

# CBSE Class 12 Chemistry Question Paper 2023 with Solution PDF-Set 56-3-1

## Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

### General Instructions

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

## Section A (18 marks)

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

1. Which of the following is not true about enantiomers?

[1 mark]

- (A) They have the same density.
- (B) They have the same melting or boiling point.
- (C) They have the same specific rotation.
- (D) They have the same chemical reactivity.

**Correct Answer:** (C) They have the same specific rotation.

### Solution:

#### Concept:

- Enantiomers are non-superimposable mirror images of the same chiral molecule.
- In an achiral environment, their physical properties are identical except for the direction of optical rotation.

**Step 1: Compare ordinary properties** The two enantiomers have the same density and the same melting and boiling points. They also have the same chemical reactivity towards achiral reagents, as intended in option (D). Thus (A), (B) and (D) are true statements in the usual comparison.

**Step 2: Compare optical rotation** Under identical conditions, enantiomers rotate plane-polarised light through equal angles in opposite directions. If one has specific rotation  $[\alpha] = +a$ , the other has  $[\alpha] = -a$ . Their magnitudes agree, but their signed specific rotations differ.

**Step 3: Conclusion** The statement that enantiomers have the same specific rotation is not true. Hence, the correct option is (C).

**Quick Tip to Solve:** For enantiomers, distinguish equal magnitude of optical rotation from equal signed specific rotation.

2. Aspirin is obtained by the acetylation of which of the following compounds?

[1 mark]

- (A) Salicylaldehyde
- (B) Salicylic acid
- (C) Acetyl salicylic acid
- (D) Phenol

**Correct Answer:** (B) Salicylic acid

### Solution:

#### Concept:

- Acetylation introduces an acetyl group into a molecule.
- Aspirin is acetylsalicylic acid, formed by acetylating the phenolic hydroxyl group of salicylic acid.

**Step 1: Identify the precursor** Salicylic acid contains both a phenolic  $\text{-OH}$  group and a  $\text{-COOH}$

**Quick Tip to Solve:** Recognise aspirin as acetylsalicylic acid: remove the acetyl group from its phenolic oxygen to find the precursor.

group on adjacent ring carbons. Acetylation converts its phenolic hydroxyl into  $-\text{OCOCH}_3$ , producing aspirin while retaining the carboxyl group.

**Step 2: Check the alternatives** Salicylaldehyde has an aldehyde group instead of the required carboxyl group. Acetylsalicylic acid is already aspirin, so it is the product, not its precursor. Phenol lacks the carboxyl group and gives phenyl acetate on acetylation.

**Step 3: Conclusion** Aspirin is obtained by acetylating salicylic acid. Hence, the correct option is (B).

**Quick Tip to Solve:** Recognise aspirin as acetylsalicylic acid: remove the acetyl group from its phenolic oxygen to find the precursor.

**3. The reactivities of the carbonyl compounds HCHO (I),  $\text{CH}_3\text{CHO}$  (II) and  $\text{CH}_3\text{COCH}_3$  (III) towards nucleophilic addition reaction decreases in the order:** [1 mark]

(A)  $\text{III} > \text{II} > \text{I}$

(B)  $\text{I} > \text{II} > \text{III}$

(C)  $\text{II} > \text{III} > \text{I}$

(D)  $\text{I} > \text{III} > \text{II}$

**Correct Answer:** (B)  $\text{I} > \text{II} > \text{III}$

**Solution:**

**Concept:**

- A nucleophile attacks the electron-deficient carbon atom of a carbonyl group.
- Alkyl groups reduce carbonyl electrophilicity by their electron-releasing effect and hinder attack sterically.

**Step 1: Compare substitution at the carbonyl carbon** Formaldehyde, HCHO (I), has no alkyl group. Ethanal,  $\text{CH}_3\text{CHO}$  (II), has one methyl group, while propanone,  $\text{CH}_3\text{COCH}_3$  (III), has two methyl groups. Increasing methyl substitution lowers the positive character of the carbonyl carbon.

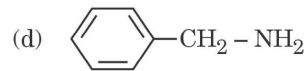
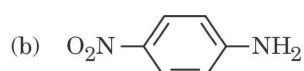
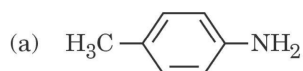
**Step 2: Include steric hindrance** Formaldehyde is also the least hindered, ethanal is more hindered, and propanone is the most hindered. Both electronic and steric effects therefore favour I over II and II over III. Options (A), (C) and (D) reverse at least one of these comparisons.

**Step 3: Conclusion** The decreasing reactivity order is  $\text{I} > \text{II} > \text{III}$ . Hence, the correct option is (B).

**Quick Tip to Solve:** Count alkyl groups attached to the carbonyl carbon: fewer groups usually mean faster nucleophilic addition.

4. Among the following, which is the strongest base?

[1 mark]



(A)  $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$  (p-toluidine)

(B)  $p\text{-O}_2\text{NC}_6\text{H}_4\text{NH}_2$  (p-nitroaniline)

(C)  $\text{C}_6\text{H}_5\text{NH}_2$  (aniline)

(D)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (benzylamine)

**Correct Answer:** (D)  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$  (benzylamine)

**Solution:**

**Concept:**

- An amine acts as a base by using the nitrogen lone pair to accept a proton.
- Delocalisation of this lone pair into a benzene ring decreases its availability for protonation.

**Step 1: Compare direct attachment to the ring** In p-toluidine (A), p-nitroaniline (B) and aniline (C), nitrogen is directly attached to the benzene ring, so its lone pair is delocalised by resonance. The methyl group increases basicity relative to aniline, whereas the nitro group strongly decreases it; neither removes the ring conjugation.

**Step 2: Identify the unconjugated lone pair** In benzylamine (D),  $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ , the intervening  $-\text{CH}_2-$  group separates nitrogen from the aromatic ring. The nitrogen lone pair is therefore not delocalised into that ring and is more available to accept a proton than in the three aniline derivatives.

**Step 3: Conclusion** Benzylamine is the strongest base among the printed compounds. Hence, the correct option is (D).

**Quick Tip to Solve:** Check whether nitrogen is bonded directly to the aromatic ring; a methylene spacer prevents lone-pair conjugation.

5. On hydrolysis, which of the following carbohydrates gives only glucose?

[1 mark]

(A) Starch

(B) Fructose

(C) Lactose

(D) Sucrose

**Correct Answer:** (A) Starch

**Solution:**

**Concept:**

- Hydrolysis cleaves glycosidic bonds in disaccharides and polysaccharides.
- Starch is a polysaccharide made entirely from glucose units.

**Quick Tip to Solve:** Recall the monomers: starch is all glucose, lactose is glucose plus galactose, and sucrose is glucose plus fructose.

**Step 1: Hydrolyse starch** Starch contains amylose and amylopectin, both composed of  $\alpha$ -D-glucose residues. Complete hydrolysis cleaves their glycosidic linkages and yields glucose as the only monosaccharide product.

**Step 2: Check the other carbohydrates** Fructose is already a monosaccharide and cannot be hydrolysed into simpler carbohydrates. Lactose gives glucose and galactose, while sucrose gives glucose and fructose. These alternatives therefore do not yield only glucose on hydrolysis.

**Step 3: Conclusion** Starch gives only glucose on complete hydrolysis. Hence, the correct option is (A).

**Quick Tip to Solve:** Recall the monomers: starch is all glucose, lactose is glucose plus galactose, and sucrose is glucose plus fructose.

**6. Which of the following vitamins is water soluble?**

[1 mark]

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

**Correct Answer:** (D) Vitamin C

**Solution:**

**Concept:**

- Vitamins are classified as water soluble or fat soluble.
- Vitamins of the B group and vitamin C are water soluble; vitamins A, D, E and K are fat soluble.

**Step 1: Identify the water-soluble vitamin** Vitamin C, also called ascorbic acid, belongs to the water-soluble class. Its several polar oxygen-containing groups allow favourable interaction with water.

**Step 2: Eliminate the other options** Vitamin A, vitamin D and vitamin E all belong to the fat-soluble class. They are absorbed along with dietary fats and are not the water-soluble choice in this list. Comparing the standard two vitamin groups therefore uniquely selects vitamin C.

**Step 3: Conclusion** Vitamin C is water soluble. Hence, the correct option is (D).

**Quick Tip to Solve:** Memorise ADEK as the fat-soluble set; vitamin C and the B group form the water-soluble set.

7. The unit of the rate of reaction is the same as that of the rate constant for a:

[1 mark]

- (A) first order reaction
- (B) second order reaction
- (C) zero order reaction
- (D) it cannot be same

**Correct Answer:** (C) zero order reaction

**Solution:**

**Concept:**

- For a reaction of order  $n$ , a rate law can be written  $r = k[A]^n$ .
- The rate has units  $\text{mol L}^{-1} \text{s}^{-1}$ , whereas  $k$  has units  $(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$ .

**Step 1: Compare the units algebraically** From  $k = r/[A]^n$ , the units of  $k$  are the units of rate divided by concentration raised to  $n$ . They equal the units of rate only when the concentration factor is dimensionless, which occurs for  $n = 0$ . Then  $r = k[A]^0 = k$ .

**Step 2: Check the listed orders** For first order,  $k$  has units  $\text{s}^{-1}$ ; for second order it has units  $\text{L mol}^{-1} \text{s}^{-1}$ . Neither matches the rate units. A zero-order rate constant has units  $\text{mol L}^{-1} \text{s}^{-1}$ , so the claim that they cannot be the same is false.

**Step 3: Conclusion** The units coincide for a zero-order reaction. Hence, the correct option is (C).

**Quick Tip to Solve:** Set the order to zero in the rate law: the concentration disappears and the rate equals the rate constant.

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

[1 mark]

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

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

**Solution:**

**Concept:**

- Molar conductivity  $\Lambda$  is related to concentration  $C$  by  $\Lambda = \Lambda_0 - A\sqrt{C}$ , where  $\Lambda_0$  is its limiting value and  $A$  is a positive constant.
- At infinite dilution, interionic interactions become negligible and molar conductivity approaches its limiting value.

**Step 1: Apply the limiting condition** For  $\Lambda = \Lambda_0$ , the correction term  $A\sqrt{C}$  must vanish. Since  $A$  is nonzero for the electrolyte, this requires  $\sqrt{C} \rightarrow 0$ , and hence  $C \rightarrow 0$ . Substitution gives  $\Lambda \rightarrow \Lambda_0 - A(0) = \Lambda_0$ .

**Step 2: Check the other limits** At  $C \rightarrow 1$ , the correction is  $A$ , so the limiting equality does not

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

follow. At  $C \rightarrow \sqrt{A}$ , a nonzero correction also remains. Increasing concentration without bound does not remove the correction; moreover, this dilute-solution relation is not valid at arbitrarily high concentrations.

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

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

**9. 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:**

- A maximum-boiling azeotrope is a constant-boiling mixture whose boiling point exceeds that of either pure component.
- Negative deviation from Raoult's law means that the actual vapour pressure is lower than the ideal value because unlike molecules attract each other strongly.

**Step 1: Relate vapour pressure to boiling point** A liquid boils when its vapour pressure equals the external pressure. Strong attractions between unlike molecules reduce their tendency to escape into the vapour. A mixture with sufficiently large negative deviation therefore needs a higher temperature to reach atmospheric pressure and forms a maximum-boiling azeotrope.

**Step 2: Compare the alternatives** Large positive deviation raises vapour pressure and produces a minimum-boiling azeotrope, whose boiling point is lower. No deviation means an ideal solution obeying Raoult's law; thus options (B) and (D) describe the same ideal behaviour and do not explain the stated maximum in boiling point.

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

**Quick Tip to Solve:** For azeotropes, remember: lower vapour pressure from negative deviation means a higher boiling point.

10. Which of the following colligative property is used to find the molar mass of proteins? [1 mark]

- (A) Osmotic pressure
- (B) Elevation in boiling point
- (C) Depression in freezing point
- (D) Relative lowering of vapour pressure

**Correct Answer:** (A) Osmotic pressure

**Solution:**

**Concept:**

- Osmotic pressure  $\pi$  of a dilute solution satisfies  $\pi = CRT$ , where  $C$  is molar concentration,  $R$  the gas constant and  $T$  absolute temperature.
- For solute mass  $w$ , solution volume  $V$  and molar mass  $M$ ,  $\pi = wRT/(MV)$ .

**Step 1: Choose a measurable property** Proteins have very large molar masses, so a given mass produces a very small number of solute particles. Changes in boiling point, freezing point and vapour pressure are consequently very small in dilute protein solutions. Osmotic pressure remains appreciable enough to measure accurately even at low concentration.

**Step 2: Use mild experimental conditions** Osmotic pressure can be measured at room temperature, avoiding heating that may denature proteins. The molar mass is then obtained from  $M = wRT/(\pi V)$ . Elevation in boiling point, depression in freezing point and relative lowering of vapour pressure are valid colligative properties, but are less suitable for such macromolecules.

**Step 3: Conclusion** Osmotic pressure is used to determine the molar mass of proteins. Hence, the correct option is (A).

**Quick Tip to Solve:** For high-molar-mass biomolecules, choose osmotic pressure because it is measurable in dilute solution at room temperature.

11. Among the following outermost configurations of transition metals which one shows the highest oxidation state? [1 mark]

- (A)  $3d^3 4s^2$
- (B)  $3d^5 4s^1$
- (C)  $3d^5 4s^2$
- (D)  $3d^6 4s^2$

**Correct Answer:** (C)  $3d^5 4s^2$

**Solution:**

**Concept:**

- For early first-row transition metals, the highest oxidation state commonly corresponds to participation of both  $3d$  and  $4s$  valence electrons.
- The maximum oxidation state rises from vanadium to manganese, then generally falls because removal or participation of further electrons becomes increasingly difficult.

**Quick Tip to Solve:** Identify manganese by its half-filled  $3d$  subshell plus two  $4s$  electrons; its maximum oxidation state is +7.

**Step 1: Identify the first three configurations**  $3d^34s^2$  corresponds to vanadium, with maximum oxidation state +5.  $3d^54s^1$  corresponds to chromium, with maximum oxidation state +6.  $3d^54s^2$  corresponds to manganese, which attains +7, as in the permanganate ion  $\text{MnO}_4^-$ .

**Step 2: Compare the iron configuration**  $3d^64s^2$  corresponds to iron. One must not simply count its eight outer electrons and infer +8: the trend does not continue beyond manganese. Iron can attain +6 in ferrate, but this is still below manganese's +7. Thus the manganese configuration has the highest oxidation state among the printed choices.

**Step 3: Conclusion**  $3d^54s^2$  shows the highest oxidation state, +7. Hence, the correct option is (C).

**Quick Tip to Solve:** Identify manganese by its half-filled 3d subshell plus two 4s electrons; its maximum oxidation state is +7.

**12. How many ions are produced in the solution from the complex  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ ?**

[1 mark]

- (A) 4
- (B) 3
- (C) 2
- (D) 5

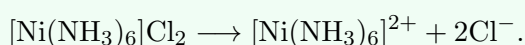
**Correct Answer:** (B) 3

**Solution:**

**Concept:**

- The species inside square brackets is a coordination entity and remains together during ordinary ionisation of a coordination salt.
- Only ions outside the coordination sphere dissociate as counterions; neutral ammonia ligands do not become separate ions.

**Step 1: Write the dissociation** The coordination entity contains six neutral ammonia ligands bonded to  $\text{Ni}^{2+}$ . The two chloride ions are outside the brackets, so dissolution gives



The charges balance: one cation of charge +2 and two anions of charge -1.

**Step 2: Count the resulting ions** Each formula unit produces one complex cation and two chloride anions, for a total of  $1 + 2 = 3$  ions. Counting only the two chlorides misses the complex cation. Counting ammonia ligands or the metal separately would incorrectly break the coordination sphere, so totals of four or five do not represent this dissociation.

**Step 3: Conclusion** Three ions are produced per formula unit. Hence, the correct option is (B).

**Quick Tip to Solve:** Count one ion for the entire bracketed complex, then add every counterion written outside the brackets.

13. Which of the following species is not expected to be a ligand?

[1 mark]

- (A) CO
- (B)  $\text{NH}_4^+$
- (C)  $\text{NH}_3$
- (D)  $\text{H}_2\text{O}$

**Correct Answer:** (B)  $\text{NH}_4^+$

**Solution:**

**Concept:**

- A ligand donates an available electron pair to a central metal atom or ion to form a coordinate bond.
- The donor atom must possess a lone pair capable of donation; a species need not carry a negative charge to act as a ligand.

**Step 1: Examine the ammonium ion** In  $\text{NH}_4^+$ , the nitrogen atom has four bonds and no available lone pair. The lone pair present in ammonia has already been used to bond to a proton during ammonium formation. Consequently, ammonium is not expected to donate an electron pair as a ligand.

**Step 2: Check every other species** Carbon monoxide, CO, donates through carbon and is a common ligand in metal carbonyls. Ammonia,  $\text{NH}_3$ , retains a lone pair on nitrogen and forms ammine complexes. Water,  $\text{H}_2\text{O}$ , has lone pairs on oxygen and forms aqua complexes. These three neutral species can therefore act as ligands despite carrying no negative charge.

**Step 3: Conclusion**  $\text{NH}_4^+$  is not expected to be a ligand. Hence, the correct option is (B).

**Quick Tip to Solve:** Look for an available donor lone pair: ammonia has one, whereas ammonium has none.

14. Which of the following is the most stable complex species?

[1 mark]

- (A)  $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (B)  $[\text{Fe}(\text{CN})_6]^{3-}$
- (C)  $[\text{Fe}(\text{CO})_5]$
- (D)  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$

**Correct Answer:** (B)  $[\text{Fe}(\text{CN})_6]^{3-}$

**Solution:**

**Concept:**

- The stability of a coordination species depends on the strength of metal-ligand bonding and the nature of the metal and ligands.
- Cyanide is a strong-field ligand and forms particularly stable iron complexes through strong metal-ligand interactions.

**Step 1: Identify the cyanide complex** In  $[\text{Fe}(\text{CN})_6]^{3-}$ , six cyanide ligands coordinate to iron(III). Cyanide produces a large ligand-field splitting and favours a low-spin  $d^5$  arrangement for iron(III).

**Quick Tip to Solve:** In this comparison of iron complexes, recognise cyanide as the strongly binding ligand in ferricyanide.

Strong bonding and this stabilisation make the ferricyanide coordination entity very stable.

**Step 2: Compare the remaining choices** The aqua complex contains water, a weaker-field ligand than cyanide, and is less stable. Oxalate is bidentate and provides chelate stabilisation, but the cyanide complex is the most stable of the listed species in this comparison. Iron pentacarbonyl contains iron in oxidation state zero and is a stable carbonyl, yet it is not the selected most stable species among these printed alternatives.

**Step 3: Conclusion**  $[\text{Fe}(\text{CN})_6]^{3-}$  is the most stable complex listed. Hence, the correct option is (B).

**Quick Tip to Solve:** In this comparison of iron complexes, recognise cyanide as the strongly binding ligand in ferricyanide.

**15.** For Questions number 15 to 18, two statements are given - one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer from the codes (a), (b), (c) and (d) given below.

- (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.

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

**Reason (R):** Complex reactions involve a sequence of elementary reactions and the slowest step is rate determining. [1 mark]

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

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

**Solution:**

**Concept:**

- Order is the sum of the experimentally determined powers of reactant concentrations in the rate law.
- Molecularity counts reacting species in one elementary step; it is a positive integer and is not defined for an overall complex reaction.

**Step 1: Judge the Assertion** The word "always" makes the Assertion false. Order and molecularity coincide for an elementary reaction obeying its elementary rate law, but this equality cannot be extended to all reactions. An overall complex reaction can have an order different from its stoichiometric

**Quick Tip to Solve:** Check "always" carefully: molecularity belongs to one elementary step, whereas order comes from the measured rate law.

coefficients.

**Step 2: Judge the Reason** The Reason is true. A complex reaction proceeds through successive elementary steps. In the standard rate-determining-step treatment, the slowest step controls the overall reaction rate.

**Step 3: Relate the statements and test the codes** The mechanism, especially its rate-determining step, determines the observed rate law. Thus the Reason does not establish the claimed universal equality. Codes (A) and (B) require a true Assertion, while (C) requires a false Reason; neither condition is satisfied.

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

**Quick Tip to Solve:** Check "always" carefully: molecularity belongs to one elementary step, whereas order comes from the measured rate law.

**16. 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.

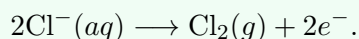
**Correct Answer:** (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

**Solution:**

**Concept:**

- At the anode, oxidation occurs; chloride ions and water compete to form chlorine and oxygen respectively.
- Overpotential is the additional electrode potential required beyond the thermodynamic potential to sustain an electrode reaction.

**Step 1: Judge the Assertion** The Assertion is true for the aqueous sodium chloride electrolysis described in the question. Chloride ions are oxidised at the anode:



Chlorine is therefore liberated.

**Step 2: Judge the Reason** The Reason is true. Oxygen evolution from water requires an appreciable overpotential. The thermodynamic electrode potentials alone therefore do not determine which gas

**Quick Tip to Solve:** For aqueous NaCl, account for the oxygen-evolution overpotential before predicting the anode gas from standard potentials.

appears in this electrolysis.

**Step 3: Check the explanation and eliminate other codes** The overpotential for oxygen evolution makes its actual discharge more difficult, so chloride oxidation can occur preferentially. This directly explains the Assertion. Code (B) incorrectly denies this explanatory link; (C) and (D) incorrectly label one of the true statements false.

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

**Quick Tip to Solve:** For aqueous NaCl, account for the oxygen-evolution overpotential before predicting the anode gas from standard potentials.

**17. 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:**

- A weaker carbon-halogen bond is more readily broken during nucleophilic substitution.
- The bond-energy order is  $C - Cl > C - I$ ; iodide is also a better leaving group than chloride.

**Step 1: Judge the Assertion** The Assertion is true. Iodoethane undergoes nucleophilic substitution more readily than chloroethane because the longer  $C - I$  bond is weaker and iodide leaves more easily.

**Step 2: Judge the Reason** The Reason reverses the actual bond-energy order. The  $C - Cl$  bond has greater, not smaller, bond energy than the  $C - I$  bond. Hence the printed Reason is false.

**Step 3: Check the explanation and the other codes** A false Reason cannot explain the true Assertion. Codes (A) and (B) both require a true Reason and are excluded. Code (D) requires a false Assertion and is also excluded. The combination is a true Assertion with a false Reason.

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

**Quick Tip to Solve:** Remember the weaker C-I bond: alkyl iodides substitute more readily even though iodine is the larger halogen.

**18. 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 characteristic oxidation states.
- Zinc has atomic configuration  $[\text{Ar}]3d^{10}4s^2$ , and  $\text{Zn}^{2+}$  has  $[\text{Ar}]3d^{10}$ .

**Step 1: Judge the Assertion** The Assertion is true. Although zinc lies in the d block, it does not satisfy the definition of a transition element because its d subshell remains completely filled.

**Step 2: Judge the Reason** The Reason is true. The ground-state zinc atom has ten electrons in its 3d subshell. On formation of its characteristic +2 ion, the two 4s electrons are removed, leaving the 3d subshell unchanged and fully occupied.

**Step 3: Check the explanation and eliminate other codes** The filled  $3d^{10}$  subshell in both the atom and its characteristic oxidised state is precisely why zinc is excluded from the transition elements. Thus (B) incorrectly denies the explanation, while (C) and (D) wrongly make a true statement false.

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

**Quick Tip to Solve:** Write Zn and  $\text{Zn}^{2+}$  configurations: removing the 4s electrons leaves  $3d^{10}$ , so neither has a partially filled d subshell.

### Section B (14 marks)

19. Write the structures and IUPAC names of the products expected from the following reactions:

(a) Reaction of methanal with  $(\text{CH}_3)_2\text{CHMgBr}$  followed by hydrolysis.

(b) Reaction of phenol with conc.  $\text{HNO}_3$ .

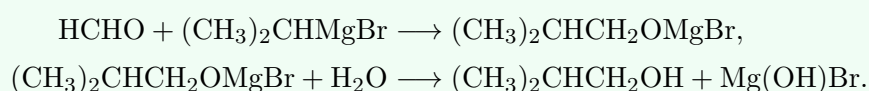
[2 marks]

#### Solution:

##### Concept:

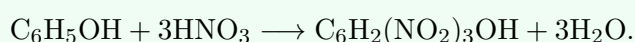
- A Grignard reagent  $\text{RMgBr}$  adds its alkyl group to methanal; hydrolysis gives the primary alcohol  $\text{RCH}_2\text{OH}$ .
- The hydroxyl group of phenol activates the ring and directs nitration to the ortho and para positions.

**Step 1: (a) Add the Grignard reagent and hydrolyse** Here  $\text{R} = (\text{CH}_3)_2\text{CH}-$ . Addition in dry ether first forms the magnesium alkoxide, which is then hydrolysed:



Number the three-carbon chain from the hydroxyl end: the methyl substituent is at carbon 2.

**Step 2: (b) Nitrate phenol with concentrated nitric acid** Concentrated nitric acid introduces three nitro groups at positions 2, 4 and 6 relative to the hydroxyl group:



The product structure is a benzene ring bearing  $-\text{OH}$  at C-1 and  $-\text{NO}_2$  at C-2, C-4 and C-6; its condensed structural representation is  $\text{HO}-\text{C}_6\text{H}_2(\text{NO}_2)_3$  with those locants.

**Step 3: Conclusion** (a)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{OH}$ : 2-methylpropan-1-ol. (b) Phenol with nitro groups at 2, 4 and 6: 2,4,6-trinitrophenol (picric acid).

**Quick Tip to Solve:** Methanal adds one carbon to the Grignard alkyl group; concentrated nitric acid gives all three activated phenol positions, 2, 4 and 6.

20. A chemical reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$  in gas phase was carried out in a closed vessel. The concentration of  $\text{NO}_2$  was found to increase by  $5 \times 10^{-3} \text{ mol L}^{-1}$  in 10 seconds. Calculate:

(a) the rate of formation of  $\text{NO}_2$ , and

(b) the rate of consumption of  $\text{N}_2\text{O}_5$ .

[2 marks]

#### Solution:

##### Concept:

- The average formation rate of a product is its concentration increase divided by the elapsed time.
- For  $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$ , the positive consumption rate of  $\text{N}_2\text{O}_5$  is half the formation rate of  $\text{NO}_2$ .

**Step 1: (a) Calculate the formation rate of nitrogen dioxide** The concentration increase is  $\Delta[\text{NO}_2] =$

**Quick Tip to Solve:** First divide the  $\text{NO}_2$  concentration increase by 10 s, then multiply by the reactant-to-product coefficient ratio 2/4.

$5 \times 10^{-3} \text{ mol L}^{-1}$  over  $\Delta t = 10 \text{ s}$ . Therefore,

$$\text{Formation rate of NO}_2 = \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{5 \times 10^{-3}}{10} = 5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}.$$

This is the species formation rate, without division by its stoichiometric coefficient.

**Step 2: (b) Use the stoichiometric ratio for consumption** Every 4 moles of  $\text{NO}_2$  formed correspond to 2 moles of  $\text{N}_2\text{O}_5$  consumed. Thus

$$\begin{aligned} -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} &= \frac{2}{4} \frac{\Delta[\text{NO}_2]}{\Delta t} \\ &= \frac{1}{2} (5 \times 10^{-4}) \\ &= 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}. \end{aligned}$$

Consumption is reported as a positive magnitude; the minus sign only indicates that the reactant concentration decreases.

**Step 3: Conclusion** (a) Rate of formation of  $\text{NO}_2 = 5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . (b) Rate of consumption of  $\text{N}_2\text{O}_5 = 2.5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ .

**Quick Tip to Solve:** First divide the  $\text{NO}_2$  concentration increase by 10 s, then multiply by the reactant-to-product coefficient ratio 2/4.

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

[2 marks]

### Solution:

#### Concept:

- A fuel cell is a galvanic cell: a spontaneous redox reaction converts chemical energy directly into electrical energy.
- Unlike a cell with a fixed store of reactants, a fuel cell receives fuel and oxidant continuously from external supplies.

**Step 1: Define a fuel cell** A fuel cell is an electrochemical cell in which the chemical energy released by the reaction of a continuously supplied fuel with an oxidant is directly converted into electrical energy. For example, a hydrogen–oxygen fuel cell uses hydrogen as fuel and oxygen as oxidant; it continues to produce electricity while these reactants are supplied.

**Step 2: State two advantages** (i) Fuel cells have high efficiency because they convert chemical energy directly into electrical energy, avoiding the intermediate conversion into heat used in a thermal power plant.

(ii) A hydrogen–oxygen fuel cell is environmentally clean during operation: its overall reaction is  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ , so the product is water and there are no carbon-containing exhaust gases.

**Step 3: Conclusion** A fuel cell generates electricity directly from continuously supplied fuel and oxidant. Its two advantages are high efficiency and, for the hydrogen–oxygen cell, clean operation with water as the product.

**Quick Tip to Solve:** Remember the two defining points: direct energy conversion and continuous supply of reactants.

**21(b).** Using  $E^\circ$  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 lose electrons and undergo oxidation.
- A sacrificial coating protects iron by oxidising preferentially, keeping iron as the cathode even if the coating is scratched.

**Step 1: Compare the reduction potentials** The given values are  $E^\circ_{X^{2+}/X} = -2.36 \text{ V}$ ,  $E^\circ_{Fe^{2+}/Fe} = -0.44 \text{ V}$ , and  $E^\circ_{Y^{2+}/Y} = -0.14 \text{ V}$ . Thus X has a more negative reduction potential than iron, whereas Y has a less negative reduction potential. X is more readily oxidised than iron; Y is less readily oxidised.

**Step 2: Explain protection by the coating** When X-coated iron is exposed to moisture, X acts as the sacrificial anode:  $X \rightarrow X^{2+} + 2e^-$ . Iron is the cathode and is protected from oxidation, including at a scratch. The potential difference favouring oxidation of X relative to iron is  $(-0.44) - (-2.36) = 1.92 \text{ V}$ . A coating of Y provides only a physical barrier while intact. At a scratch, iron becomes the anode relative to Y and corrodes; the corresponding difference is  $(-0.14) - (-0.44) = 0.30 \text{ V}$ .

**Step 3: Conclusion** X is the better coating because its more negative standard reduction potential makes it oxidise preferentially and provide sacrificial protection to iron.

**Quick Tip to Solve:** For sacrificial protection, choose a coating metal with a reduction potential more negative than iron.

**22(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 carbohydrate as glycogen, a highly branched polymer of glucose.
- Starch is formed from alpha-D-glucose units, whereas cellulose is formed from beta-D-glucose units.

**Step 1: (i) Identify the storage carbohydrate and organ** Carbohydrates are stored in the animal body in the form of glycogen, often called animal starch. One organ containing glycogen is the liver. Liver glycogen can be broken down to supply glucose when required. Glycogen is also present in skeletal muscles, where it serves as a local source of energy.

**Step 2: (ii) Compare the basic structures** Starch is a polymer of  $\alpha$ -D-glucose: amylose contains  $\alpha(1 \rightarrow 4)$  glycosidic linkages, and amylopectin has these chains with  $\alpha(1 \rightarrow 6)$  branch linkages.

**Quick Tip to Solve:** Use the alpha/beta distinction for starch versus cellulose; use glycogen, not starch, for animal storage.

Cellulose is a linear polymer of  $\beta$ -D-glucose joined by  $\beta(1 \rightarrow 4)$  glycosidic linkages. The different configuration at the anomeric carbon gives starch and cellulose different chain arrangements; therefore they are not structurally identical merely because both contain glucose.

**Step 3: Conclusion** (i) Animal carbohydrates are stored as glycogen, for example in the liver. (ii) Starch contains alpha-D-glucose units, while cellulose contains beta-D-glucose units.

**Quick Tip to Solve:** Use the alpha/beta distinction for starch versus cellulose; use glycogen, not starch, for animal storage.

OR

**22(b). Differentiate between:**

(i) Peptide linkage and Glycosidic linkage

(ii) Nucleoside and Nucleotide

[2 marks]

**Solution:**

**Concept:**

- Biomolecule linkages join monomer units: peptide bonds join amino acids, whereas glycosidic bonds join sugar units.
- A nucleoside contains a nitrogenous base and a pentose sugar; adding phosphate gives a nucleotide.

**Step 1: (i) Distinguish peptide and glycosidic linkages** A peptide linkage is the amide linkage  $-CO - NH-$  formed by condensation between the carboxyl group of one amino acid and the amino group of another, with elimination of water. It joins amino acids in peptides and proteins. A glycosidic linkage is an oxygen bridge  $C - O - C$  joining monosaccharide units, formed by condensation involving the anomeric hydroxyl group of one sugar and a hydroxyl group of another. It occurs in disaccharides and polysaccharides.

**Step 2: (ii) Distinguish nucleoside and nucleotide** A nucleoside consists of a nitrogenous base linked to a pentose sugar, such as ribose or deoxyribose; it has no phosphate group. A nucleotide consists of the same base-sugar unit together with a phosphate group attached to the sugar. Thus a nucleotide is a phosphorylated nucleoside. For example, adenosine is a nucleoside and adenosine monophosphate is a nucleotide.

**Step 3: Conclusion** (i) Peptide linkage:  $-CO - NH-$  between amino acids; glycosidic linkage:  $C - O - C$  between sugar units. (ii) Nucleoside = base + sugar; nucleotide = base + sugar + phosphate.

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

23. 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.

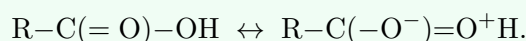
[2 marks]

**Solution:**

**Concept:**

- Electrophilicity is the tendency of an electron-deficient atom to accept an electron pair from a nucleophile.
- Resonance donation from the hydroxyl oxygen reduces the positive character of the carboxylic carbon; alkyl groups also donate electron density by their +I effect.

**Step 1: (a) Compare the carboxylic and carbonyl carbons** In a carboxylic acid, a lone pair on the hydroxyl oxygen is delocalised towards the carbonyl group:



This resonance donation reduces the electron deficiency of the carbonyl carbon. Aldehydes and ketones have no adjacent hydroxyl oxygen providing this additional resonance donation. Hence, their carbonyl carbon is more electrophilic than the carboxylic carbon.

**Step 2: (b) Compare propanal and propanone towards HCN** Addition of HCN begins with attack of the nucleophile  $\text{CN}^-$  on the carbonyl carbon. Propanal,  $\text{CH}_3\text{CH}_2\text{CHO}$ , has one alkyl group and one hydrogen attached to that carbon, whereas propanone,  $\text{CH}_3\text{COCH}_3$ , has two alkyl groups. The two alkyl groups in propanone donate more electron density, decreasing electrophilicity, and offer greater steric hindrance to the approaching nucleophile. Propanal therefore undergoes HCN addition more readily.

**Step 3: Conclusion** The carboxylic carbon is less electrophilic because of resonance donation by  $-\text{OH}$ . Propanal is more reactive than propanone because it has less electron donation and less steric hindrance.

**Quick Tip to Solve:** For nucleophilic carbonyl addition, compare both electron donation to the carbonyl carbon and crowding around it.

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

(a) Carbylamine reaction

(b) Gabriel phthalimide synthesis

[2 marks]

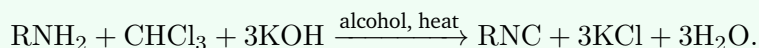
**Solution:**

**Concept:**

- The carbylamine reaction converts a primary amine into an isocyanide on heating with chloroform and alcoholic potassium hydroxide.
- Gabriel synthesis uses the nucleophilic nitrogen of potassium phthalimide to replace halide in an alkyl halide, followed by hydrolysis to a primary amine.

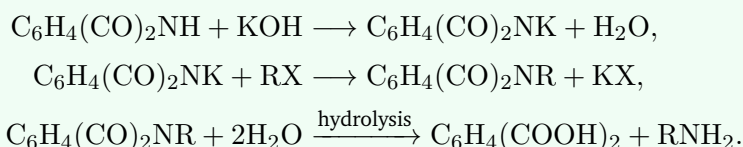
**Quick Tip to Solve:** In the carbylamine equation balance three KOH; in Gabriel synthesis show salt formation, alkylation and hydrolysis.

**Step 1: (a) Carbylamine reaction** The general chemical equation is



Here  $\text{RNH}_2$  is a primary amine and  $\text{RNC}$  is an isocyanide with a characteristic unpleasant odour. Both aliphatic and aromatic primary amines give this test; secondary and tertiary amines do not.

**Step 2: (b) Gabriel phthalimide synthesis** Let  $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$  denote cyclic phthalimide. Its nitrogen lies between the two carbonyl groups. The reaction sequence is



$\text{RX}$  is an alkyl halide. The final products are phthalic acid and a primary aliphatic amine. The method does not prepare aniline because aryl halides do not undergo the required nucleophilic substitution readily.

**Step 3: Conclusion** Carbylamine formation gives  $\text{RNC}$ ; Gabriel synthesis gives  $\text{RNH}_2$  after alkylation and hydrolysis of phthalimide.

**Quick Tip to Solve:** In the carbylamine equation balance three  $\text{KOH}$ ; in Gabriel synthesis show salt formation, alkylation and hydrolysis.

## 25. Give reasons for the following:

(a) Aquatic animals are more comfortable in cold water in comparison to warm water.

(b) Sprinkling of salt helps in clearing the snow-covered roads in hilly areas.

[2 marks]

### Solution:

#### Concept:

- Henry's law is  $p = K_H x$ , where  $p$  is the partial pressure of the gas and  $x$  its mole fraction in water.
- Freezing-point depression is a colligative property:  $\Delta T_f = iK_f m$ , with  $i$  the van't Hoff factor,  $K_f$  the cryoscopic constant and  $m$  the solute molality.

**Step 1: (a) Oxygen availability in cold water** Dissolution of oxygen in water is favoured at lower temperature. At the same oxygen partial pressure, cold water therefore contains more dissolved oxygen than warm water. Equivalently, the Henry constant for oxygen is smaller at lower temperature, so  $x = p/K_H$  is greater. Aquatic animals obtain oxygen for respiration from the water; the greater dissolved oxygen supply makes cold water more comfortable for them.

**Step 2: (b) Salt lowers the freezing point** Salt dissolves in the thin film of liquid water present on snow or ice and forms a solution. The dissolved ions lower the freezing point of water, according to  $\Delta T_f = iK_f m$ . Thus the salt solution can remain liquid below  $0^\circ\text{C}$ , the freezing point of pure water. Snow or ice consequently melts under suitable temperature conditions, helping clear the road. This effect concerns freezing-point depression, rather than an increase in the temperature caused by salt.

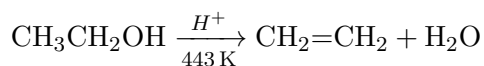
**Quick Tip to Solve:** Link cold water to increased gas solubility, and salt on snow specifically to freezing-point depression.

**Step 3: Conclusion** Cold water supplies more dissolved oxygen to aquatic animals. Salt clears snow by depressing the freezing point of the water formed on it.

**Quick Tip to Solve:** Link cold water to increased gas solubility, and salt on snow specifically to freezing-point depression.

### Section C (15 marks)

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



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

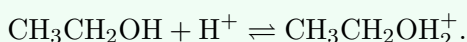
[3 marks]

**Solution:**

**Concept:**

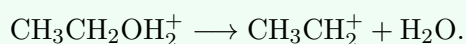
- Acid-catalysed dehydration of ethanol eliminates water to form ethene at 443 K; protonation converts the poor leaving group  $-\text{OH}$  into water.
- The acid catalyst is regenerated after removal of a proton. Cumene first forms cumene hydroperoxide by air oxidation, then undergoes acid cleavage to phenol and acetone.

**Step 1: (a) Step 1: Protonate ethanol** The oxygen lone pair of ethanol accepts a proton from the acid, producing the ethyl oxonium ion:



The  $-\text{OH}_2^+$  group can depart as neutral water, whereas an unprotonated hydroxyl group would have to leave as the much less favourable hydroxide ion.

**Step 2: (a) Step 2: Remove water** In the standard board-level representation, the protonated alcohol loses a water molecule to give the carbocation intermediate:



This is the slow step in the conventional stepwise mechanism. The intermediate carries a positive charge on the carbon that was originally bonded to oxygen.

**Step 3: (a) Step 3: Eliminate a proton** A proton is lost from the neighbouring carbon. The electrons of that C–H bond form the carbon–carbon double bond:

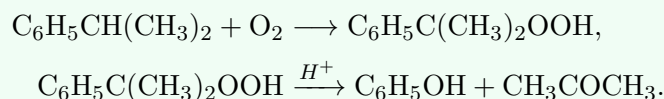


The regenerated proton shows that the acid acts as a catalyst. Combining the steps gives  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[443\text{ K}]{\text{H}^+} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$ .

**Step 4: (b) Prepare phenol from cumene** Cumene is isopropylbenzene,  $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$ . Oxidation

**Quick Tip to Solve:** At 443 K identify ethanol dehydration; for the cumene route always include the hydroperoxide and acetone coproduct.

with oxygen from air produces cumene hydroperoxide, which is cleaved in acidic medium:



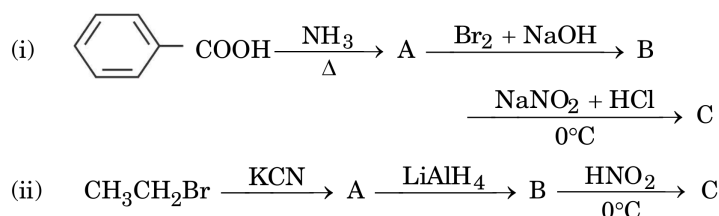
Phenol is obtained together with acetone as a useful coproduct; the acid-catalysed cleavage retains all the carbon atoms in these two products.

**Step 5: Conclusion** Ethanol undergoes protonation, loss of water and elimination of a proton to form ethene. Cumene gives phenol and acetone through its hydroperoxide.

**Quick Tip to Solve:** At 443 K identify ethanol dehydration; for the cumene route always include the hydroperoxide and acetone coproduct.

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

[3 marks]

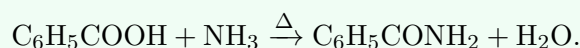


**Solution:**

**Concept:**

- Heating a carboxylic acid with ammonia gives an amide through its ammonium salt. Hofmann bromamide degradation converts  $\text{RCONH}_2$  into  $\text{RNH}_2$ , losing the carbonyl carbon.
- An aromatic primary amine forms a diazonium salt with  $\text{NaNO}_2/\text{HCl}$  at  $0^\circ\text{C}$ . Cyanide substitution adds one carbon; reduction of a nitrile gives a primary amine.
- A primary aliphatic amine reacts with nitrous acid to give an alcohol with evolution of nitrogen; its aliphatic diazonium intermediate is unstable.

**Step 1: Identify the amide and amine in sequence (i)** Benzoic acid first gives ammonium benzoate with ammonia. On heating, this loses water and forms benzamide:



Thus A has structure  $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH}_2$ . Bromine in aqueous sodium hydroxide causes Hofmann degradation:

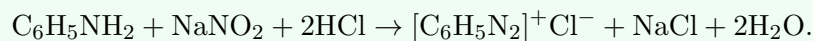


B is aniline,  $\text{C}_6\text{H}_5 - \text{NH}_2$ ; the benzene ring is retained, while the carbonyl carbon is removed.

**Step 2: Diazotise the aromatic amine in sequence (i)** Nitrous acid is generated in situ from sodium nitrite and hydrochloric acid. At the printed low temperature, aniline gives benzenediazonium

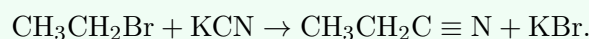
**Quick Tip to Solve:** Track carbon count: KCN adds one carbon,  $\text{LiAlH}_4$  retains it, and Hofmann degradation removes the amide carbonyl carbon.

chloride:



C therefore has structure  $[\text{C}_6\text{H}_5 - \text{N} \equiv \text{N}]^+\text{Cl}^-$ . The low temperature preserves the aromatic diazonium salt.

**Step 3: Follow cyanide substitution and reduction in sequence (ii)** Potassium cyanide replaces bromide through carbon attachment and introduces an additional carbon:

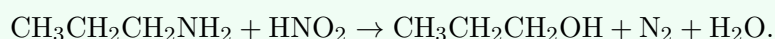


A is propanenitrile,  $\text{CH}_3\text{CH}_2 - \text{C} \equiv \text{N}$ . Lithium aluminium hydride reduces the nitrile group without removing its carbon:



B is propan-1-amine,  $\text{CH}_3\text{CH}_2\text{CH}_2 - \text{NH}_2$ .

**Step 4: React the aliphatic amine with nitrous acid** Unlike the aromatic diazonium salt in (i), the aliphatic diazonium intermediate decomposes even at low temperature. The amino group is replaced by hydroxyl:



Thus C is propan-1-ol, with the same three-carbon chain as B.

**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:  $[\text{C}_6\text{H}_5\text{N}_2]^+\text{Cl}^-$ . (ii) A:  $\text{CH}_3\text{CH}_2\text{CN}$ , B:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ , C:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ .

**Quick Tip to Solve:** Track carbon count: KCN adds one carbon,  $\text{LiAlH}_4$  retains it, and Hofmann degradation removes the amide carbonyl carbon.

OR

**27(b). How will you convert the following:**

(i) Aniline to p-bromoaniline

(ii) Ethanoic acid to methanamine

(iii) Butanenitrile to 1-aminobutane

[3 marks]

**Solution:**

**Concept:**

- Acetylation protects aniline's strongly activating amino group. The acetamido group remains ortho/para directing, but bromination becomes controlled and predominantly gives the para product.
- Hofmann bromamide degradation converts an amide  $\text{RCONH}_2$  to a primary amine  $\text{RNH}_2$  containing one fewer carbon atom.
- Lithium aluminium hydride reduces a nitrile  $\text{R} - \text{C} \equiv \text{N}$  to  $\text{R} - \text{CH}_2\text{NH}_2$ ; the nitrile carbon remains in the product.

**Quick Tip to Solve:** Protect aniline before selective monobromination; use Hofmann degradation only when the desired amine has one fewer carbon.

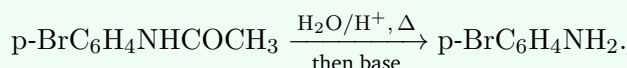
**Step 1: Convert aniline into p-bromoaniline** First protect the amino group by acetylating aniline with acetic anhydride:



Brominate the resulting acetanilide using bromine in ethanoic acid. Steric hindrance near the acetamido group favours substitution at the para position:

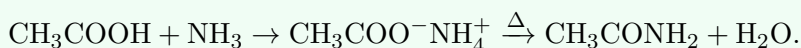


Finally hydrolyse the protected product with aqueous acid and heat, then make the solution alkaline to obtain the free amine:

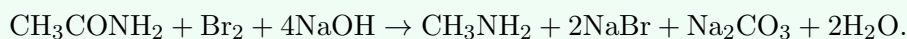


Direct bromination of aniline with bromine water is unsuitable because it gives 2,4,6-tribromoaniline.

**Step 2: Convert ethanoic acid into methanamine** Treat ethanoic acid with ammonia and heat the ammonium ethanoate formed to obtain ethanamide:

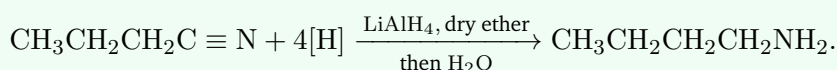


Now use bromine and aqueous sodium hydroxide for Hofmann degradation:



The carbonyl carbon is lost, so the two-carbon acid yields one-carbon methanamine. Reducing the amide instead would retain both carbons and give ethanamine, so degradation is essential.

**Step 3: Convert butanenitrile into 1-aminobutane** Reduce butanenitrile with lithium aluminium hydride in dry ether, followed by aqueous work-up:



The nitrile carbon becomes the terminal  $\text{CH}_2$  carbon bonded to  $\text{NH}_2$ . Consequently all four carbons are retained, and the amino group is on carbon 1 of the chain.

**Step 4: Conclusion** (i) Acetylate aniline, brominate acetanilide, then hydrolyse to p-bromoaniline. (ii) Form ethanamide, then use  $\text{Br}_2/\text{NaOH}$  to obtain  $\text{CH}_3\text{NH}_2$ . (iii) Reduce butanenitrile with  $\text{LiAlH}_4$  to obtain  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ .

**Quick Tip to Solve:** Protect aniline before selective monobromination; use Hofmann degradation only when the desired amine has one fewer carbon.

**28.** 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  $0.45^\circ\text{C}$ . Calculate the percentage association of acid if it forms a dimer in the solution. (Given:  $K_f$  for benzene =  $5.12 \text{ K kg mol}^{-1}$ ) [3 marks]

**Solution:**

**Concept:**

- Freezing-point depression is  $\Delta T_f = iK_fm$ , where  $i$  is the van't Hoff factor,  $K_f$  is the solvent's cryoscopic constant and  $m$  is the molality calculated from the initial amount of solute.
- Dimerisation combines two solute molecules into one particle. If the fraction of acid molecules associating is  $\alpha$ , the particle count gives  $i = 1 - \alpha/2$ .

**Step 1: Calculate the initial molality** The amount of acetic acid, using the given molar mass, is

$$n = \frac{0.3 \text{ g}}{60 \text{ g mol}^{-1}} = 0.005 \text{ mol.}$$

Convert the mass of benzene to kilograms before using molality:

$$m_{\text{benzene}} = 30 \text{ g} = 0.030 \text{ kg}, \quad m = \frac{0.005}{0.030} = \frac{1}{6} \text{ mol kg}^{-1}.$$

This is the analytical molality before accounting for association, not the reduced molality of independently moving particles.

**Step 2: Obtain the van't Hoff factor from the observed depression** If no association occurred, the expected depression would be

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

The measured depression is  $0.45 \text{ K}$ , since a temperature difference of one degree Celsius equals one kelvin. Therefore,

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

Its value below unity indicates that association reduces the number of solute particles.

**Step 3: Relate the particle count to percentage association** For dimer formation,  $2\text{CH}_3\text{COOH} \rightleftharpoons (\text{CH}_3\text{COOH})_2$ . Starting with one mole of acid molecules,  $1 - \alpha$  mole remains unassociated, while  $\alpha/2$  mole of dimers forms. The total particle amount is

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

Hence,

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

Multiplying the fraction by 100 gives the percentage of original acid molecules incorporated into dimers. The result is physically consistent: complete dimerisation would give  $i = 0.5$ , close to the observed value.

**Step 4: Conclusion** The percentage association of acetic acid is  $\alpha \times 100 = 94.53125\% \approx \boxed{94.5\%}$ .

**Quick Tip to Solve:** For dimerisation use percentage association =  $200(1-i)$ ; convert the 30 g of solvent into 0.030 kg before finding molality.

29. 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,  $A$  is the pre-exponential factor and  $E_a$  is activation energy.
- For unchanged reactant concentrations, reaction rate is proportional to  $k$ . Use absolute temperatures in kelvin and take  $A$  as constant over the small temperature interval.

**Step 1: Convert temperatures and identify the ratio** At the same reactant concentrations, doubling the rate means  $k_2/k_1 = 2$ . The temperatures are  $T_1 = 27 + 273 = 300 \text{ K}$  and  $T_2 = 37 + 273 = 310 \text{ K}$ . A Celsius temperature must not be inserted directly into the reciprocal-temperature expression.

**Step 2: Apply the two-temperature Arrhenius equation** Taking common logarithms of the Arrhenius equations and subtracting gives

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

Thus

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

The difference  $1/300 - 1/310$  is positive, consistent with a positive activation energy and a rate that rises on heating.

**Step 3: Substitute the supplied values** Using  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\log 2 = 0.3010$ ,

$$E_a = \frac{2.303(8.314)(0.3010)(300)(310)}{10} = 53597.5 \text{ J mol}^{-1}.$$

Dividing by 1000 converts joules to kilojoules. The supplied values of  $\log 3$  and  $\log 4$  are unnecessary because the measured rate ratio is two.

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

**Quick Tip to Solve:** Convert both Celsius temperatures to kelvin first; use only the logarithm of the actual rate ratio.

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

(a) HI

(b) Conc.  $\text{HNO}_3$

(c)  $\text{Br}_2$  water

(d) HCN

[3 marks]

**Solution:**

**Concept:**

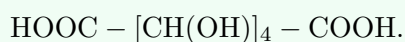
- Open-chain D-glucose has the structure  $\text{CHO} - [\text{CH}(\text{OH})]_4 - \text{CH}_2\text{OH}$ ; its aldehyde and terminal primary alcohol groups undergo different reactions.
- Bromine water oxidises only the aldehyde group, whereas concentrated nitric acid oxidises both terminal groups. Hydrogen cyanide adds across the aldehyde carbonyl.

**Step 1: (a) Reaction with HI** On prolonged heating with HI, all oxygen-containing groups of glucose are removed while its unbranched six-carbon skeleton is retained. The organic product is n-hexane, with structure



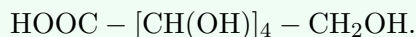
This reaction supports the presence of a straight chain of six carbon atoms in glucose.

**Step 2: (b) Reaction with concentrated nitric acid** The aldehyde group  $-\text{CHO}$  and the terminal primary alcohol group  $-\text{CH}_2\text{OH}$  are both oxidised to carboxyl groups. The product is saccharic acid (D-glucaric acid):



The four intermediate hydroxyl-bearing carbons retain their configuration.

**Step 3: (c) Reaction with bromine water** Bromine water is a mild oxidising agent. It changes the aldehyde group to a carboxyl group without oxidising the terminal primary alcohol. The product is D-gluconic acid:



Its difference from saccharic acid is therefore the unchanged terminal  $-\text{CH}_2\text{OH}$  group.

**Step 4: (d) Reaction with HCN** Cyanide attacks the aldehyde carbonyl carbon and the resulting oxygen is protonated. The cyanohydrin product has the structure



The original aldehyde carbon now carries  $-\text{OH}$ ,  $-\text{CN}$ , hydrogen and the glucose chain. A new stereogenic centre is formed, so two cyanohydrin configurations at that centre can result.

**Step 5: Conclusion** Any three required products are: (a) n-hexane, (b) saccharic acid, (c) gluconic acid and (d) glucose cyanohydrin, with the structures given above.

**Quick Tip to Solve:** Count the carbon atoms: HCN adds one carbon, while oxidation by bromine water or nitric acid preserves the six-carbon chain.

## Section D (8 marks)

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

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

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

Answer the following questions:

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

[1 mark]

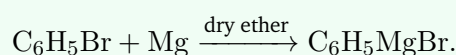
**Solution:**

**Concept:**

- Magnesium reacts with an organic halide in dry ether to form a Grignard reagent, represented by  $RMgX$ .
- Ether provides a suitable medium for the organomagnesium compound; moisture destroys it by protonating its organic group.

**Step 1: Identify the organic group** Bromobenzene is  $C_6H_5Br$ . Its phenyl group  $C_6H_5-$  is retained, and magnesium inserts into the carbon-bromine bond.

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



The product is an organomagnesium halide, not benzene. Keeping the ether dry prevents reaction with water, which would otherwise consume the Grignard reagent.

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

**Quick Tip to Solve:** Insert Mg between the organic group and halogen; remember that Grignard preparation requires dry ether.

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

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

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

[1 mark]

**Solution:**

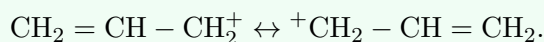
**Concept:**

- In an  $S_N1$  reaction, the slow step is carbon-halogen bond ionisation to form a carbocation.

**Quick Tip to Solve:** For an  $S_N1$  comparison, first draw the carbocation after halide loss and look for resonance or tertiary stabilisation.

- Greater carbocation stability favours faster ionisation. Resonance stabilises allylic carbocations, and hyperconjugation and the electron-releasing inductive effect stabilise tertiary carbocations.

**Step 1: Compare the first pair**  $\text{CH}_2 = \text{CH} - \text{CH}_2\text{Cl}$  forms an allylic carbocation whose positive charge is delocalised by resonance:



Propyl chloride would form an unstabilised primary carbocation. Therefore allyl chloride ionises more readily.

**Step 2: Compare the second pair**  $(\text{CH}_3)_3\text{CCl}$  forms a tertiary carbocation stabilised by three methyl groups.  $\text{CH}_3\text{Cl}$  would require a highly unstable methyl carbocation and has negligible ordinary  $\text{S}_{\text{N}}1$  reactivity. Hydroxide attacks after the slow ionisation step; its strength does not reverse this carbocation-stability comparison.

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

**Quick Tip to Solve:** For an  $\text{S}_{\text{N}}1$  comparison, first draw the carbocation after halide loss and look for resonance or tertiary stabilisation.

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

(1) 1-chlorobutane

(2) but-1-ene.

[2 marks]

#### Solution:

##### Concept:

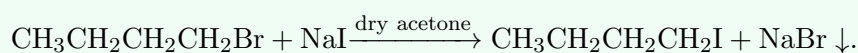
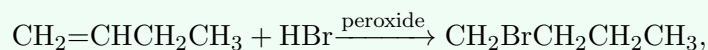
- Finkelstein reaction replaces chlorine or bromine in an alkyl halide by iodine using sodium iodide in dry acetone.
- Addition of  $\text{HBr}$  in the presence of peroxide follows the anti-Markovnikov rule; the peroxide effect does not operate with  $\text{HI}$ .

**Step 1: From 1-chlorobutane** Treat 1-chlorobutane with sodium iodide in dry acetone. The primary carbon permits nucleophilic substitution by iodide:



Sodium chloride precipitates from acetone, driving the halogen-exchange reaction towards 1-iodobutane.

**Step 2: From but-1-ene** First add  $\text{HBr}$  in the presence of peroxide to put bromine on the terminal carbon, producing 1-bromobutane. Then perform halogen exchange:



Direct addition of  $\text{HI}$  gives mainly 2-iodobutane by Markovnikov addition, so it cannot give the

**Quick Tip to Solve:** For a terminal iodide from an alkene, use  $\text{HBr}$ /peroxide first and then exchange  $\text{Br}$  for  $\text{I}$ .

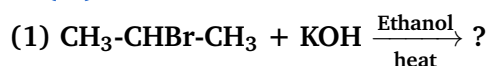
required terminal iodo compound by this route.

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

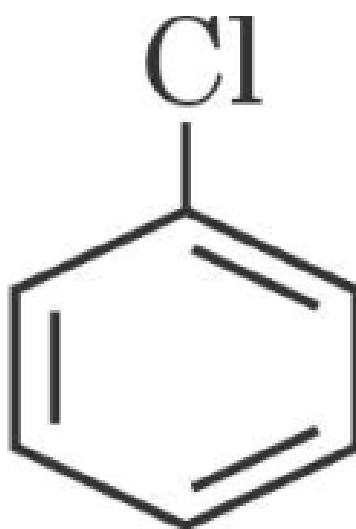
**Quick Tip to Solve:** For a terminal iodide from an alkene, use HBr/peroxide first and then exchange Br for I.

OR

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



[2 marks]

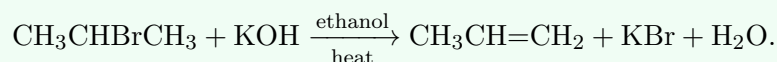


**Solution:**

**Concept:**

- Hot alcoholic KOH favours elimination of a hydrogen halide from a haloalkane, forming an alkene.
- Chlorine deactivates the benzene ring inductively but directs electrophilic substitution to the ortho and para positions through resonance.

**Step 1: Elimination from 2-bromopropane** Ethanolic KOH on heating removes a hydrogen from an adjacent carbon and bromine from the central carbon. The two adjacent methyl groups are equivalent, so either elimination gives the same alkene:



The major product is propene. Aqueous KOH would favour substitution to propan-2-ol, but the specified hot ethanolic conditions favour elimination.

**Step 2: Acylation of chlorobenzene** Acetyl chloride with anhydrous aluminium chloride introduces

**Quick Tip to Solve:** Check the solvent for elimination, and choose the less crowded para position for bulky acyl substitution.

an acetyl group,  $-\text{COCH}_3$ , on the ring. Chlorine directs substitution to the ortho and para positions; the para product predominates because it has less steric crowding:



The major product is 4-chloroacetophenone, with the chlorine and acetyl group at the 1,4 positions. The ortho isomer is the minor product.

**Step 3: Conclusion** (1) Propene,  $\text{CH}_3\text{CH}=\text{CH}_2$ . (2) 4-Chloroacetophenone,  $\text{p-ClC}_6\text{H}_4\text{COCH}_3$ .

**Quick Tip to Solve:** Check the solvent for elimination, and choose the less crowded para position for bulky acyl substitution.

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

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

Answer the following questions:

When a coordination compound  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  is mixed with  $\text{AgNO}_3$  solution, 2 moles of  $\text{AgCl}$  are precipitated per mole of the compound. Write the structural formula of the complex and secondary valency for Nickel ion.

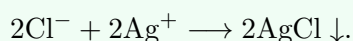
[1 mark]

**Solution:**

**Concept:**

- Only ionisable chloride ions outside the coordination sphere precipitate immediately with  $\text{AgNO}_3$ .
- Werner secondary valency is the coordination number: the number of donor atoms directly attached to the metal.

**Step 1: Locate the chloride ions** Two moles of  $\text{AgCl}$  per mole of compound account for both chloride ions. Thus both chlorides are outside the coordination sphere:



They balance the charge of the nickel(II) complex cation.

**Step 2: Identify the coordinated ligands** The six water molecules are neutral, monodentate ligands coordinated to  $\text{Ni}^{2+}$ . Therefore the formula is  $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ , and six oxygen donor atoms give nickel a secondary valency of six. The primary valency is two and should not be confused with this coordination number.

**Quick Tip to Solve:** Count precipitated chloride outside the brackets before counting ligands inside them.

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

**Quick Tip to Solve:** Count precipitated chloride outside the brackets before counting ligands inside them.

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

[1 mark]

**Solution:**

**Concept:**

- Ionisation isomers exchange a coordinated anionic ligand with a counter-ion outside the coordination sphere.
- In IUPAC naming, neutral  $\text{NH}_3$  is ammine and coordinated  $\text{Cl}^-$  is chlorido.

**Step 1: Construct the ionisation isomer** Exchange the coordinated sulphate and the outer chloride in  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$ . The ionisation isomer is  $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ . Its sulphate counter-ion has charge  $-2$ , so the complex ion has charge  $+2$ .

**Step 2: Determine the name** If the cobalt oxidation state is  $x$ , the five neutral ammine ligands and the chlorido ligand give  $x - 1 = +2$ , hence  $x = +3$ . Name ammine before chlorido alphabetically, specify cobalt(III), and then name the sulphate counter-ion. The metal retains the name cobalt because the coordination entity is cationic.

**Step 3: Conclusion** The IUPAC name is  $\boxed{\text{pentaamminechloridocobalt(III) sulphate}}$ .

**Quick Tip to Solve:** Exchange only the inner anion and the counter-ion, then recalculate the complex charge before naming.

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

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

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

[Atomic number: Ni = 28, Fe = 26]

[2 marks]

**Solution:**

**Concept:**

- In VBT,  $sp^3$  hybridisation gives tetrahedral geometry, whereas  $d^2sp^3$  hybridisation gives inner-orbital octahedral geometry.
- A complex with no unpaired electrons is diamagnetic; a complex with unpaired electrons is paramagnetic.

**Step 1: Tetracarbonylnickel** CO is neutral, so nickel has oxidation state zero. Free nickel has configuration  $[\text{Ar}]3d^84s^2$ . In the presence of strong-field CO, the valence electrons pair in the  $3d$  orbitals to give  $3d^{10}$ , leaving the  $4s$  and three  $4p$  orbitals available for  $sp^3$  hybridisation. Four CO ligands donate lone pairs into these four hybrid orbitals. Thus  $[\text{Ni}(\text{CO})_4]$  is tetrahedral and all its electrons are paired, making it diamagnetic.

**Quick Tip to Solve:** Determine oxidation state and d-electron count before applying pairing and assigning VBT hybridisation.

**Step 2: Hexacyanidoferrate(III)** For  $[\text{Fe}(\text{CN})_6]^{3-}$ , let iron have oxidation state  $x$ . Then  $x - 6 = -3$ , so  $x = +3$ .  $\text{Fe}^{3+}$  has configuration  $[\text{Ar}]3d^5$ . Strong-field cyanide pairs these five electrons in three  $3d$  orbitals, leaving two  $3d$  orbitals vacant, but one electron remains unpaired. Two inner  $3d$ , one  $4s$  and three  $4p$  orbitals form six  $d^2sp^3$  hybrids. Hence the complex is octahedral and paramagnetic with one unpaired electron.

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

**Quick Tip to Solve:** Determine oxidation state and d-electron count before applying pairing and assigning VBT hybridisation.

OR

**32(iii). Give reasons:**

(1) Low spin tetrahedral complexes are not formed.

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

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

[2 marks]

**Solution:**

**Concept:**

- Crystal-field splitting competes with pairing energy  $P$ . Electrons pair in lower orbitals only when the energy saved exceeds  $P$ .
- In octahedral valence bond theory,  $d^2sp^3$  uses two inner  $3d$  orbitals, whereas  $sp^3d^2$  uses outer  $4d$  orbitals.

**Step 1: (1) Explain the absence of low-spin tetrahedral complexes** Tetrahedral splitting  $\Delta_t$  is small; for the same metal and ligands,  $\Delta_t = \frac{4}{9}\Delta_o$ , where  $\Delta_o$  is octahedral splitting. Normally  $\Delta_t < P$ . It therefore costs less energy to occupy the higher tetrahedral orbitals singly than to pair electrons in the lower orbitals. Hence tetrahedral complexes are high spin whenever a high-spin/low-spin distinction is possible.

**Step 2: (2) Compare the orbitals used by cobalt and nickel** Cobalt has atomic number 27, so  $\text{Co}^{3+}$  is  $[\text{Ar}]3d^6$ . With ammonia and the high charge of cobalt(III), the six  $3d$  electrons pair in three orbitals, leaving two inner  $3d$  orbitals vacant. These combine with one  $4s$  and three  $4p$  orbitals to form six  $d^2sp^3$  orbitals in  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Nickel has atomic number 28, so  $\text{Ni}^{2+}$  is  $[\text{Ar}]3d^8$ . Eight electrons cannot be accommodated in just three  $3d$  orbitals, whose capacity is six. Thus two vacant inner  $3d$  orbitals cannot be produced even by pairing. The six-coordinate nickel complex instead uses one  $4s$ , three  $4p$  and two  $4d$  orbitals for  $sp^3d^2$  hybridisation.

**Step 3: Conclusion** Small tetrahedral splitting prevents low-spin pairing.  $[\text{Co}(\text{NH}_3)_6]^{3+}$  is an inner-orbital  $d^2sp^3$  complex, while  $[\text{Ni}(\text{NH}_3)_6]^{2+}$  is an outer-orbital  $sp^3d^2$  complex.

**Quick Tip to Solve:** Count the metal-ion d electrons first: a d8 ion cannot leave two inner d orbitals empty.

### Section E (15 marks)

**33(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)  $\text{Cu}^{+}$  ion is unstable in aqueous solution.

(ii) Write the equations involved in the preparation of  $\text{KMnO}_4$  from Pyrolusite ore ( $\text{MnO}_2$ ). [5 marks]

#### Solution:

##### Concept:

- Transition-metal ions accept lone pairs from ligands to form coordinate bonds. Small size, high charge density and suitable vacant orbitals favour complex formation.
- The half-filled  $3d^5$  configuration of  $\text{Mn}^{2+}$  is especially stable. Standard reduction potentials describe the tendency of the written reduction to occur.
- Hydration stabilises aqueous ions; a sufficiently favourable hydration enthalpy can compensate for the energy needed to form a more highly charged ion.
- In potassium permanganate manufacture, manganese is oxidised from +4 in the ore to +6 in manganate and then to +7 in permanganate.

**Step 1: (i)(1) Explain complex formation by transition metals** Transition-metal ions have relatively small radii and high ionic charges, giving them high charge density. They attract electron pairs strongly and have suitable vacant orbitals to accept ligand lone pairs. Each ligand therefore forms a coordinate bond with the central ion, producing a coordination complex. For example, ammonia supplies nitrogen lone pairs to a metal ion in an ammine complex.

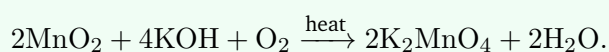
**Step 2: (i)(2) Explain the two manganese reduction potentials** Manganese has configuration  $[\text{Ar}]3d^54s^2$ , and  $\text{Mn}^{2+}$  has the stable half-filled  $[\text{Ar}]3d^5$  configuration. The reduction  $\text{Mn}^{2+} + 2e^{-} \rightarrow \text{Mn}$  removes this especially stable ionic state and is relatively unfavourable, so  $E_{\text{Mn}^{2+}/\text{Mn}}^{\circ}$  is highly negative. Conversely,  $\text{Mn}^{3+}$  is  $3d^4$ ; the reduction  $\text{Mn}^{3+} + e^{-} \rightarrow \text{Mn}^{2+}$  produces stable  $3d^5$ . Its strong tendency to occur accounts for the highly positive  $E_{\text{Mn}^{3+}/\text{Mn}^{2+}}^{\circ}$ .

**Step 3: (i)(3) Explain instability of aqueous copper(I)** Although  $\text{Cu}^{+}$  has a filled  $3d^{10}$  configuration,  $\text{Cu}^{2+}$  has a much more negative hydration enthalpy. This hydration stabilisation more than compensates for the energy needed to remove the second electron when disproportionation is considered. Consequently, aqueous copper(I) undergoes simultaneous oxidation and reduction:



One copper(I) ion loses an electron and the other gains it; thus copper(I) is unstable in aqueous solution.

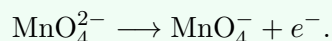
**Step 4: (ii) Prepare manganate from pyrolusite** Fuse pyrolusite,  $\text{MnO}_2$ , with potassium hydroxide in the presence of air or oxygen. The manganese(IV) oxide is oxidised to green potassium manganate:



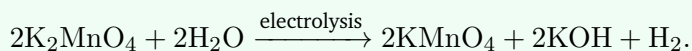
**Quick Tip to Solve:** Track manganese oxidation states as +4 to +6 to +7, and write both manganese potentials as reductions before explaining their signs.

Oxygen acts as the oxidising agent in the alkaline fusion.

**Step 5: (ii) Convert manganate into permanganate** Oxidise the manganate solution electrolytically. At the anode, manganese(VI) loses one electron to form manganese(VII):



The overall electrolytic conversion, including hydrogen evolution at the cathode, can be written as



Concentrating the resulting solution gives purple potassium permanganate crystals.

**Step 6: Conclusion** Complex formation follows from high charge density and lone-pair acceptance; manganese potentials reflect stable  $3d^5 \text{Mn}^{2+}$ ; aqueous  $\text{Cu}^+$  disproportionates because copper(II) is strongly hydrated. Pyrolusite is converted to  $\text{K}_2\text{MnO}_4$  by alkaline oxidative fusion and then to  $\text{KMnO}_4$  by electrolytic oxidation.

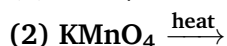
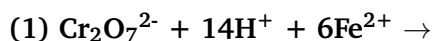
**Quick Tip to Solve:** Track manganese oxidation states as +4 to +6 to +7, and write both manganese potentials as reductions before explaining their signs.

OR

**33(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:**

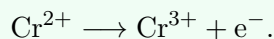
- Oxidation states depend on the electrons available for bonding and the stability of the resulting electronic configuration. Scandium forms  $\text{Sc}^{3+}$ , with the noble-gas configuration  $[\text{Ar}]$ .
- A reducing agent loses electrons. Aqueous  $\text{Cr}^{2+}$  is readily oxidised to  $\text{Cr}^{3+}$ , whose  $3d^3$  configuration is comparatively stable.
- Redox equations conserve both atoms and total charge. In acidic solution, dichromate is reduced to  $\text{Cr}^{3+}$ , while  $\text{Fe}^{2+}$  is oxidised to  $\text{Fe}^{3+}$ .
- Misch metal is a lanthanoid-rich alloy. Its useful mechanical properties arise from combining rare-earth metals with iron and small amounts of other elements.

**Step 1: (i)(1) Identify the metal with one oxidation state** The metal is **scandium (Sc)**. Its atomic

**Quick Tip to Solve:** For dichromate, two Cr atoms each gain three electrons: match this with six Fe(II) ions. For heated permanganate, remember the three products manganate, manganese dioxide and oxygen.

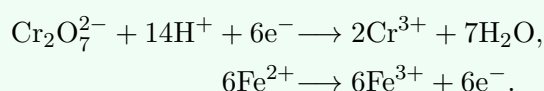
electronic configuration is  $[\text{Ar}]3d^14s^2$ . Loss of the two  $4s$  electrons and the one  $3d$  electron gives  $\text{Sc}^{3+}$ , with configuration  $[\text{Ar}]$ . Thus scandium exhibits the +3 oxidation state in its compounds. Zinc is not the required transition metal: its atom and its usual ion both have a completely filled  $3d$  subshell.

**Step 2: (i)(2) Identify the strong reducing agent** The metal is **chromium (Cr)**. In aqueous solution its +2 ion has configuration  $3d^4$  and readily loses an electron to form the more stable  $3d^3$  chromium(III) ion:

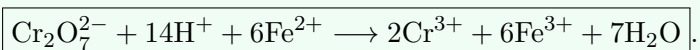


Since  $\text{Cr}^{2+}$  supplies an electron to another species, it acts as a strong reducing agent. The identification is based on oxidation of the +2 ion, rather than reduction of that ion to the metal.

**Step 3: (ii)(1) Complete the dichromate reaction** The reduction and oxidation half-equations are

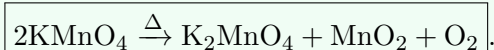


Cancelling the six electrons gives



Each chromium atom changes from +6 to +3, so two chromium atoms accept six electrons in total. Six iron(II) ions each release one electron. There are two Cr, seven O, fourteen H and six Fe atoms on each side; the total charge is +24 on each side.

**Step 4: (ii)(2) Write the thermal decomposition equation** On heating, potassium permanganate forms potassium manganate, manganese dioxide and oxygen:



The two potassium atoms appear together in  $\text{K}_2\text{MnO}_4$ ; the two manganese atoms are divided between manganate and manganese dioxide. The eight oxygen atoms on the left equal  $4 + 2 + 2$  on the right. Manganese is reduced from +7 to +6 and +4, while some oxide oxygen is oxidised to molecular oxygen.

**Step 5: (iii) Describe Misch metal and give a use** **Misch metal** is an alloy containing about 95% lanthanoid metals and about 5% iron, with traces of sulphur, carbon, calcium and aluminium. The lanthanoid portion is principally a mixture of metals such as cerium and lanthanum. One use is in **magnesium-based alloys used to make bullets and shells**. Incorporating Misch metal improves the properties of these magnesium alloys for such applications.

**Step 6: Conclusion** (i) The metals are **Sc** and **Cr**, respectively. (ii) The balanced reactions produce  $2\text{Cr}^{3+} + 6\text{Fe}^{3+} + 7\text{H}_2\text{O}$  from the stated dichromate reactants, and  $\text{K}_2\text{MnO}_4 + \text{MnO}_2 + \text{O}_2$  from  $2\text{KMnO}_4$  on heating. (iii) Misch metal is a lanthanoid-rich alloy containing iron, used in magnesium-based alloys for bullets and shells.

**Quick Tip to Solve:** For dichromate, two Cr atoms each gain three electrons: match this with six Fe(II) ions. For heated permanganate, remember the three products manganate, manganese dioxide and oxygen.

**34(a).** (i) An organic compound (X) having molecular formula  $C_5H_{10}O$  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

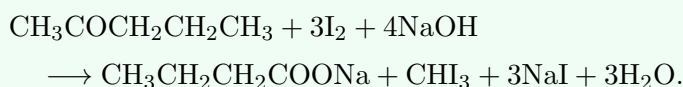
[5 marks]

**Solution:**

**Concept:**

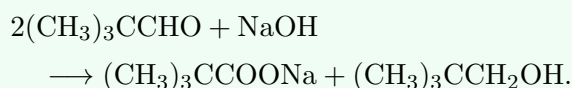
- A methyl ketone contains the group  $CH_3CO-$  and gives yellow iodoform,  $CHI_3$ , with iodine and alkali.
- Cannizzaro disproportionation is shown by aldehydes without any hydrogen on the carbon adjacent to the  $-CHO$  group. Tollens' reagent oxidises an aldehyde to carboxylate while silver ions form metallic silver.
- A chiral carbon has four different substituents. Wolff-Kishner reduction converts a carbonyl group into a methylene group; the Hell-Volhard-Zelinsky reaction replaces an  $\alpha$  hydrogen of a carboxylic acid by halogen.

**Step 1: (i)(1) Select a methyl ketone** One suitable structure is pentan-2-one,  $CH_3COCH_2CH_2CH_3$ . Its molecular formula is  $C_5H_{10}O$ , and its  $CH_3CO-$  group gives the iodoform test:



The yellow precipitate is iodoform. Another valid structure is the branched methyl ketone 3-methylbutan-2-one. Its formula is  $CH_3COCH(CH_3)_2$ , and it also gives this test. Pentan-3-one does not contain a methyl group directly bonded to its carbonyl carbon, so it does not satisfy this test.

**Step 2: (i)(2) Select an aldehyde with no  $\alpha$  hydrogen** The required structure is 2,2-dimethylpropanal,  $(CH_3)_3CCHO$ . The carbon next to the aldehyde group is attached to three methyl groups and the aldehyde carbon, and therefore carries no hydrogen. It undergoes Cannizzaro's reaction with concentrated alkali:

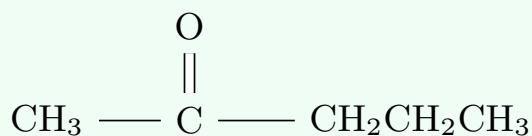


One aldehyde molecule is oxidised to the carboxylate and the other is reduced to the primary alcohol. Ordinary aldehydes with  $\alpha$  hydrogens instead favour aldol reactions under the appropriate alkaline conditions.

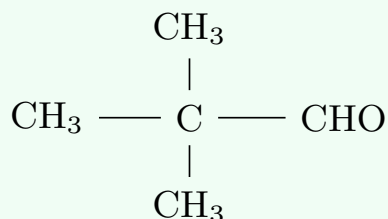
**Step 3: (i)(3) Select a chiral aldehyde** The structure is 2-methylbutanal,  $CH_3CH_2CH(CH_3)CHO$ . Its aldehyde group reduces Tollens' reagent to give a silver mirror. Its carbon at position 2, marked with an asterisk in the drawing, has four different groups:  $H$ ,  $CH_3$ ,  $CH_2CH_3$  and  $CHO$ . It is therefore a chiral carbon. The total carbon count is five and the hydrogen count is ten, as required.

**Quick Tip to Solve:** For the three structures, check in order for a methyl ketone, no  $\alpha$  hydrogen, and an aldehyde with four different groups on one carbon.

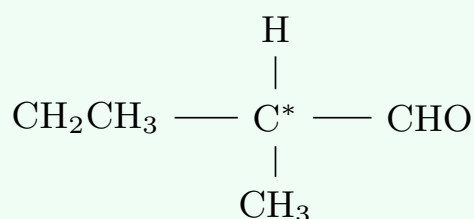
(1) Pentan-2-one



(2) 2,2-Dimethylpropanal

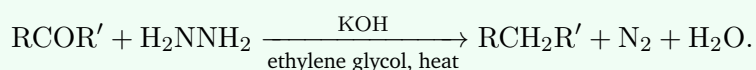


(3) 2-Methylbutanal



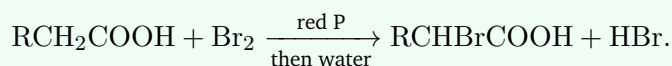
Structures satisfying the three tests; the asterisk identifies the chiral carbon.

**Step 4: (ii)(1) Write Wolff-Kishner reduction** An aldehyde or ketone first forms a hydrazone with hydrazine. Heating with potassium hydroxide in a high-boiling solvent such as ethylene glycol then removes the oxygen functionality, with evolution of nitrogen. The overall ketone reaction is



For an aldehyde, take  $\text{R}' = \text{H}$ , giving  $\text{RCHO} \rightarrow \text{RCH}_3$ . Thus the carbon skeleton is retained while the carbonyl oxygen is replaced by two hydrogens.

**Step 5: (ii)(2) Write Hell-Volhard-Zelinsky reaction** A carboxylic acid containing an alpha hydrogen reacts with bromine in the presence of red phosphorus, followed by hydrolysis, to form an alpha-bromocarboxylic acid:



Chlorine can similarly give the alpha-chloro acid. The substitution occurs at the carbon immediately adjacent to  $-\text{COOH}$ , rather than on the hydroxyl group. An alpha hydrogen is essential for this reaction.

**Step 6: Conclusion** The structures are pentan-2-one (or 3-methylbutan-2-one), 2,2-dimethylpropanal and 2-methylbutanal for (i)(1), (2) and (3), respectively. Wolff-Kishner reduction gives  $\text{RCH}_2\text{R}'$  from  $\text{RCOR}'$ ; the Hell-Volhard-Zelinsky reaction gives  $\text{RCHBrCOOH}$  from  $\text{RCH}_2\text{COOH}$ .

**Quick Tip to Solve:** For the three structures, check in order for a methyl ketone, no alpha hydrogen, and an aldehyde with four different groups on one carbon.

34(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:

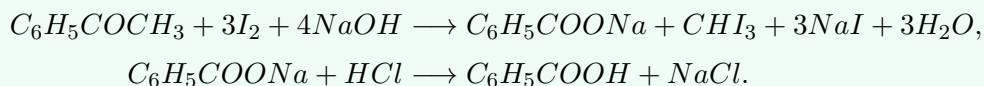
- (1)  $\text{O}_2\text{N}-\text{CH}_2-\text{COOH}$ ,  $\text{F}-\text{CH}_2-\text{COOH}$ ,  $\text{CN}-\text{CH}_2\text{COOH}$  (Acidic character)
- (2) Ethanal, Propanal, Butanone, Propanone (Reactivity in nucleophilic addition reactions) [5 marks]

### Solution:

#### Concept:

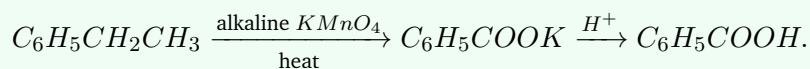
- A methyl ketone,  $\text{RCOCH}_3$ , undergoes the haloform reaction with iodine and alkali to give the carboxylate  $\text{RCOO}^-$ ; acidification gives  $\text{RCOOH}$ .
- An alkylbenzene containing a benzylic hydrogen undergoes vigorous side-chain oxidation to benzoic acid. An aryl Grignard reagent reacts with  $\text{CO}_2$ , adding one carbon to form a carboxylate on hydrolysis.
- Electron-withdrawing groups exert a negative inductive effect ( $-I$ ) and stabilise the carboxylate conjugate base, increasing acidity. Carbonyl addition is favoured by a more electrophilic and less sterically hindered carbonyl carbon.

**Step 1: (i)(1) Convert acetophenone by the haloform reaction** Acetophenone,  $\text{C}_6\text{H}_5\text{COCH}_3$ , is a methyl ketone. Treat it with iodine in aqueous sodium hydroxide, then acidify the sodium benzoate obtained:



Cleavage of the methyl ketone removes its methyl carbon as iodoform while retaining the carbonyl carbon in the carboxyl group.

**Step 2: (i)(2) Oxidise the side chain of ethylbenzene** Heat ethylbenzene with alkaline potassium permanganate, followed by acidification:

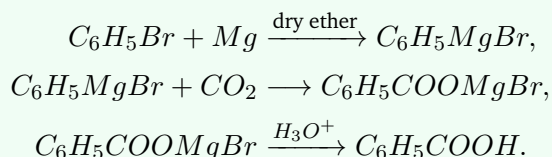


Ethylbenzene has benzylic hydrogen atoms, so strong oxidation converts its side chain into a carboxyl group. The benzene ring remains intact; the terminal carbon is removed during oxidation.

**Step 3: (i)(3) Carboxylate a Grignard reagent from bromobenzene** React bromobenzene with magnesium in dry ether to prepare phenylmagnesium bromide. Treat this reagent with dry carbon

**Quick Tip to Solve:** Use haloform cleavage for the methyl ketone, side-chain oxidation for the alkylbenzene, and Grignard carboxylation for the aryl halide; rank carbonyl reactivity by both alkyl donation and steric hindrance.

dioxide and then hydrolyse with dilute acid:

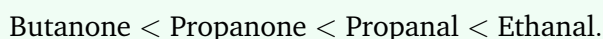


The carbon of carbon dioxide becomes the carboxyl carbon. Dry conditions are essential during Grignard preparation and carboxylation because water destroys the reagent.

**Step 4: (ii)(1) Compare acidic character** All three acids contain the substituent on the carbon adjacent to  $COOH$ , so their relative electron-withdrawing effects can be compared directly. For these groups the relevant  $-I$  strength increases as  $F < CN < NO_2$ . Greater electron withdrawal stabilises the negative charge of the conjugate carboxylate and facilitates proton loss. The increasing acidity order is therefore



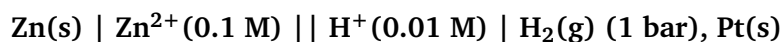
**Step 5: (ii)(2) Compare nucleophilic addition reactivity** Alkyl groups donate electron density by the  $+I$  effect, reducing the partial positive charge on the carbonyl carbon. They also hinder the approach of a nucleophile. Ketones have two alkyl groups and are less reactive than aldehydes, which have one alkyl group and one hydrogen. Within each pair, an ethyl group gives greater donation and steric hindrance than a methyl group. Thus butanone is less reactive than propanone, while propanal is less reactive than ethanal:



**Step 6: Conclusion** Acetophenone gives benzoic acid by haloform reaction followed by acidification; ethylbenzene by alkaline  $KMnO_4$  oxidation followed by acidification; and bromobenzene via its Grignard reagent,  $CO_2$  and acidic hydrolysis. Increasing acidic character:  $FCH_2COOH < CNCH_2COOH < O_2NCH_2COOH$ . Increasing nucleophilic addition reactivity: butanone  $<$  propanone  $<$  propanal  $<$  ethanal.

**Quick Tip to Solve:** Use haloform cleavage for the methyl ketone, side-chain oxidation for the alkylbenzene, and Grignard carboxylation for the aryl halide; rank carbonyl reactivity by both alkyl donation and steric hindrance.

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



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

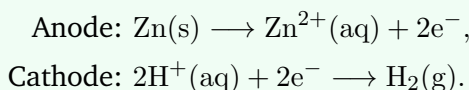
(b) State Kohlrausch law of independent migration of ions. Why does the conductivity of a solution decrease with dilution? [5 marks]

### Solution:

#### Concept:

- A galvanic cell has oxidation at the anode and reduction at the cathode. Using reduction potentials,  $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$ .
- At 25°C, the Nernst equation is  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log Q$ , where  $n$  is the number of electrons transferred and  $Q$  is the reaction quotient. Pure solids have unit activity.
- At infinite dilution, the limiting molar conductivity of an electrolyte is the sum of the independent ionic contributions. Conductivity  $\kappa$  measures conduction by the ions present per unit volume of solution.

**Step 1: (a) Identify the electrode reactions and standard emf** Zinc is the anode and the hydrogen electrode is the cathode. The balanced half-reactions are



Thus the overall reaction is  $\text{Zn(s)} + 2\text{H}^{+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ , and  $n = 2$ . The standard cell potential is

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

The electrode potentials given are reduction potentials, so the negative zinc value is subtracted when calculating the cell potential.

**Step 2: (a) Calculate the reaction quotient and apply the Nernst equation** For the balanced cell reaction, hydrogen-ion concentration occurs squared in the denominator. Taking concentrations relative to 1 M and hydrogen pressure relative to 1 bar,

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

Since  $\log 10 = 1$ ,  $\log Q = 3$ . Therefore,

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

The dilute hydrogen-ion solution lowers the hydrogen electrode's reduction potential; the calculated cell emf is consequently below its standard value.

**Step 3: (b) State Kohlrausch's law** At infinite dilution, each ion makes a definite contribution to the limiting molar conductivity of an electrolyte, independent of the nature of the other ion present.

**Quick Tip to Solve:** Balance the cell reaction before forming  $Q$ : the coefficient 2 of hydrogen ions gives the square in the denominator, while the two electrons give  $n = 2$ .

Hence, for an electrolyte giving  $\nu_+$  cations and  $\nu_-$  anions per formula unit,

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

where  $\lambda_+^\circ$  and  $\lambda_-^\circ$  are the limiting ionic molar conductivities of the cation and anion, respectively. The coefficients count the ions produced by one formula unit of the electrolyte.

**Step 4: (b) Explain the effect of dilution on conductivity** Dilution increases the volume of the solution and reduces the number of ions per unit volume. Fewer charge carriers are then available within a given volume to carry electric current, so the conductivity  $\kappa$  decreases. Although ionic mobility can increase as interionic interactions diminish, the reduction in ion concentration makes conductivity fall. This differs from molar conductivity, which generally increases on dilution because it refers to the conductivity associated with one mole of electrolyte; weak electrolytes also undergo increased ionisation.

**Step 5: Conclusion** (a) The emf of the cell at 25°C is 0.671 V. (b) Kohlrausch's law expresses limiting molar conductivity as the sum of 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 forming Q: the coefficient 2 of hydrogen ions gives the square in the denominator, while the two electrons give  $n = 2$ .