}_5\text{H}_{10}\text{O}$, a methyl ketone has the form $\text{CH}_3\text{COC}_3\text{H}_7$. The propyl group can be straight or branched, giving pentan-2-one and 3-methylbutan-2-one, respectively. Both structures below contain the required $\text{CH}_3\text{CO}-$ group and have the stated

Quick Tip to Solve: With five carbons fixed, look for $\text{CH}_3\text{CO}-$ for iodoform, remove all α -hydrogens for Cannizzaro, and attach four different groups to a carbon in an aldehyde for the chiral Tollens-positive structure.

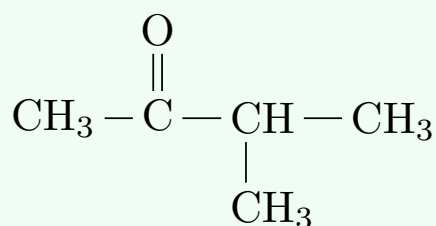
molecular formula. The test cleaves this group to give yellow iodoform:



Here R is either propyl group. Pentan-3-one lacks a methyl group directly bonded to the carbonyl carbon and does not give this test.



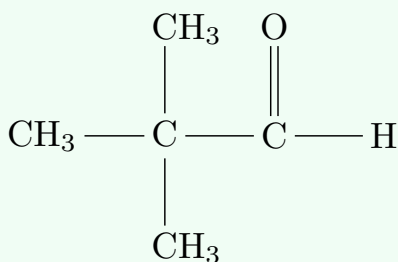
Pentan-2-one



3-Methylbutan-2-one

The two methyl ketones with molecular formula $\text{C}_5\text{H}_{10}\text{O}$.

Step 2: (i)(2) Choose an aldehyde without an alpha hydrogen The required structure is 2,2-dimethylpropanal, $(\text{CH}_3)_3\text{CCHO}$. Its carbon adjacent to the aldehyde group is bonded to three methyl groups and the aldehyde carbon, so it has no hydrogen. Consequently, concentrated alkali causes Cannizzaro disproportionation: one aldehyde molecule is oxidised to carboxylate and another is reduced to an alcohol. Its carbon count is $3 + 1 + 1 = 5$, and its hydrogen count is $9 + 1 = 10$, agreeing with $\text{C}_5\text{H}_{10}\text{O}$.

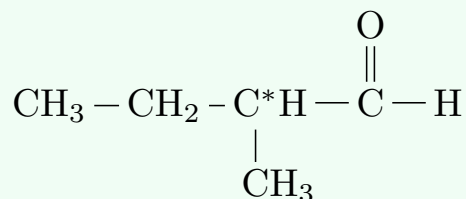


2,2-Dimethylpropanal has no hydrogen on the alpha carbon.

Step 3: (i)(3) Identify the chiral aldehyde Choose 2-methylbutanal, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$. The aldehyde group reduces Tollens' reagent and gives the silver-mirror test. The carbon next to CHO is chiral because it is bonded to four different groups: H, CH_3 , CH_2CH_3 and CHO. The star in the structure below identifies this carbon. Either enantiomer has the required properties; a particular

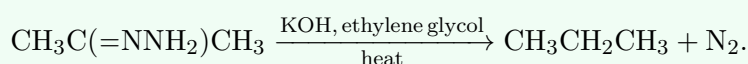
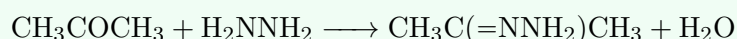
Quick Tip to Solve: With five carbons fixed, look for $\text{CH}_3\text{CO}-$ for iodoform, remove all α -hydrogens for Cannizzaro, and attach four different groups to a carbon in an aldehyde for the chiral Tollens-positive structure.

absolute configuration is not specified.



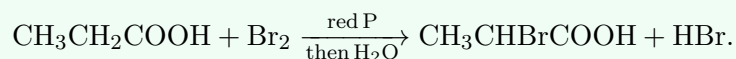
2-Methylbutanal; the starred carbon has four different substituents.

Step 4: (ii)(1) Write the Wolff-Kishner reduction The aldehyde or ketone first reacts with hydrazine to form a hydrazone. Heating this with potassium hydroxide in ethylene glycol replaces the carbonyl oxygen by two hydrogen atoms, with nitrogen evolved. For example, propanone is reduced to propane:



This reduction is performed under strongly basic conditions.

Step 5: (ii)(2) Write the Hell-Volhard-Zelinsky reaction A carboxylic acid containing at least one α -hydrogen reacts with bromine in the presence of a small amount of red phosphorus, followed by hydrolysis, to give an α -bromocarboxylic acid. For example, propanoic acid gives 2-bromopropanoic acid:



Bromine replaces the hydrogen on the carbon immediately adjacent to the carboxyl group. Chlorine may be used for the corresponding α -chlorination.

Step 6: Conclusion The structures in (i) are: (1) pentan-2-one or 3-methylbutan-2-one; (2) 2,2-dimethylpropanal; and (3) 2-methylbutanal. In (ii), Wolff-Kishner reduction converts carbonyl compounds into hydrocarbons, while the Hell-Volhard-Zelinsky reaction gives α -halocarboxylic acids.

Quick Tip to Solve: With five carbons fixed, look for $\text{CH}_3\text{CO}-$ for iodoform, remove all α -hydrogens for Cannizzaro, and attach four different groups to a carbon in an aldehyde for the chiral Tollens-positive structure.

35(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:

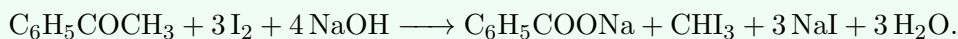
- (1) $\text{O}_2\text{N}-\text{CH}_2-\text{COOH}$, $\text{F}-\text{CH}_2-\text{COOH}$, $\text{CN}-\text{CH}_2\text{COOH}$ (Acidic character)
- (2) Ethanal, Propanal, Butanone, Propanone (Reactivity in nucleophilic addition reactions) [5 marks]

Solution:

Concept:

- A methyl ketone undergoes the haloform reaction with iodine and alkali, giving a carboxylate salt. Acidification converts the salt into the carboxylic acid.
- A benzene side chain containing a benzylic hydrogen is oxidised to a carboxyl group by hot alkaline KMnO_4 . A Grignard reagent reacts with CO_2 , followed by acidic hydrolysis, to form a carboxylic acid.
- Electron-withdrawing substituents strengthen a carboxylic acid by stabilising its conjugate base through the negative inductive effect. Carbonyl compounds undergo nucleophilic addition more readily when their carbonyl carbon is less crowded and more electrophilic.

Step 1: (i)(1) Convert acetophenone by the haloform reaction Acetophenone contains the methyl ketone group $-\text{COCH}_3$. Warm it with iodine and aqueous sodium hydroxide to form sodium benzoate and yellow iodoform:

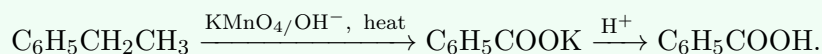


Acidify the sodium benzoate solution with dilute hydrochloric acid:



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

Step 2: (i)(2) Oxidise the side chain of ethylbenzene Ethylbenzene has hydrogen atoms on the carbon directly attached to the benzene ring. Heat it with alkaline potassium permanganate, then acidify. The entire side chain is shortened to a single carboxyl group attached to the ring:

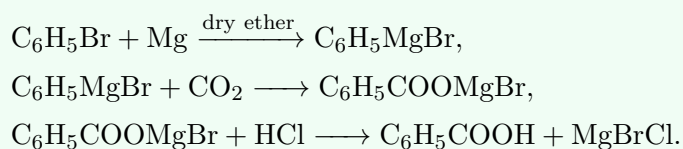


Thus, vigorous side-chain oxidation gives the benzoate salt first; the final acidification is essential to obtain benzoic acid.

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

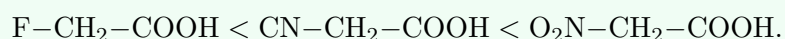
Quick Tip to Solve: For the three conversions, identify a methyl ketone, a benzylic hydrogen and an aryl halide respectively: they suggest haloform cleavage, side-chain oxidation and Grignard carboxylation. Finish each route with acidification.

with dilute acid:

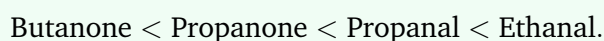


Dry conditions are necessary until the carboxylation is complete because water destroys a Grignard reagent. Carbon dioxide supplies the new carboxyl carbon.

Step 4: (ii)(1) Compare the electron-withdrawing groups Each acid has its substituent on the carbon adjacent to the carboxyl group, so the distance of the inductive effect is the same. The electron-withdrawing influence increases in the order fluoro, cyano, nitro for these compounds. Increasing stabilisation of the carboxylate ion makes loss of a proton more favourable. Hence the increasing acidic character is



Step 5: (ii)(2) Compare carbonyl electrophilicity and steric hindrance Ketones have two electron-releasing alkyl groups attached to the carbonyl carbon, whereas aldehydes have only one. The ketone carbonyl is therefore less electrophilic and more hindered toward a nucleophile. Within each pair, the larger ethyl group donates electron density and obstructs approach more than a methyl group. Thus butanone reacts less readily than propanone, and propanal less readily than ethanal. The increasing reactivity is



Step 6: Conclusion Benzoic acid is obtained by haloform cleavage and acidification of acetophenone, side-chain oxidation and acidification of ethylbenzene, and Grignard formation followed by carboxylation and acidic hydrolysis of bromobenzene. The required orders are fluoroacetic acid < cyanoacetic acid < nitroacetic acid, and butanone < propanone < propanal < ethanal.

Quick Tip to Solve: For the three conversions, identify a methyl ketone, a benzylic hydrogen and an aryl halide respectively: they suggest haloform cleavage, side-chain oxidation and Grignard carboxylation. Finish each route with acidification.