

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

## Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

### General Instructions

- (i) This Question Paper contains **35** questions. **All** questions are compulsory.
- (ii) Question Paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.
- (iii) **In section A** – question number **1** to **18** are Multiple Choice (MCQ) type questions carrying **1** mark each.
- (iv) **In section B** – question number **19** to **25** are Very Short Answer (VSA) type questions carrying **2** marks each.
- (v) **In section C** – question number **26** to **30** are Short Answer (SA) type questions carrying **3** marks each.
- (vi) **In section D** – question number **31 & 32** are case-based questions carrying **4** marks each.
- (vii) **In section E** – question number **33** to **35** are Long Answer (LA) 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 calculator is **NOT** allowed.

### Section A (18 marks)

1. Which of the following belongs to the class of Vinyl halides?

[1 mark]

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

**Correct Answer:** (B)  $\text{CH}_2 = \text{C}(\text{Br}) - \text{CH}_3$

#### Solution:

##### Concept:

- A vinyl halide has its halogen directly bonded to an  $sp^2$ -hybridised carbon of a carbon-carbon double bond.
- An allylic halide has the halogen on an  $sp^3$  carbon adjacent to the double bond.

**Step 1: Inspect the halogen-bearing carbon** In option (B),  $\text{CH}_2 = \text{C}(\text{Br}) - \text{CH}_3$ , bromine is bonded directly to a carbon of the  $\text{C} = \text{C}$  bond. That carbon is  $sp^2$ -hybridised, so the compound is a vinyl halide.

**Step 2: Exclude the other structures** In (A), chlorine is on a saturated carbon separated from the double bond by another carbon. In (C), bromine is on the saturated carbon next to the double bond, so this is an allylic halide. In (D), bromine is attached to a carbon of a triple bond, which is  $sp$ -hybridised; this is not a vinyl halide.

**Step 3: Conclusion**  $\text{CH}_2 = \text{C}(\text{Br}) - \text{CH}_3$  is the vinyl halide. Hence, the correct option is (B).

**Quick Tip to Solve:** Locate the carbon directly attached to the halogen; a double-bond carbon identifies a vinyl halide.

2. What is the secondary valency of Cobalt in  $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ?

[1 mark]

- (A) 6  
(B) 4  
(C) 2  
(D) 8

**Correct Answer:** (A) 6

#### Solution:

##### Concept:

- Werner secondary valency is the coordination number: the number of donor atoms bonded directly to the metal.
- Ethylenediamine, en, is bidentate; each ligand supplies two nitrogen donor atoms. Chloride is monodentate.

**Step 1: Count the donor atoms** The two en ligands contribute  $2 \times 2 = 4$  donor atoms. The two

**Quick Tip to Solve:** For secondary valency, count donor atoms rather than the number of ligand names inside the brackets.

coordinated chloride ligands contribute  $2 \times 1 = 2$  donor atoms. Thus the total coordination number is  $4 + 2 = 6$ .

**Step 2: Distinguish coordination number from ligand count** There are four ligand molecules or ions, but each ethylenediamine binds through two atoms, so option (B), 4, is not the secondary valency. Option (C), 2, counts only chlorides. Option (D), 8, exceeds the actual number of donor atoms. The positive charge outside the brackets does not alter this count.

**Step 3: Conclusion** The secondary valency of cobalt is 6. Hence, the correct option is (A).

**Quick Tip to Solve:** For secondary valency, count donor atoms rather than the number of ligand names inside the brackets.

**3. When Benzene diazonium chloride reacts with phenol, it forms a dye. This reaction is called**

[1 mark]

- (A) Diazotisation reaction
- (B) Condensation reaction
- (C) Coupling reaction
- (D) Acetylation reaction

**Correct Answer:** (C) Coupling reaction

**Solution:**

**Concept:**

- Aromatic diazonium salts undergo azo coupling with activated aromatic rings such as phenol.
- The product contains an azo linkage,  $-\text{N} = \text{N}-$ , joining two aromatic rings.

**Step 1: Identify the dye-forming process** Benzene diazonium chloride couples with the activated phenol ring, mainly at the para position, to form an azo dye. The new linkage between the aromatic rings is  $-\text{N} = \text{N}-$ ; this characteristic dye-forming reaction is azo coupling.

**Step 2: Check the alternative names** Diazotisation converts a primary aromatic amine into a diazonium salt; the salt is already present here. Condensation is not the specific name for this azo dye-forming reaction. Acetylation introduces an acetyl group,  $\text{CH}_3\text{CO}-$ , which is not the transformation described.

**Step 3: Conclusion** This is a coupling reaction. Hence, the correct option is (C).

**Quick Tip to Solve:** When a diazonium salt reacts with phenol to make an azo dye, identify the reaction as coupling.

4. The slope in the plot of  $[R]$  vs. time for a zero order reaction is

[1 mark]

- (A)  $\frac{+k}{2.303}$
- (B)  $-k$
- (C)  $\frac{-k}{2.303}$
- (D)  $+k$

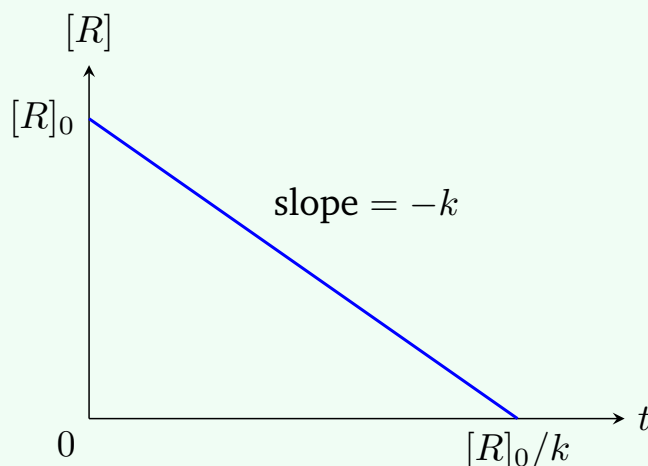
**Correct Answer:** (B)  $-k$

**Solution:**

**Concept:**

- For a zero-order reaction, the rate is independent of reactant concentration:  $-d[R]/dt = k$ .
- The integrated rate law is  $[R] = [R]_0 - kt$ , where  $[R]_0$  is the initial concentration and  $k$  is the positive rate constant.

**Step 1: Compare with the equation of a straight line** Write the integrated law as  $[R] = (-k)t + [R]_0$ . Comparing with  $y = mx + c$ , the vertical axis is  $[R]$ , the horizontal axis is time  $t$ , the intercept is  $[R]_0$ , and the slope is  $-k$ .



*Zero-order reactant concentration decreases linearly with time.*

**Step 2: Check the sign and logarithmic factor** Reactant concentration decreases as time increases, so a positive slope, as in (A) or (D), is impossible for disappearance of the reactant. The factor 2.303 appears in the common-logarithm form of the first-order law, not in this zero-order concentration plot; therefore (C) is also incorrect.

**Step 3: Conclusion** The slope of the  $[R]$  versus time plot is  $-k$ . Hence, the correct option is (B).

**Quick Tip to Solve:** Use the plotted variables first: concentration against time gives slope  $-k$  for zero order.

### 5. Proteins are polymers of

[1 mark]

- (A) Nucleic acids
- (B) Amino acids
- (C) Monosaccharides
- (D) Amines

**Correct Answer:** (B) Amino acids

#### **Solution:**

#### **Concept:**

- Proteins are polypeptides formed from  $\alpha$ -amino acid monomers.
- Adjacent amino acids join through peptide bonds,  $-\text{CO} - \text{NH}-$ , formed between a carboxyl group and an amino group.

**Step 1: Identify the repeating units** Each amino acid provides an amino group and a carboxyl group. Condensation between these groups produces peptide bonds, and repeated linking gives a polypeptide chain. Proteins consist of one or more such chains, so their monomers are amino acids.

**Step 2: Exclude the other biomolecules** Nucleic acids are themselves polymers of nucleotides and are not protein monomers. Monosaccharides form carbohydrate polymers such as starch and cellulose. Amines contain an amino group but lack the complete amino-acid structure needed for the standard peptide backbone.

**Step 3: Conclusion** Proteins are polymers of amino acids. Hence, the correct option is (B).

**Quick Tip to Solve:** Recall that a protein backbone contains peptide bonds joining amino-acid units, not sugar units.

### 6. Retention of configuration is observed in

[1 mark]

- (A)  $\text{S}_{\text{N}}1$  reaction
- (B)  $\text{S}_{\text{N}}2$  reaction
- (C) Neither  $\text{S}_{\text{N}}1$  nor  $\text{S}_{\text{N}}2$  reaction
- (D)  $\text{S}_{\text{N}}2$  reaction as well as  $\text{S}_{\text{N}}1$  reaction

**Correct Answer:** (A)  $\text{S}_{\text{N}}1$  reaction

#### **Solution:**

#### **Concept:**

- Retention means that a substitution product preserves the spatial configuration at the reacting stereogenic centre.
- An  $\text{S}_{\text{N}}1$  reaction forms a planar carbocation; an  $\text{S}_{\text{N}}2$  reaction proceeds by backside attack.

**Step 1: Examine the  $\text{S}_{\text{N}}1$  pathway** In an  $\text{S}_{\text{N}}1$  reaction, departure of the leaving group forms an approximately planar  $sp^2$  carbocation. The nucleophile can attack either face. Attack from one face gives inversion and attack from the other gives retention; hence retained product is observed as part of the racemised mixture.

**Quick Tip to Solve:** Distinguish retention as one  $\text{S}_{\text{N}}1$  product from exclusive retention:  $\text{S}_{\text{N}}1$  usually gives racemisation.

**Step 2: Examine the  $S_N2$  pathway and options** An  $S_N2$  substitution occurs in one step by backside attack, giving Walden inversion at the reacting stereogenic centre. It does not give retention in a single substitution. Thus (B) and (D) incorrectly include  $S_N2$ , while (C) incorrectly excludes the retained product formed by  $S_N1$ .

**Step 3: Conclusion** Retention is observed in an  $S_N1$  reaction, along with inversion. Hence, the correct option is (A).

**Quick Tip to Solve:** Distinguish retention as one  $S_N1$  product from exclusive retention:  $S_N1$  usually gives racemisation.

**7. An azeotropic mixture of two liquids will have a boiling point lower than either of the two liquids when it** [1 mark]

- (A) shows a negative deviation from Raoult's law
- (B) forms an ideal solution
- (C) shows a positive deviation from Raoult's law
- (D) is saturated

**Correct Answer:** (C) shows a positive deviation from Raoult's law

**Solution:**

**Concept:**

- Raoult's law relates a component's partial vapour pressure to its mole fraction in an ideal solution.
- Positive deviation means the total vapour pressure exceeds the ideal value because unlike inter-molecular attractions are weaker.

**Step 1: Identify the deviation** A minimum-boiling azeotrope boils below both pure liquids. Weaker attractions between unlike molecules let them escape more readily into the vapour, so the mixture shows a sufficiently large positive deviation from Raoult's law.

**Step 2: Check the alternatives** A higher vapour pressure reaches atmospheric pressure at a lower temperature. Negative deviation instead leads to maximum-boiling azeotropes, while an ideal solution does not form an azeotrope. Saturation alone does not establish this boiling-point behaviour.

**Step 3: Conclusion** The mixture shows a positive deviation from Raoult's law. Hence, the correct option is (C).

**Quick Tip to Solve:** Associate a minimum boiling point with high vapour pressure and positive deviation.

8. Which of the following solutions of KCl will have the highest value of molar conductivity? [1 mark]

- (A) 0.01 M
- (B) 1 M
- (C) 0.5 M
- (D) 0.1 M

**Correct Answer:** (A) 0.01 M

**Solution:**

**Concept:**

- Molar conductivity is  $\Lambda_m = 1000\kappa/c$ , when conductivity  $\kappa$  is in  $\text{S cm}^{-1}$  and concentration  $c$  is in  $\text{mol L}^{-1}$ .
- For strong electrolytes,  $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$  at low concentrations, with  $A > 0$ .

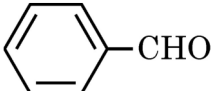
**Step 1: Use the dilution trend** KCl is a strong electrolyte. On dilution, interionic interactions weaken and the ions move more freely, increasing the conductivity contributed per mole of electrolyte. Thus molar conductivity increases as concentration decreases.

**Step 2: Compare all concentrations** The concentrations satisfy  $0.01 < 0.1 < 0.5 < 1 \text{ mol L}^{-1}$ . Therefore the 0.01 M solution has the greatest molar conductivity; each of (B), (C) and (D) is more concentrated. Specific conductivity generally falls on dilution, but that is a different quantity.

**Step 3: Conclusion** 0.01 M KCl has the highest molar conductivity. Hence, the correct option is (A).

**Quick Tip to Solve:** For the same strong electrolyte, choose the smallest concentration for maximum molar conductivity.

9. Which of the following does not give Cannizzaro reaction? [1 mark]

- (A)  $(\text{CH}_3)_3\text{C} - \text{CHO}$
- (B)  $(\text{CH}_3)_2\text{CH} - \text{CHO}$
- (C) 
- (D)  $\text{HCHO}$

**Correct Answer:** (B)  $(\text{CH}_3)_2\text{CH} - \text{CHO}$

**Solution:**

**Concept:**

- Cannizzaro reaction is the disproportionation of an aldehyde without an  $\alpha$ -hydrogen in concentrated alkali.
- The  $\alpha$ -carbon is the carbon immediately next to the aldehyde carbonyl carbon.

**Step 1: Find the alpha-hydrogen** In  $(\text{CH}_3)_2\text{CHCHO}$ , the carbon adjacent to  $-\text{CHO}$  is  $\text{CH}$ , so it bears one  $\alpha$ -hydrogen. This aldehyde undergoes aldol reaction under the usual basic conditions rather than Cannizzaro reaction.

**Step 2: Check the other aldehydes** In  $(\text{CH}_3)_3\text{CCHO}$ , the adjacent carbon has no hydrogen. Benzaldehyde,  $\text{C}_6\text{H}_5\text{CHO}$ , also has no  $\alpha$ -hydrogen, and formaldehyde,  $\text{HCHO}$ , has no  $\alpha$ -carbon at all.

**Quick Tip to Solve:** Inspect only the carbon directly beside  $\text{CHO}$ ; hydrogens on more distant methyl groups do not count.

Therefore options (A), (C) and (D) can undergo Cannizzaro reaction.

**Step 3: Conclusion**  $(\text{CH}_3)_2\text{CHCHO}$  does not give Cannizzaro reaction. Hence, the correct option is (B).

**Quick Tip to Solve:** Inspect only the carbon directly beside CHO; hydrogens on more distant methyl groups do not count.

**10. Which of the following reactions are feasible?**

[1 mark]

- (A)  $\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3 \longrightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$   
(B)  $(\text{CH}_3)_3\text{C} - \text{Cl} + \text{Na}^+ \text{ } ^-\text{OCH}_2\text{CH}_3 \longrightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$   
(C) Both (a) and (b)  
(D) Neither (a) nor (b)

**Correct Answer:** (A)  $\text{CH}_3\text{CH}_2\text{Br} + \text{Na}^+ \text{ } ^-\text{OC}(\text{CH}_3)_3 \longrightarrow \text{CH}_3\text{CH}_2 - \text{O} - \text{C}(\text{CH}_3)_3$

**Solution:**

**Concept:**

- Williamson ether synthesis involves an alkoxide attacking an alkyl halide by an  $\text{S}_{\text{N}}2$  mechanism.
- A primary alkyl halide permits substitution; a tertiary alkyl halide with a strong base mainly undergoes elimination.

**Step 1: Assess reaction (a)** Ethyl bromide,  $\text{CH}_3\text{CH}_2\text{Br}$ , is a primary halide. tert-Butoxide can displace bromide from its accessible primary carbon to give ethyl tert-butyl ether. Hence the proposed Williamson preparation in (a) is feasible.

**Step 2: Assess reaction (b) and the combined choices** tert-Butyl chloride has a tertiary carbon bonded to chlorine. Steric hindrance prevents the required backside  $\text{S}_{\text{N}}2$  attack by ethoxide. As a strong base, ethoxide instead promotes elimination to 2-methylpropene. Thus (b) is not a feasible Williamson route to the stated ether; neither the choice containing both reactions nor the choice containing neither is correct.

**Step 3: Conclusion** Only reaction (a) is feasible for the stated ether synthesis. Hence, the correct option is (A).

**Quick Tip to Solve:** Put the less hindered alkyl group in the halide and the bulky group in the alkoxide.

**11. Aldehydes and ketones react with hydroxylamine to form**

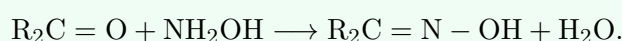
[1 mark]

- (A) hydrazones  
(B) cyanohydrins  
(C) semicarbazones  
(D) Oxime

**Correct Answer:** (D) Oxime**Solution:****Concept:**

- Hydroxylamine is  $\text{NH}_2\text{OH}$ ; it condenses with aldehydes and ketones with loss of water.
- The product contains the oxime group  $>\text{C}=\text{N}-\text{OH}$ .

**Step 1: Identify the condensation product** The carbonyl oxygen is replaced by  $\text{N}-\text{OH}$  through addition followed by dehydration. For a ketone, the overall reaction is



An aldehyde similarly gives  $\text{RCH}=\text{N}-\text{OH}$ .

**Step 2: Distinguish the other derivatives** Hydrazones are obtained with hydrazine,  $\text{NH}_2\text{NH}_2$ ; semicarbazones with semicarbazide,  $\text{NH}_2\text{NHCONH}_2$ . Cyanohydrins result from addition of hydrogen cyanide to a carbonyl compound. These different reagents rule out (A), (B) and (C).

**Step 3: Conclusion** Aldehydes and ketones form oximes with hydroxylamine. Hence, the correct option is (D).

**Quick Tip to Solve:** Remember the reagent ending  $\text{NH}_2\text{OH}$  produces a carbonyl derivative ending  $\text{C}=\text{N}-\text{OH}$ .

**12. For a reaction  $2\text{A} \rightarrow 3\text{B}$ , rate of reaction  $-\frac{d[\text{A}]}{dt}$  is equal to**

[1 mark]

- (A)  $\frac{+3}{2} \frac{d[\text{B}]}{dt}$   
(B)  $\frac{+2}{3} \frac{d[\text{B}]}{dt}$   
(C)  $\frac{+1}{3} \frac{d[\text{B}]}{dt}$   
(D)  $+2 \frac{d[\text{B}]}{dt}$

**Correct Answer:** (B)  $\frac{+2}{3} \frac{d[\text{B}]}{dt}$ **Solution:****Concept:**

- For  $a\text{A} \rightarrow b\text{B}$ , the normalized reaction rate is  $r = -\frac{1}{a} \frac{d[\text{A}]}{dt} = \frac{1}{b} \frac{d[\text{B}]}{dt}$ .
- Reactant concentration decreases, while product concentration increases; the minus sign makes the disappearance rate positive.

**Quick Tip to Solve:** For the disappearance rate of A relative to formation of B, use the coefficient of A divided by that of B.

**Step 1: Apply the stoichiometric coefficients** For  $2A \rightarrow 3B$ , two moles of A disappear for every three moles of B produced. Hence

$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{1}{3} \frac{d[B]}{dt}.$$

**Step 2: Isolate the requested expression** Multiplying both sides by 2 gives

$$-\frac{d[A]}{dt} = \frac{2}{3} \frac{d[B]}{dt}.$$

The question asks for the unnormalized disappearance rate of A. The factor  $3/2$  reverses the ratio;  $1/3$  belongs to the normalized rate, and the factor 2 ignores the product coefficient 3.

**Step 3: Conclusion**  $-d[A]/dt = (2/3)d[B]/dt$ . Hence, the correct option is (B).

**Quick Tip to Solve:** For the disappearance rate of A relative to formation of B, use the coefficient of A divided by that of B.

**13. The formula of the complex dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate is:** [1 mark]

- (A)  $[\text{PtCl}_2(\text{en})_2(\text{NO}_3)_2]$
- (B)  $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$
- (C)  $[\text{PtCl}_2(\text{en})_2(\text{NO}_3)]\text{NO}_3$
- (D)  $[\text{Pt}(\text{en})_2(\text{NO}_3)_2]\text{Cl}_2$

**Correct Answer:** (B)  $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$

**Solution:**

**Concept:**

- The oxidation state of platinum is +4; each chlorido ligand has charge  $-1$ , while ethane-1,2-diamine (en) is neutral.
- Ligands named before the metal lie inside the coordination sphere; nitrate named afterward is a counter-ion.

**Step 1: Find the complex charge** Dichlorido gives two coordinated  $\text{Cl}^-$  ligands, and bis(ethane-1,2-diamine) gives two neutral en ligands. Therefore the complex charge is  $+4 - 2 = +2$ , so the coordination entity is  $[\text{PtCl}_2(\text{en})_2]^{2+}$ .

**Step 2: Balance with nitrate and check options** Two nitrate ions, each of charge  $-1$ , are needed outside the brackets to balance the complex cation. Options (A) and (C) incorrectly put nitrate inside the coordination sphere; (D) puts chloride outside and nitrate inside, contrary to the ligand names. Only (B) has the named ligands inside and both nitrates outside.

**Step 3: Conclusion** The formula is  $[\text{PtCl}_2(\text{en})_2](\text{NO}_3)_2$ . Hence, the correct option is (B).

**Quick Tip to Solve:** First calculate the bracket charge from metal and ligands, then add counter-ions outside the brackets.

14. Which one among the following metals of 3d series has the lowest melting point?

[1 mark]

- (A) Fe
- (B) Mn
- (C) Zn
- (D) Cu

**Correct Answer:** (C) Zn

**Solution:**

**Concept:**

- Melting a metal requires disruption of the ordered metallic lattice; weaker metallic bonding generally gives a lower melting point.
- Zinc has the electronic configuration  $[\text{Ar}] 3d^{10}4s^2$ , with a completely filled 3d subshell.

**Step 1: Compare zinc with the listed metals** Zinc has comparatively weak metallic bonding and melts at approximately 420 °C. Its filled 3d subshell does not provide the same contribution to strong metallic bonding as the partly filled d subshells of many transition metals.

**Step 2: Check the other options** Copper melts at about 1085 °C, manganese at about 1246 °C, and iron at about 1538 °C. Although manganese shows a dip in the melting-point trend within the transition series, its melting point is still much higher than that of zinc. Thus Fe, Mn and Cu cannot be the lowest among these four.

**Step 3: Conclusion** Zinc has the lowest melting point among the given metals. Hence, the correct option is (C).

**Quick Tip to Solve:** Compare all the listed metals: the manganese dip does not make Mn lower-melting than Zn.

15. Assertion (A): Elevation in boiling point is a colligative property.

Reason (R): The lowering of vapour pressure of solution causes elevation in boiling point.

Select the most appropriate answer from the options given below:

[1 mark]

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

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

**Solution:**

**Concept:**

- A colligative property depends on the number of dissolved solute particles rather than their chemical identity, for a dilute solution.
- For a non-volatile solute,  $\Delta T_b = iK_b m$ , where  $m$  is molality,  $K_b$  is the solvent boiling-point elevation constant and  $i$  counts the effective particles.

**Quick Tip to Solve:** Link boiling to vapour pressure reaching atmospheric pressure, then use particle concentration.

**Step 1: Judge Assertion (A)** Elevation of boiling point is a colligative property. For a given solvent, the expression  $\Delta T_b = iK_b m$  shows dependence on the concentration of solute particles. Therefore Assertion (A) is true.

**Step 2: Judge Reason (R)** A non-volatile solute lowers the solvent vapour pressure at a given temperature. A liquid boils when its vapour pressure equals the external pressure; the solution must therefore be heated to a higher temperature to boil. Reason (R) is true.

**Step 3: Test whether the reason explains the assertion** The lowering of vapour pressure is itself determined by the solute particle concentration through Raoult's law. This lowering produces the rise in boiling temperature and accounts for its colligative nature. Thus the reason correctly explains the assertion; the options declaring either statement false or denying the explanatory connection do not apply.

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

**Quick Tip to Solve:** Link boiling to vapour pressure reaching atmospheric pressure, then use particle concentration.

**16. Assertion (A):** Chlorobenzene is resistant to electrophilic substitution reaction.

**Reason (R):** C-Cl bond in chlorobenzene acquires partial double bond characters due to resonance.

Select the most appropriate answer from the options given below:

[1 mark]

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

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

**Solution:**

**Concept:**

- Chlorobenzene undergoes electrophilic aromatic substitution, although chlorine deactivates the ring through its electron-withdrawing inductive effect.
- Resonance donation of a chlorine lone pair gives the C – Cl bond partial double-bond character; this helps explain resistance to nucleophilic substitution.

**Step 1: Judge Assertion (A)** Chlorobenzene can undergo electrophilic substitution such as nitration, giving mainly ortho and para products under suitable conditions. It is less reactive than benzene, but the printed assertion calls it resistant to electrophilic substitution. That is not the characteristic resistance being explained by the reason. Assertion (A) is false.

**Step 2: Judge Reason (R)** A lone pair on chlorine overlaps with the aromatic system. The resulting resonance contribution gives the carbon-chlorine bond partial double-bond character and makes that bond shorter and stronger than a typical carbon-chlorine single bond. Reason (R) is true.

**Step 3: Relate the statements to the correct reaction type** The strong carbon-chlorine bond is

**Quick Tip to Solve:** Read the reaction type carefully: partial C-Cl double-bond character hinders nucleophilic displacement.

associated with the difficulty of nucleophilic displacement in chlorobenzene. Electrophilic aromatic substitution replaces a ring hydrogen and does not require breaking this bond. Therefore the true reason does not make the printed electrophilic-substitution assertion true.

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

**Quick Tip to Solve:** Read the reaction type carefully: partial C-Cl double-bond character hinders nucleophilic displacement.

**17. Assertion (A): Conductivity decreases with decrease in concentration of electrolyte.**

**Reason (R): Number of ions per unit volume that carry the current in a solution decreases on dilution.**

**Select the most appropriate answer from the options given below:**

[1 mark]

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

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

**Solution:**

**Concept:**

- Conductivity  $\kappa$  describes conduction by the ions present in a unit volume of electrolyte solution.
- Molar conductivity  $\Lambda_m = \kappa \times 1000/c$ , with  $c$  in  $\text{mol L}^{-1}$ , is a different quantity and increases on dilution.

**Step 1: Judge Assertion (A)** On dilution, electrolyte concentration decreases and conductivity decreases because a unit volume contains fewer mobile charge carriers. Thus Assertion (A), which refers to conductivity rather than molar conductivity, is true.

**Step 2: Judge Reason (R)** Dilution increases the solution volume, so the number of ions available to carry current per unit volume decreases. Even when ionisation increases for a weak electrolyte, the conductivity falls on dilution. Reason (R) is true.

**Step 3: Check the explanatory link** Ions carry the electric current through the solution. Their reduced number per unit volume directly explains the reduced conductivity. Consequently the reason explains the assertion, and options denying the truth of a statement or the causal connection are unsuitable. The increase in molar conductivity on dilution does not contradict this result.

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

**Quick Tip to Solve:** Check whether the question says conductivity or molar conductivity before applying the dilution trend.

**18. Assertion (A):** Transition metals have high enthalpy of atomisation.

**Reason (R):** Greater number of unpaired electrons in transition metals results in weak metallic bonding.

Select the most appropriate answer from the options given below:

[1 mark]

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

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

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

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

**Correct Answer:** (C) (A) is true, but (R) is false.

**Solution:**

**Concept:**

- Enthalpy of atomisation is the enthalpy required to form gaseous atoms from the element in its standard state.
- Strong metallic bonding in transition metals involves participation of valence *s* and *d* electrons and requires considerable energy to overcome.

**Step 1: Judge Assertion (A)** Transition metals generally have high enthalpies of atomisation because their metallic bonding is strong. Separating atoms from the metallic lattice into gaseous atoms requires a large energy input. Hence Assertion (A) is true.

**Step 2: Judge Reason (R)** The printed reason says that a greater number of unpaired electrons results in weak metallic bonding. This reverses the standard explanation: more unpaired valence electrons generally permit stronger interatomic interaction and stronger metallic bonding. Therefore Reason (R) is false.

**Step 3: Select the truth combination** The assertion agrees with the general properties of transition metals, whereas the reason incorrectly describes the effect of unpaired electrons. Neither option with both statements true can apply, and the option declaring the assertion false also fails. The appropriate combination is a true assertion and a false reason.

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

**Quick Tip to Solve:** For atomisation, stronger metallic bonding means more energy is needed to separate gaseous atoms.

## Section B (14 marks)

19(a). Give reasons:

(i) Mercury cell delivers a constant potential during its lifetime.

(ii) In the experimental determination of electrolytic conductance, Direct Current (DC) is not used.

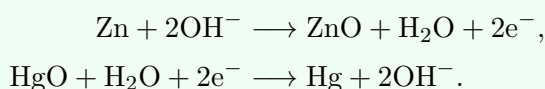
[2 marks]

**Solution:**

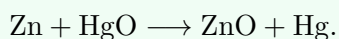
**Concept:**

- The potential of an electrochemical cell depends on the activities appearing in its net cell reaction, as described by the Nernst equation.
- An accurate conductance measurement requires the electrolyte composition and the electrode conditions to remain stable during measurement.

**Step 1: (i) Explain the constant potential of a mercury cell** The mercury cell uses a zinc amalgam anode and a cathode containing mercury(II) oxide. Its electrode reactions in alkaline medium are



Adding these reactions cancels water and hydroxide ions:



No dissolved ion appears in the overall reaction, so the electrolyte concentration does not change in a way that changes the cell potential during normal operation. The activities of the solid phases remain essentially constant. Thus the cell delivers a nearly constant potential of about 1.35 V during its useful lifetime.

**Step 2: (ii) Explain why direct current is avoided** Direct current flows continually in one direction and produces electrolysis at the electrodes. It changes the electrolyte concentration near the electrodes and can cause deposition or gas formation. The resulting electrode polarisation introduces an opposing potential, so the measured resistance no longer represents only the electrolyte resistance. Alternating current is therefore used: its rapidly reversing direction minimises net electrolysis and electrode polarisation, allowing reliable measurement of electrolytic conductance.

**Step 3: Conclusion** (i) The mercury cell has a net reaction involving no dissolved ions, keeping its potential nearly constant. (ii) DC causes electrolysis and electrode polarisation; AC is used to minimise these effects.

**Quick Tip to Solve:** Add the mercury-cell half-reactions first; cancellation of hydroxide ions shows why concentration stays stable.

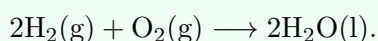
**19(b). Define fuel cell with an example. What advantages do the fuel cells have over primary and secondary batteries?** [2 marks]

**Solution:**

**Concept:**

- A fuel cell is a galvanic cell that converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy.
- The electrode reactions are redox reactions: oxidation releases electrons at the anode and reduction consumes electrons at the cathode.

**Step 1: Define the cell and give an example** A fuel cell produces electricity as long as fuel and oxidant are supplied to its electrodes. The hydrogen–oxygen fuel cell is an example: hydrogen is the fuel and oxygen is the oxidant. Their overall reaction is



The released chemical energy is converted directly into electrical energy through the external circuit.

**Step 2: State the advantages** Fuel cells have high energy-conversion efficiency and can operate continuously with an external supply of reactants. Unlike primary batteries, they need not be discarded when a fixed internal supply of reactants is exhausted; unlike secondary batteries, they do not need periodic electrical recharging. The hydrogen–oxygen fuel cell also produces water, so it causes much less pollution during operation.

**Step 3: Conclusion** A hydrogen–oxygen fuel cell converts continuously supplied hydrogen and oxygen into electricity. Its advantages include high efficiency, continuous operation without recharging and clean operation with water as the product.

**Quick Tip to Solve:** Relate continuous operation to the external fuel supply; do not describe a fuel cell as a rechargeable battery.

**20. The vapour pressure of pure liquid X and pure liquid Y at 25°C are 120 mm Hg and 160 mm Hg respectively. If equal moles of X and Y are mixed to form an ideal solution, calculate the vapour pressure of the solution.** [2 marks]

**Solution:**

**Concept:**

- For an ideal solution, Raoult's law gives  $p_X = x_X p_X^\circ$  and  $p_Y = x_Y p_Y^\circ$ , where  $x_i$  is the liquid-phase mole fraction and  $p_i^\circ$  the pure-liquid vapour pressure.
- The total vapour pressure is the sum of the partial pressures:  $p = p_X + p_Y$ .

**Step 1: Calculate the mole fractions** Let each liquid contribute  $n$  moles. The total amount is  $2n$ , so

$$x_X = \frac{n}{2n} = \frac{1}{2}, \quad x_Y = \frac{n}{2n} = \frac{1}{2}.$$

**Quick Tip to Solve:** For equal moles of two ideal volatile liquids, the total pressure is the arithmetic mean of their pure vapour pressures.

Equal moles therefore give equal mole fractions, irrespective of the molar masses or densities of the liquids.

**Step 2: Apply Raoult's law to both components** At 25°C, substitute  $p_X^\circ = 120 \text{ mm Hg}$  and  $p_Y^\circ = 160 \text{ mm Hg}$ :

$$\begin{aligned}p_X &= \frac{1}{2}(120) = 60 \text{ mm Hg}, \\p_Y &= \frac{1}{2}(160) = 80 \text{ mm Hg}, \\p &= 60 + 80 = 140 \text{ mm Hg}.\end{aligned}$$

Both liquids are volatile, so both partial pressures must be included. The result lies between the two pure-liquid vapour pressures, as expected for an ideal mixture.

**Step 3: Conclusion** The vapour pressure of the ideal solution at 25°C is 140 mm Hg.

**Quick Tip to Solve:** For equal moles of two ideal volatile liquids, the total pressure is the arithmetic mean of their pure vapour pressures.

**21(a). Write the IUPAC names of the following:**

(i)  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$

(ii)  $\text{K}_2[\text{NiCl}_4]$

[2 marks]

**Solution:**

**Concept:**

- Name ligands before the central metal, placing ligand names in alphabetical order while ignoring multiplicative prefixes.
- An anionic coordination entity uses the metal name ending in -ate; the metal oxidation state is written in Roman numerals.

**Step 1: Name the cobalt complex** In  $[\text{Co}(\text{NH}_3)_5(\text{ONO})]^{2+}$ , ammonia is neutral and the  $\text{ONO}^-$  ligand has charge  $-1$ . If the cobalt oxidation state is  $z$ , then

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

Five ammonia ligands give pentaammine. The written ONO indicates coordination through oxygen, hence nitrito-O. Ammine precedes nitrito alphabetically. The cation is named pentaammine(nitrito-O)cobalt(III) ion.

**Step 2: Name the potassium salt** In  $\text{K}_2[\text{NiCl}_4]$ , the two potassium ions require the complex ion to have charge  $-2$ . Each chlorido ligand has charge  $-1$ , hence

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

Four chlorido ligands give tetrachlorido, and the anionic complex takes the metal name nickelate. Name the potassium cation first, followed by the complex anion.

**Step 3: Conclusion** (i) Pentaammine(nitrito-O)cobalt(III) ion.

(ii) Potassium tetrachloridonickelate(II).

**Quick Tip to Solve:** Read ONO as oxygen-bound nitrito and calculate the metal oxidation state from the charge of the whole coordination entity.

21(b). (i) What is a chelate complex? Give one example.

(ii) What are heteroleptic complexes? Give one example.

[2 marks]

**Solution:**

**Concept:**

- A ligand is a species that donates one or more electron pairs to a central metal ion to form coordinate bonds.
- Chelation describes ring formation by a multidentate ligand; heteroleptic describes the presence of more than one kind of ligand.

**Step 1: Define a chelate complex and give an example** A chelate complex is a coordination complex in which a bidentate or polydentate ligand attaches to the same central metal ion through two or more donor atoms, forming one or more rings. For example,  $[\text{Co}(\text{en})_3]^{3+}$  is a chelate complex, where en is ethane-1,2-diamine,  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ . Each en ligand coordinates through its two nitrogen atoms and forms a ring containing the cobalt ion.

**Step 2: Define a heteroleptic complex and give an example** A heteroleptic complex contains more than one type of ligand coordinated to its central metal atom or ion. For example,  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  is heteroleptic because it contains both neutral ammonia ligands and chlorido ligands. The number of ligand types, rather than the number of individual ligands, determines whether the complex is heteroleptic. Chelation and heteroleptic character are separate properties of a complex.

**Step 3: Conclusion** (i) A chelate complex has ring-forming multidentate ligands; example:  $[\text{Co}(\text{en})_3]^{3+}$ .

(ii) A heteroleptic complex has different types of ligands; example:  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ .

**Quick Tip to Solve:** For chelation, check multiple donor atoms and ring formation; for heteroleptic complexes, count the different ligand types.

22. (a) The conversion of molecule A to B follows second order kinetics. If concentration of A is increased to three times, how will it affect the rate of formation of B?

(b) Define Pseudo first order reaction with an example.

[2 marks]

**Solution:**

**Concept:**

- For a second order conversion involving one reactant A, the rate law is  $r = k[A]^2$ , where  $k$  is the rate constant and  $[A]$  is the concentration of A.
- A pseudo first order reaction has a higher actual order but behaves as first order because the concentration of one reactant, present in large excess, remains practically constant.

**Step 1: (a) Compare the two rates** At the same temperature,  $k$  remains unchanged. Initially,

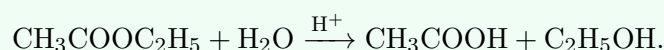
**Quick Tip to Solve:** Tripling concentration multiplies a second order rate by  $3^2$ ; for pseudo first order behaviour, identify the reactant in large excess.

$r_1 = k[A]^2$ . When the concentration is tripled,

$$r_2 = k(3[A])^2 = 9k[A]^2 = 9r_1.$$

Thus, the rate of formation of B increases ninefold; the rate depends on the square of concentration, not directly on concentration.

**Step 2: (b) Define and illustrate pseudo first order behaviour** A reaction of higher order that behaves kinetically as a first order reaction when one reactant is in large excess is called a pseudo first order reaction. For example, acid-catalysed hydrolysis of ethyl acetate in excess water is



With the acid concentration fixed,  $r = k[\text{ester}][\text{H}_2\text{O}]$ . Since excess water has almost constant concentration,  $r = k_{\text{obs}}[\text{ester}]$ , where  $k_{\text{obs}} = k[\text{H}_2\text{O}]$ .

**Step 3: Conclusion** (a) The rate becomes nine times its original value. (b) Hydrolysis of ethyl acetate in excess water is a pseudo first order reaction.

**Quick Tip to Solve:** Tripling concentration multiplies a second order rate by  $3^2$ ; for pseudo first order behaviour, identify the reactant in large excess.

**23. (a) What is the difference between a nucleoside and nucleotide?**

**(b) What products would be formed when a nucleotide from DNA containing thymine is hydrolysed?**

[2 marks]

**Solution:**

**Concept:**

- A nucleoside consists of a nitrogenous base linked to a pentose sugar by a glycosidic bond.
- A nucleotide is a phosphorylated nucleoside: it contains a nitrogenous base, a pentose sugar and a phosphate group. DNA contains 2-deoxyribose as its sugar.

**Step 1: (a) Distinguish the two units** A nucleoside contains only two components: a nitrogenous base and a pentose sugar. A nucleotide contains these same components along with a phosphate group, attached through a phosphate ester linkage. Thus, addition of phosphate to a nucleoside gives a nucleotide. For example, thymidine is a nucleoside, whereas thymidine monophosphate is a nucleotide; phosphate is the distinguishing component.

**Step 2: (b) Identify the products of complete hydrolysis** The given nucleotide belongs to DNA, so its pentose sugar is 2-deoxyribose, not ribose. Its specified nitrogenous base is thymine. On complete hydrolysis, the glycosidic bond joining the base to the sugar and the phosphate ester linkage are broken. Therefore the three products are thymine, 2-deoxyribose and phosphoric acid (phosphate). The identity of the base follows directly from the question, while the identity of the sugar follows from DNA.

**Step 3: Conclusion** (a) Nucleoside = base + sugar; nucleotide = base + sugar + phosphate. (b) Complete hydrolysis yields thymine, 2-deoxyribose and phosphoric acid.

**Quick Tip to Solve:** Use DNA to select deoxyribose; the extra phosphate group is what distinguishes a nucleotide from a nucleoside.

24. Write the chemical equation involved in the following:

(a) Kolbe's reaction

(b) Williamson synthesis

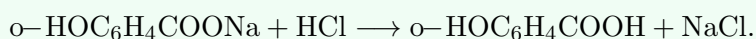
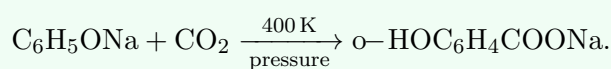
[2 marks]

**Solution:**

**Concept:**

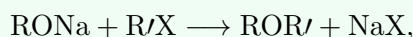
- Kolbe's reaction of sodium phenoxide with carbon dioxide introduces a carboxyl group predominantly at the ortho position; acidification yields salicylic acid.
- Williamson synthesis forms an ether by nucleophilic substitution of an alkyl halide with a sodium alkoxide. A primary alkyl halide favours substitution.

**Step 1: (a) Write Kolbe's reaction** Sodium phenoxide is heated with carbon dioxide under pressure at about 400 K. Sodium salicylate is formed and then acidified:

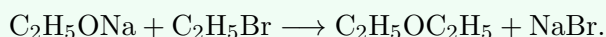


The product is 2-hydroxybenzoic acid (salicylic acid). Here Kolbe's reaction refers to carboxylation of phenoxide in the phenol chapter.

**Step 2: (b) Write Williamson synthesis** The general equation is



where  $R$  and  $R'$  are alkyl groups and  $X$  is a halogen. For example, sodium ethoxide reacts with bromoethane to give ethoxyethane:



The alkoxide ion attacks the carbon bonded to halogen, which leaves as halide. The ether oxygen comes from the alkoxide.

**Step 3: Conclusion** Kolbe's reaction yields salicylic acid after acidification; Williamson synthesis yields an ether from a sodium alkoxide and an alkyl halide.

**Quick Tip to Solve:** For Kolbe's reaction, include both carbon dioxide under pressure and acidification; for Williamson synthesis, show the alkoxide and halide.

25. Do the following conversions in not more than two steps:

(a)  $\text{CH}_3\text{CN}$  to  $\text{CH}_3\text{COCH}_3$

(b) Benzoic acid ( $\text{C}_6\text{H}_5\text{COOH}$ ) to Benzene ( $\text{C}_6\text{H}_6$ )

[2 marks]

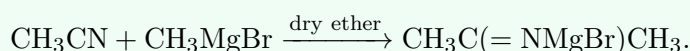


**Solution:**

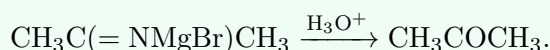
**Concept:**

- A nitrile reacts with a Grignard reagent to form an imine magnesium salt; acidic hydrolysis gives a ketone.
- Heating a sodium carboxylate with soda lime ( $\text{NaOH} + \text{CaO}$ ) removes the carboxyl carbon as carbonate and gives a hydrocarbon with one fewer carbon atom.

**Step 1: (a) Convert acetonitrile into acetone** Step 1: Treat acetonitrile with methylmagnesium bromide in dry ether. The methyl group adds to the nitrile carbon, giving an imine magnesium salt:

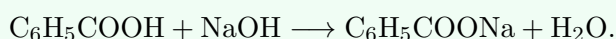


Step 2: Hydrolyse this intermediate with water and dilute acid:

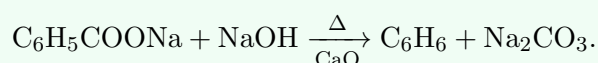


The nitrile carbon becomes the carbonyl carbon, and the Grignard reagent supplies the second methyl group. Dry conditions are needed during addition because water destroys the Grignard reagent.

**Step 2: (b) Convert benzoic acid into benzene** Step 1: Neutralise benzoic acid with sodium hydroxide to form sodium benzoate:



Step 2: Heat dry sodium benzoate with soda lime:



This is decarboxylation. The six-carbon benzene ring remains intact, while the carboxyl carbon is removed. Calcium oxide is the solid component of soda lime used with sodium hydroxide.

**Step 3: Conclusion** (a) Use  $\text{CH}_3\text{MgBr}$  in dry ether, followed by acidic hydrolysis. (b) Form sodium benzoate, then heat it with soda lime to obtain benzene.

**Quick Tip to Solve:** A methyl Grignard reagent adds the extra methyl group needed for acetone; soda lime removes the entire carboxyl group from sodium benzoate.

### Section C (15 marks)

26. (a) Draw the geometrical isomers of  $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$ . Which geometrical isomer of  $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$  is not optically active and why?

(b) Write the hybridisation and magnetic behaviour of  $[\text{CoF}_6]^{3-}$ .

[Given: Atomic number of Co = 27]

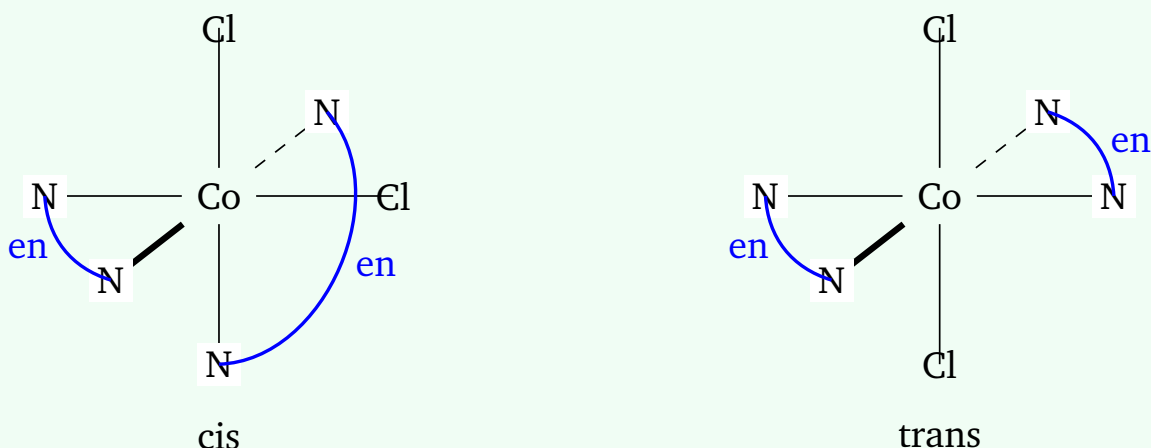
[3 marks]

#### Solution:

##### Concept:

- An octahedral complex has six coordination positions. Each ethane-1,2-diamine (en) ligand is bidentate and occupies two adjacent positions.
- Geometrical isomers differ in the relative positions of the chloride ligands: cis has adjacent chlorides, whereas trans has opposite chlorides.
- Optical activity requires chirality. A plane of symmetry makes a structure achiral; weak-field ligands favour a high-spin electronic arrangement.

**Step 1: (a) Draw and distinguish the geometrical isomers** In  $[\text{Co}(\text{en})_2\text{Cl}_2]^{2+}$ , the two en ligands provide four nitrogen donor atoms and the two chloride ligands occupy the remaining two sites. In the cis form, the  $\text{Cl} - \text{Co} - \text{Cl}$  angle is  $90^\circ$ ; in the trans form it is  $180^\circ$ . In the drawings, the curved links join the two nitrogen donors belonging to the same en ligand. The en ligands therefore chelate through adjacent sites in both structures.



*Octahedral cis and trans isomers; curved links denote en chelate ligands.*

**Step 2: (a) Identify the optically inactive isomer** The trans isomer is optically inactive because it has a plane of symmetry and its mirror image is superimposable on it. The cis arrangement lacks such a plane of symmetry and occurs as a pair of non-superimposable mirror images. Thus an individual cis optical isomer can rotate plane-polarised light, while the trans structure is achiral.

**Step 3: (b) Determine hybridisation and magnetic behaviour** For  $[\text{CoF}_6]^{3-}$ , let the cobalt oxidation state be  $x$ . Then  $x + 6(-1) = -3$ , giving  $x = +3$ . Cobalt has atomic number 27, so  $\text{Co}^{3+}$  has configuration  $[\text{Ar}]3d^6$ . Fluoride is a weak-field ligand and does not force pairing in the  $3d$  orbitals. The octahedral ion is high spin, with  $t_{2g}^4 e_g^2$  occupancy and four unpaired electrons. It uses outer  $d$

**Quick Tip to Solve:** First locate the two Cl ligands: adjacent means cis and opposite means trans. For the fluoride complex, count Co(III) as  $d^6$  before applying the weak-field rule.

orbitals for  $sp^3d^2$  hybridisation and is paramagnetic.

**Step 4: Conclusion** (a) The geometrical isomers are cis and trans; the trans isomer is optically inactive due to its plane of symmetry. (b)  $[\text{CoF}_6]^{3-}$  is  $sp^3d^2$ -hybridised and paramagnetic, with four unpaired electrons.

**Quick Tip to Solve:** First locate the two Cl ligands: adjacent means cis and opposite means trans. For the fluoride complex, count Co(III) as d6 before applying the weak-field rule.

**27.** When 19.5 g of  $\text{F}-\text{CH}_2-\text{COOH}$  (Molar mass =  $78 \text{ g mol}^{-1}$ ), is dissolved in 500 g of water, the depression in freezing point is observed to be  $1^\circ\text{C}$ . Calculate the degree of dissociation of  $\text{F}-\text{CH}_2-\text{COOH}$ .

[Given:  $K_f$  for water =  $1.86 \text{ K kg mol}^{-1}$ ]

[3 marks]

**Solution:**

**Concept:**

- The depression in freezing point is  $\Delta T_f = iK_fm$ , where  $i$  is the van't Hoff factor,  $K_f$  is the molal freezing-point depression constant and  $m$  is molality.
- For a monoprotic acid dissociating into two ions,  $i = 1 + \alpha$ , where  $\alpha$  is the fraction of acid molecules dissociated.

**Step 1: Calculate the analytical molality** The number of moles of fluoroacetic acid initially dissolved is

$$n = \frac{19.5 \text{ g}}{78 \text{ g mol}^{-1}} = 0.250 \text{ mol.}$$

The mass of solvent is 500 g = 0.500 kg. Molality uses the mass of solvent, so

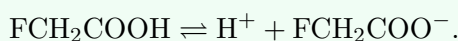
$$m = \frac{0.250}{0.500} = 0.500 \text{ mol kg}^{-1}.$$

This is the initial molality of acid, before accounting for the extra particles produced by dissociation.

**Step 2: Obtain the van't Hoff factor from the observed depression** A temperature difference of  $1^\circ\text{C}$  equals 1 K. The expected depression for undissociated acid would be  $K_fm = 1.86 \times 0.500 = 0.930 \text{ K}$ . Since the observed depression is larger, dissociation increases the number of dissolved particles. Thus

$$i = \frac{\Delta T_f}{K_fm} = \frac{1.00}{1.86 \times 0.500} = \frac{100}{93} = 1.07527.$$

**Step 3: Relate particle formation to dissociation** The acid dissociates as



Starting with one mole, the undissociated acid contributes  $1 - \alpha$  mole and the two ions contribute

**Quick Tip to Solve:** For a monoprotic acid producing two ions, calculate  $i$  from the observed freezing-point depression and then use  $\alpha = i - 1$ ; convert solvent grams to kilograms first.

$\alpha + \alpha$  moles. The total is  $1 + \alpha$ , hence  $i = 1 + \alpha$ . Therefore

$$\alpha = i - 1 = \frac{100}{93} - 1 = \frac{7}{93} = 0.07527.$$

Multiplying this fraction by 100 gives the percentage dissociation.

**Step 4: Conclusion** The degree of dissociation is  $\alpha \approx 0.0753$ , corresponding to approximately 7.53% dissociation.

**Quick Tip to Solve:** For a monoprotic acid producing two ions, calculate  $i$  from the observed freezing-point depression and then use  $\alpha = i - 1$ ; convert solvent grams to kilograms first.

**28. Answer any 3 of the following:**

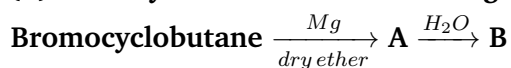
(a) Which isomer of  $C_5H_{10}$  gives a single monochloro compound  $C_5H_9Cl$  in bright sunlight?

(b) Arrange the following compounds in increasing order of reactivity towards  $S_N2$  reaction:

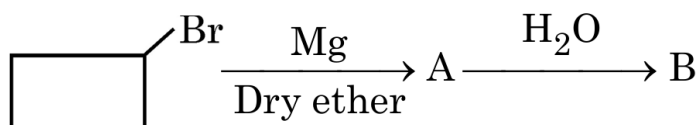
2-Bromopentane, 1-Bromopentane, 2-Bromo-2-methylbutane

(c) Why p-dichlorobenzene has higher melting point than those of ortho- and meta-isomers?

(d) Identify A and B in the following:



[3 marks]



### Solution:

#### Concept:

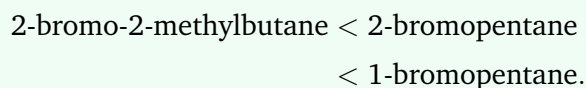
- Photochemical chlorination replaces hydrogen by chlorine through a free-radical substitution process. Equivalent substitution sites give the same constitutional product.
- The  $S_N2$  mechanism requires backside attack: increasing crowding at the carbon bonded to the leaving group decreases its reactivity.
- Crystal packing affects melting point, while a Grignard reagent  $RMgBr$  yields  $RH$  on reaction with water.

**Step 1: (a) Identify the isomer giving one monochloro product** The required isomer of  $C_5H_{10}$  is cyclopentane. Its five carbon positions are equivalent, so replacing one hydrogen by chlorine at any ring carbon gives the same constitutional product, chlorocyclopentane,  $C_5H_9Cl$ . Bright sunlight initiates the radical substitution of chlorine into a C-H bond.

**Step 2: (b) Arrange the substrates by increasing  $S_N2$  reactivity** 2-Bromo-2-methylbutane is a tertiary alkyl bromide, 2-bromopentane is secondary and 1-bromopentane is primary. Because the nucleophile must approach the carbon bearing bromine from the opposite side of the C-Br bond, tertiary substitution creates the greatest steric obstruction and primary substitution the least. The

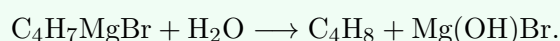
**Quick Tip to Solve:** Classify each bromide as primary, secondary or tertiary before ordering  $S_N2$  reactivity; in the Grignard sequence, preserve the ring and replace  $MgBr$  by H.

increasing order is therefore



**Step 3: (c) Explain the higher melting point of the para isomer** Para-dichlorobenzene has a more symmetrical molecular arrangement than the ortho and meta isomers. Its molecules pack more efficiently in the crystal lattice. The resulting stronger overall lattice stabilisation requires more thermal energy to disrupt on melting, giving the para isomer the higher melting point.

**Step 4: (d) Identify the products A and B** Magnesium inserts into the carbon-bromine bond in dry ether, giving the Grignard reagent A, cyclobutylmagnesium bromide,  $\text{C}_4\text{H}_7\text{MgBr}$ . Water then protonates the cyclobutyl group to give B, cyclobutane,  $\text{C}_4\text{H}_8$ :



The four-membered carbon ring remains intact in both steps; water replaces the organomagnesium group by hydrogen.

**Step 5: Conclusion** (a) Cyclopentane. (b) 2-Bromo-2-methylbutane < 2-bromopentane < 1-bromopentane. (c) Better symmetry gives more efficient crystal packing. (d) A is cyclobutylmagnesium bromide; B is cyclobutane. Solutions to all four alternatives are provided.

**Quick Tip to Solve:** Classify each bromide as primary, secondary or tertiary before ordering  $\text{S}_\text{N}2$  reactivity; in the Grignard sequence, preserve the ring and replace  $\text{MgBr}$  by  $\text{H}$ .

**29. A first order reaction is 50% complete in 30 minutes at 300 K and in 10 minutes at 320 K. Calculate activation energy ( $E_a$ ) 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:**

- For a first-order reaction, the time for 50% completion is the half-life:  $t_{1/2} = 0.693/k$ , where  $k$  is the rate constant. Thus a shorter half-life means a larger rate constant.
- The two-temperature Arrhenius equation is  $\log(k_2/k_1) = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$ , where  $E_a$  is activation energy and both temperatures are absolute temperatures.

**Step 1: Identify the half-lives and calculate the rate-constant ratio** At  $T_1 = 300 \text{ K}$ ,  $t_{1/2,1} = 30 \text{ min}$ ; at  $T_2 = 320 \text{ K}$ ,  $t_{1/2,2} = 10 \text{ min}$ . Therefore,

$$k_1 = \frac{0.693}{30} = 0.0231 \text{ min}^{-1}, \quad k_2 = \frac{0.693}{10} = 0.0693 \text{ min}^{-1}.$$

Hence  $k_2/k_1 = 3$ , so the given value  $\log 3 = 0.4771$  applies. The time units cancel in this ratio; conversion of minutes to seconds is unnecessary.

**Step 2: Substitute in the Arrhenius equation** Rearrange for the activation energy and insert  $R =$

**Quick Tip to Solve:** Use the inverse half-life ratio directly:  $k_2/k_1 = t_{1/2,1}/t_{1/2,2} = 3$ .

$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ :

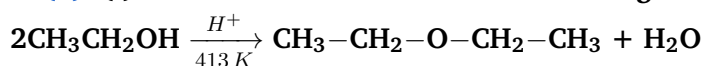
$$\begin{aligned} E_a &= \frac{2.303R \log(k_2/k_1)}{1/T_1 - 1/T_2} \\ &= \frac{2.303 \times 8.314 \times 0.4771 \times 300 \times 320}{320 - 300} \\ &= 4.385 \times 10^4 \text{ J mol}^{-1}. \end{aligned}$$

The reciprocal-temperature difference is positive because  $T_2 > T_1$ , and the logarithm is positive because the rate increases on heating. Thus the computed activation energy is positive, as expected.

**Step 3: Conclusion** The activation energy is  $E_a \approx 43.85 \text{ kJ mol}^{-1}$ .

**Quick Tip to Solve:** Use the inverse half-life ratio directly:  $k_2/k_1 = t_{1/2,1}/t_{1/2,2} = 3$ .

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



**(ii) Why ortho-nitrophenol is steam volatile while para-nitrophenol is not?**

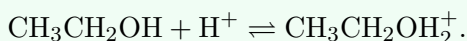
[3 marks]

**Solution:**

**Concept:**

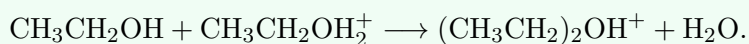
- Acid-catalysed intermolecular dehydration of a primary alcohol at 413 K produces an ether. Protonation turns the hydroxyl group into water, a good leaving group.
- Intramolecular hydrogen bonding occurs within one molecule; intermolecular hydrogen bonding associates different molecules and reduces their volatility.

**Step 1: (i) Protonate ethanol** The oxygen lone pair of ethanol accepts a proton from the acid catalyst:



The protonated hydroxyl group can now depart as neutral water. For a primary alcohol, the substitution proceeds by attack of another ethanol molecule, rather than by formation of an unstable free primary carbocation.

**Step 2: (i) Form the ether bond and regenerate the catalyst** The oxygen lone pair of a second ethanol molecule attacks the primary carbon of protonated ethanol. The carbon–oxygen bond to water breaks in the same substitution step:

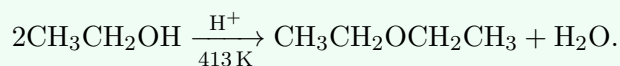


The protonated ether then loses a proton:



**Quick Tip to Solve:** For the ethanol mechanism, show water leaving from protonated ethanol and show  $\text{H}^+$  regenerated in the last step.

Thus the acid is regenerated and the overall reaction is



**Step 3: (ii) Compare hydrogen bonding in the nitrophenols** In ortho-nitrophenol, the adjacent hydroxyl and nitro groups form an intramolecular  $\text{O} - \text{H} \cdots \text{O}$  hydrogen bond. Consequently, intermolecular association is weaker and the compound is steam volatile. In para-nitrophenol, the groups are too far apart for this intramolecular bond; instead, molecules form intermolecular hydrogen bonds. Their stronger association raises the boiling point and makes para-nitrophenol non-volatile in steam.

**Step 4: Conclusion** (i) Ethanol forms ethoxyethane through protonation, nucleophilic substitution and deprotonation. (ii) Ortho-nitrophenol is steam volatile because of intramolecular hydrogen bonding, whereas para-nitrophenol forms intermolecular hydrogen bonds.

**Quick Tip to Solve:** For the ethanol mechanism, show water leaving from protonated ethanol and show  $\text{H}^+$  regenerated in the last step.

OR

**30(b). What happens when:**

(i) Anisole is treated with  $\text{CH}_3\text{Cl}$ /anhydrous  $\text{AlCl}_3$ ?

(ii) Phenol is oxidised with  $\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}^+$ ?

(iii)  $(\text{CH}_3)_3\text{C}-\text{OH}$  is heated with  $\text{Cu}/573\text{ K}$ ?

Write chemical equation in support of your answer.

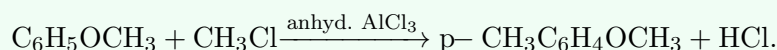
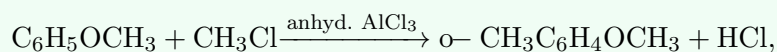
[3 marks]

**Solution:**

**Concept:**

- The methoxy group in anisole activates the benzene ring and directs electrophilic substitution to the ortho and para positions.
- Phenol undergoes oxidation to a quinone. A tertiary alcohol has no hydrogen on the carbon bearing  $-\text{OH}$ , so it cannot undergo the usual dehydrogenation to a carbonyl compound.

**Step 1: (i) Friedel-Crafts alkylation of anisole** Anisole reacts with methyl chloride in the presence of anhydrous aluminium chloride to give a mixture of ortho- and para-methylanisole. The para isomer is the major product because the para position offers less steric hindrance. The equations for the two substitution pathways are

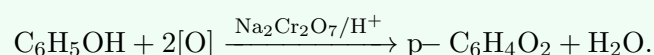


The methyl group substitutes a ring hydrogen; it does not replace the methoxy group.

**Step 2: (ii) Oxidation of phenol** Acidified sodium dichromate oxidises phenol to para-benzoquinone

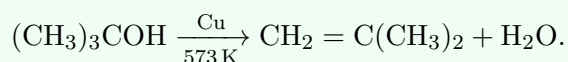
**Quick Tip to Solve:** Before assigning a carbonyl product for heated alcohols, check whether the carbon bearing  $-\text{OH}$  has a hydrogen.

(1,4-benzoquinone). An equation using the usual oxidation notation is



Here [O] represents oxygen supplied by the oxidising agent. The product contains two carbonyl groups in the 1,4 positions of the six-membered ring.

**Step 3: (iii) Heat the tertiary alcohol over copper** When tert-butyl alcohol vapour is passed over heated copper at 573 K, it undergoes dehydration to 2-methylpropene:



A hydrogen from an adjacent methyl group and the hydroxyl group are eliminated as water. Since the hydroxyl-bearing carbon has no hydrogen, dehydrogenation to a ketone cannot occur; the product is an alkene.

**Step 4: Conclusion** The products are (i) ortho- and para-methylanisole, with the para isomer major; (ii) para-benzoquinone; and (iii) 2-methylpropene with water.

**Quick Tip to Solve:** Before assigning a carbonyl product for heated alcohols, check whether the carbon bearing –OH has a hydrogen.

### Section D (8 marks)

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

**31(i). Case Study:** Carbohydrates are optically active polyhydroxy aldehydes and ketones. They are also called saccharides. All those carbohydrates which reduce Fehling's solution and Tollen's reagent are referred to as reducing sugars. Glucose, the most important source of energy for mammals, is obtained by the hydrolysis of starch. Vitamins are accessory food factors required in the diet. Proteins are the polymers of  $\alpha$ -amino acids and perform various structural and dynamic functions in the organisms. Deficiency of vitamins leads to many diseases.

(a) The penta-acetate of glucose does not react with Hydroxylamine. What does it indicate? [1 mark]

**Solution:**

**Concept:**

- Hydroxylamine,  $\text{NH}_2\text{OH}$ , reacts with a free aldehyde or ketone carbonyl group to form an oxime.
- In cyclic glucose, the aldehyde group is involved in forming a hemiacetal; acetylation of its hydroxyl groups gives the penta-acetate.

**Step 1: Interpret the negative hydroxylamine test** If glucose penta-acetate contained a free –CHO group, hydroxylamine would form the corresponding oxime. Its failure to react therefore indicates the absence of a free aldehydic carbonyl group.

**Step 2: Relate the result to the cyclic form** The aldehydic group of glucose is masked in the cyclic structure. Acetylation of the anomeric hydroxyl group prevents the usual ring opening that would

**Quick Tip to Solve:** A negative oxime test points to absence of a free carbonyl group, not absence of oxygen atoms.

expose the aldehyde. Hence the penta-acetate cannot give the carbonyl reaction with hydroxylamine.

**Step 3: Conclusion** It indicates that glucose penta-acetate has no free aldehyde group, supporting the cyclic structure of glucose.

**Quick Tip to Solve:** A negative oxime test points to absence of a free carbonyl group, not absence of oxygen atoms.

**31(ii). (b) Why cannot vitamin C be stored in our body?**

[1 mark]

**Solution:**

**Concept:**

- Water-soluble vitamins dissolve in body fluids, and excess quantities are eliminated in urine.
- Vitamin C (ascorbic acid) is a water-soluble vitamin and must be supplied regularly through food.

**Step 1: Identify the solubility** Vitamin C belongs to the water-soluble group of vitamins. It therefore dissolves in the aqueous fluids of the body.

**Step 2: Relate solubility to storage** Excess vitamin C is excreted through urine instead of accumulating in a long-term body store. Hence a regular dietary supply is necessary.

**Step 3: Conclusion** Vitamin C cannot be stored in our body because it is water-soluble and its excess is readily excreted in urine.

**Quick Tip to Solve:** Link vitamin C to water solubility and urinary excretion; mention both in the answer.

**31(iii). (c) Define the following as related to proteins:**

**(i) Peptide linkage**

**(ii) Denaturation**

[2 marks]

**Solution:**

**Concept:**

- Proteins are polymers of  $\alpha$ -amino acids connected by amide bonds called peptide linkages.
- The biological activity of a protein depends on its specific three-dimensional structure.

**Step 1: Define peptide linkage** A peptide linkage is the amide linkage  $-\text{CO} - \text{NH}-$  formed when the carboxyl group of one amino acid reacts with the amino group of another amino acid with elimination of one molecule of water. Thus two amino acids form a dipeptide, and repetition of this condensation connects many amino-acid units into a polypeptide chain.

**Step 2: Define denaturation** Denaturation is the loss of the native conformation and biological activity of a protein due to heat, change in pH or other physical or chemical agents. The secondary and tertiary structures are disrupted, while the primary structure, that is, the amino-acid sequence and peptide bonds, remains intact. For example, the coagulation of egg white on heating is denaturation.

**Step 3: Conclusion** Peptide linkage: the  $-\text{CO} - \text{NH}-$  bond joining amino acids. Denaturation: loss

**Quick Tip to Solve:** For denaturation, explicitly distinguish disruption of folding from cleavage of peptide bonds.

of native protein structure and biological activity without breaking its primary structure.

**Quick Tip to Solve:** For denaturation, explicitly distinguish disruption of folding from cleavage of peptide bonds.

OR

**31(iii). (c) Define the following as related to carbohydrates:**

(i) Anomers

(ii) Glycosidic linkage

[2 marks]

**Solution:**

**Concept:**

- Cyclisation of a monosaccharide creates an anomeric carbon: the former carbonyl carbon becomes a new stereogenic centre.
- A glycosidic linkage connects monosaccharide units through an oxygen atom after elimination of water.

**Step 1: Define anomers** Anomers are cyclic stereoisomers of a carbohydrate that differ only in configuration at the anomeric carbon. For glucose this is carbon 1, which was the aldehyde carbon in the open-chain form. Thus  $\alpha$ -D-glucopyranose and  $\beta$ -D-glucopyranose differ in the orientation of the hydroxyl group at carbon 1; their configurations at the other stereogenic carbons are the same.

**Step 2: Define glycosidic linkage** A glycosidic linkage is the C – O – C linkage joining two monosaccharide units, formed by condensation of their hydroxyl groups with elimination of water. At least one participating group is the hydroxyl group at an anomeric carbon. For example, maltose contains an  $\alpha(1 \rightarrow 4)$  glycosidic linkage between its two glucose units.

**Step 3: Conclusion** Anomers differ only at the anomeric carbon. A glycosidic linkage is the oxygen bridge joining monosaccharide units after loss of water.

**Quick Tip to Solve:** In anomers, name the anomeric carbon; in glycosidic linkage, identify the oxygen bridge.

**32(i). Case Study:** The carbon-oxygen double bond is polarised in aldehydes and ketones due to higher electronegativity of oxygen relative to carbon. Therefore they undergo nucleophilic addition reactions with a number of nucleophiles such as HCN, NaHSO<sub>3</sub>, alcohols, ammonia derivatives and Grignard reagents. Aldehydes are easily oxidised by mild oxidising agents as compared to ketones. The carbonyl group of carboxylic acid does not give reactions of aldehydes and ketones. Carboxylic acids are considerably more acidic than alcohols and most of simple phenols.

(a) Write the name of the product when an aldehyde reacts with excess alcohol in presence of dry HCl. [1 mark]

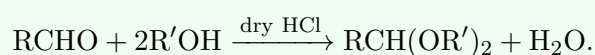
**Solution:**

**Concept:**

- In acid-catalysed addition of alcohol to an aldehyde, a hemiacetal forms first.
- Excess alcohol converts the hemiacetal into an acetal containing two alkoxy groups on the former carbonyl carbon.

**Step 1: Follow the alcohol addition** The first alcohol molecule adds to the aldehyde carbonyl group in the presence of acid, producing a hemiacetal containing one hydroxyl group and one alkoxy group.

**Step 2: Identify the final product** With excess alcohol and dry HCl, the hydroxyl group is replaced by a second alkoxy group. The overall reaction is



**Step 3: Conclusion** The product is an acetal.

**Quick Tip to Solve:** Excess alcohol gives an acetal; the intermediate after one alcohol addition is a hemiacetal.

**32(ii). (b) Why carboxylic acid is a stronger acid than phenol?**

[1 mark]

**Solution:**

**Concept:**

- Acid strength increases with the stability of the conjugate base formed on loss of H<sup>+</sup>.
- Carboxylate ions have two equivalent resonance structures, with negative charge shared between two oxygen atoms.

**Step 1: Compare conjugate-base stabilisation** A carboxylic acid loses H<sup>+</sup> to form a carboxylate ion. Its two equivalent resonance structures delocalise the negative charge equally over two electronegative oxygen atoms, giving strong stabilisation.

**Step 2: Contrast the phenoxide ion** Phenol forms a phenoxide ion. Its resonance structures are non-equivalent, and some place the negative charge on less electronegative carbon atoms of the ring. Phenoxide is therefore less effectively stabilised than carboxylate.

**Step 3: Conclusion** Carboxylic acid is stronger than phenol because its conjugate base, the carboxylate ion, is more strongly resonance-stabilised than the phenoxide ion.

**Quick Tip to Solve:** Compare the conjugate bases: equivalent oxygen-centred resonance favours carboxylate stability.

**32(iii).** (c) (i) Arrange the following compounds in increasing order of their reactivity towards  $\text{CH}_3\text{MgBr}$ :

$\text{CH}_3\text{CHO}$ ,  $(\text{CH}_3)_3\text{C}-\text{CO}-\text{CH}_3$ ,  $\text{CH}_3-\text{CO}-\text{CH}_3$

(ii) Write a chemical test to distinguish between propanal and propanone.

[2 marks]

**Solution:**

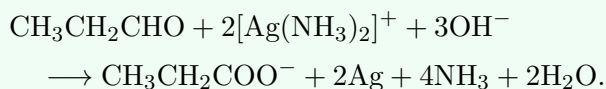
**Concept:**

- Grignard reagents supply a nucleophilic carbon atom that attacks the electron-deficient carbonyl carbon. Alkyl groups lower its electrophilicity through their electron-releasing effect.
- Bulky groups also hinder nucleophilic attack. Tollens' reagent oxidises an aldehyde to a carboxylate ion while silver ions are reduced to metallic silver; ordinary ketones do not give this test.

**Step 1: (c)(i) Compare electronic and steric effects** Ethanal,  $\text{CH}_3\text{CHO}$ , has only one alkyl group and one small hydrogen attached to its carbonyl carbon, so it is attacked most readily. Propanone has two methyl groups, which increase electron donation and steric hindrance. The ketone  $(\text{CH}_3)_3\text{C}-\text{CO}-\text{CH}_3$  contains a bulky tert-butyl group and is least reactive. Thus increasing reactivity towards  $\text{CH}_3\text{MgBr}$  is



**Step 2: (c)(ii) Apply Tollens' test** Warm each compound separately with freshly prepared Tollens' reagent in a clean test tube. Propanal gives a silver mirror, whereas propanone gives no silver mirror. The aldehyde reaction is

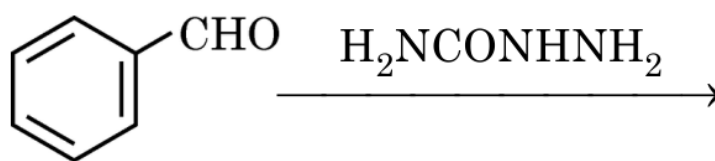
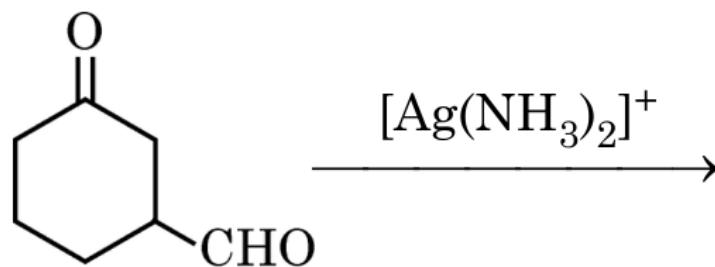


**Step 3: Conclusion** The reactivity order is tert-butyl methyl ketone < propanone < ethanal. In Tollens' test, propanal gives a silver mirror and propanone does not.

**Quick Tip to Solve:** For Grignard addition compare both alkyl donation and crowding; distinguish an aldehyde from a ketone using the silver-mirror test.

32(iii). (c) Write the main product in the following reactions:

[2 marks]



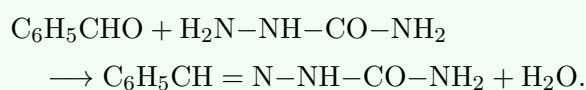
### Solution:

#### Concept:

- Tollens' reagent,  $[\text{Ag}(\text{NH}_3)_2]^+$  in alkaline medium, selectively oxidises an aldehyde group to a carboxylate group. A ketone group remains unchanged.
- Semicarbazide,  $\text{H}_2\text{NCONHNH}_2$ , condenses with an aldehyde or ketone through its terminal hydrazino  $-\text{NH}_2$  group, forming a semicarbazone and water.

**Step 1: (c)(i) Oxidise the aldehyde group selectively** The first substrate contains a cyclic ketone and an attached  $-\text{CHO}$  group. Tollens' reagent converts only  $-\text{CHO}$  into  $-\text{COO}^-$  in the alkaline reaction mixture; the ring carbonyl is retained. The main organic product is therefore 3-oxocyclohexane-1-carboxylate. Its acid form after acidification is 3-oxocyclohexane-1-carboxylic acid, commonly drawn with  $-\text{COOH}$  replacing the original  $-\text{CHO}$ . Silver metal is deposited during the reaction.

**Step 2: (c)(ii) Form the benzaldehyde semicarbazone** The second substrate is benzaldehyde. Its carbonyl oxygen is replaced by  $=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$  on condensation with semicarbazide:



The product is benzaldehyde semicarbazone. The amide nitrogen next to  $\text{CO}$  is not the nitrogen that forms the new carbon-nitrogen double bond.

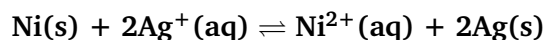
**Step 3: Conclusion** (i) The aldehyde substituent becomes carboxylate ( $-\text{COOH}$  after acidification), with the cyclohexanone group unchanged. (ii) The product is  $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{NH}-\text{CO}-\text{NH}_2$ , benzaldehyde semicarbazone.

**Quick Tip to Solve:** In a molecule containing both  $\text{CHO}$  and a ketone, Tollens' reagent changes only  $\text{CHO}$ ; semicarbazide reacts through its terminal hydrazino nitrogen.

### Section E (15 marks)

**33. (a)** Conductivity of  $2 \times 10^{-3}$  M methanoic acid is  $8 \times 10^{-5} \text{ S cm}^{-1}$ . Calculate its molar conductivity and degree of dissociation if  $\Lambda_m^\circ$  for methanoic acid is  $404 \text{ S cm}^2 \text{ mol}^{-1}$ .

**(b)** Calculate the  $\Delta_r G^\circ$  and  $\log K_c$  for the given reaction at 298 K:



Given:  $E^\circ_{\text{Ni}^{2+}/\text{Ni}} = -0.25 \text{ V}$ ,  $E^\circ_{\text{Ag}^+/\text{Ag}} = +0.80 \text{ V}$ ;  $1 \text{ F} = 96500 \text{ C mol}^{-1}$ .

[5 marks]

#### Solution:

##### Concept:

- For conductivity  $\kappa$  in  $\text{S cm}^{-1}$  and concentration  $c$  in  $\text{mol L}^{-1}$ , molar conductivity is  $\Lambda_m = 1000\kappa/c$ , in  $\text{S cm}^2 \text{ mol}^{-1}$ .
- For a weak electrolyte, the degree of dissociation is  $\alpha = \Lambda_m/\Lambda_m^\circ$ , where  $\Lambda_m^\circ$  is the molar conductivity at infinite dilution.
- Standard cell potential is  $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$ , using reduction potentials. The relations  $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$  and  $\Delta_r G^\circ = -RT \ln K_c$  connect electrical work and equilibrium.

**Step 1: (a) Calculate molar conductivity** Substitute  $\kappa = 8 \times 10^{-5} \text{ S cm}^{-1}$  and  $c = 2 \times 10^{-3} \text{ mol L}^{-1}$ :

$$\Lambda_m = \frac{1000(8 \times 10^{-5})}{2 \times 10^{-3}} = 40 \text{ S cm}^2 \text{ mol}^{-1}.$$

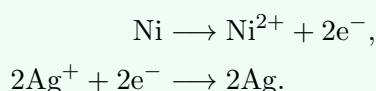
The factor 1000 converts the volume unit from litres to cubic centimetres; omitting it would give an incorrect molar conductivity.

**Step 2: (a) Obtain the degree of dissociation** Methanoic acid is a weak electrolyte, so its conductivity at the stated concentration is reduced by incomplete ionisation. Using the limiting value supplied,

$$\alpha = \frac{40}{404} = 0.0990.$$

Thus the fraction dissociated is approximately 0.0990, or 9.90%. This is dimensionless because the conductivity units cancel.

**Step 3: (b) Determine the cell potential and electron number** Nickel is oxidised and silver ions are reduced:



Hence  $n = 2$  electrons per reaction as written. Using the given reduction potentials,

$$E^\circ_{\text{cell}} = 0.80 - (-0.25) = 1.05 \text{ V}.$$

Electrode potentials are not multiplied by the stoichiometric coefficients.

**Quick Tip to Solve:** Keep the litre-to-cubic-centimetre factor in conductivity, and count two electrons for nickel oxidation before applying either thermodynamic formula.

**Step 4: (b) Calculate standard Gibbs energy and equilibrium constant** With  $F = 96500 \text{ C mol}^{-1}$ ,

$$\begin{aligned}\Delta_r G^\circ &= -2(96500)(1.05) \\ &= -202650 \text{ J mol}^{-1} \\ &= -202.65 \text{ kJ mol}^{-1}.\end{aligned}$$

At 298 K, using  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ,

$$\log K_c = \frac{nFE_{\text{cell}}^\circ}{2.303RT} = \frac{202650}{2.303(8.314)(298)} \approx 35.51.$$

The commonly rounded 0.0591 V form gives approximately 35.53. The negative Gibbs energy and large positive logarithm are consistent with a strongly product-favoured standard reaction.

**Step 5: Conclusion** (a)  $\Lambda_m = 40 \text{ S cm}^2 \text{ mol}^{-1}$  and  $\alpha = 0.0990$  (9.90%). (b)  $\Delta_r G^\circ = -202.65 \text{ kJ mol}^{-1}$  and  $\log K_c \approx 35.5$ .

**Quick Tip to Solve:** Keep the litre-to-cubic-centimetre factor in conductivity, and count two electrons for nickel oxidation before applying either thermodynamic formula.

**34(a). (I) Account for the following:**

(i)  $E^\circ$  value for  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple is much more positive than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$ .

(ii)  $\text{Sc}^{3+}$  is colourless whereas  $\text{Ti}^{3+}$  is coloured in an aqueous solution.

(iii) Actinoids show wide range of oxidation states.

(II) Write the chemical equations for the preparation of  $\text{KMnO}_4$  from  $\text{MnO}_2$ .

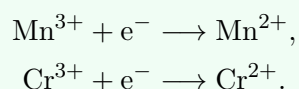
[5 marks]

**Solution:**

**Concept:**

- A standard reduction potential describes the tendency of the oxidised species to gain electrons. Particularly stable electronic configurations can favour either the reactant or the product of a reduction.
- In aqueous transition-metal ions, splitting of the d orbitals permits visible-light absorption by d-d transitions when suitable occupied and vacant d orbitals are present.
- Actinoid valence orbitals have comparable energies. Preparation of permanganate involves oxidation of manganese from +4 to +6 and then to +7.

**Step 1: (I)(i) Compare the two reduction couples** The relevant reductions are



$\text{Mn}^{3+}$  has configuration  $3d^4$ , whereas  $\text{Mn}^{2+}$  has the especially stable half-filled  $3d^5$  configuration. Reduction of  $\text{Mn}^{3+}$  therefore produces a particularly stable ion and is strongly favoured. In contrast,  $\text{Cr}^{3+}$  has the stable  $3d^3$  configuration ( $t_{2g}^3$  in an octahedral aqueous complex); reduction gives  $\text{Cr}^{2+}$ , with  $3d^4$ , and loses this stability. Thus the standard reduction potential of the manganese couple is

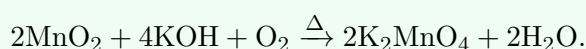
**Quick Tip to Solve:** Write the d-electron counts before comparing potentials or colours, and track manganese as +4, +6, then +7 in the preparation.

much more positive than that of the chromium couple.

**Step 2: (I)(ii) Explain the colours of the aqueous ions** Scandium has atomic number 21 and titanium has atomic number 22. Their tripositive ions have configurations  $\text{Sc}^{3+} : [\text{Ar}] 3d^0$  and  $\text{Ti}^{3+} : [\text{Ar}] 3d^1$ , respectively. In  $\text{Sc}^{3+}$ , no d electron is available for a d–d transition, so its aqueous solution is colourless. In hydrated  $\text{Ti}^{3+}$ , the d electron can absorb visible radiation and move from a lower-energy to a higher-energy split d orbital. The transmitted light consequently gives the solution its colour.

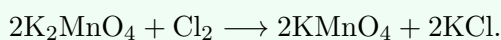
**Step 3: (I)(iii) Explain the range of actinoid oxidation states** The 5*f*, 6*d* and 7*s* orbitals of actinoids have comparable energies. Different numbers of electrons from these orbitals can therefore participate in bonding or be removed. Participation of the 5*f* electrons in addition to the 6*d* and 7*s* electrons accounts for their wide range of oxidation states, especially among the earlier actinoids.

**Step 4: (II) Prepare potassium manganate from manganese dioxide** Fuse  $\text{MnO}_2$  with potassium hydroxide in the presence of air or oxygen. The manganese oxidation state increases from +4 to +6, forming green potassium manganate:



Oxygen acts as the oxidising agent in this stage; the equation conserves potassium, manganese, oxygen and hydrogen atoms.

**Step 5: (II) Oxidise manganate to permanganate** Oxidise the manganate solution with chlorine to obtain potassium permanganate, in which manganese is in the +7 oxidation state:



Each of the two manganese atoms loses one electron, while one chlorine molecule gains two electrons to form two chloride ions. This balances both the electron transfer and the molecular equation. The resulting permanganate solution is concentrated to obtain  $\text{KMnO}_4$  crystals.

**Step 6: Conclusion** The manganese reduction gains stable  $3d^5$ , whereas the chromium reduction loses stable  $3d^3$ . Aqueous  $\text{Sc}^{3+}$  is  $d^0$  and colourless;  $\text{Ti}^{3+}$  is  $d^1$  and coloured. Comparable 5*f*, 6*d*, 7*s* energies explain actinoid oxidation states. The preparation proceeds as  $\text{MnO}_2 \rightarrow \text{K}_2\text{MnO}_4 \rightarrow \text{KMnO}_4$  by the balanced equations above.

**Quick Tip to Solve:** Write the d-electron counts before comparing potentials or colours, and track manganese as +4, +6, then +7 in the preparation.

34(b). (I) Account for the following:

(i) Transition metals form alloys.

(ii)  $\text{Ce}^{4+}$  is a strong oxidising agent.

(II) Write one similarity and one difference between chemistry of Lanthanoids and Actinoids.

(III) Complete the following ionic equation:



[5 marks]

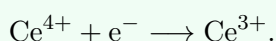
### Solution:

#### Concept:

- An alloy is a metallic mixture in which atoms of one metal can replace atoms of another in the crystal lattice when their atomic sizes are similar.
- An oxidising agent accepts electrons. The relative stability of oxidation states determines whether reduction is favourable.
- Lanthanoids involve progressive filling of  $4f$  orbitals, whereas actinoids involve progressive filling of  $5f$  orbitals; both commonly exhibit the +3 oxidation state.
- Dichromate and chromate ions interconvert with a change in the acidity of the medium, without changing the oxidation state of chromium.

**Step 1: (I)(i) Explain alloy formation** Transition metals have similar atomic radii. Therefore, an atom of one transition metal can replace an atom of another transition metal in its metallic crystal lattice without greatly disturbing the structure. Their similar metallic bonding allows the resulting mixture to retain a metallic structure. Consequently, transition metals readily form alloys with one another. For example, chromium and nickel can be incorporated into iron to make stainless steel. The essential reason is the similarity of atomic sizes and the ability of the atoms to occupy equivalent positions in a metal lattice.

**Step 2: (I)(ii) Explain the oxidising action of cerium(IV)** The +3 oxidation state is the common, stable state of lanthanoids. Cerium in the +4 state has a strong tendency to accept an electron and change to  $\text{Ce}^{3+}$ :



The standard reduction potential of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  couple is highly positive, approximately +1.74 V. Thus,  $\text{Ce}^{4+}$  readily undergoes reduction while oxidising another substance, which accounts for its strong oxidising character.

**Step 3: (II) Compare lanthanoids and actinoids Similarity:** Both series commonly form compounds in the +3 oxidation state. The loss of three electrons gives their characteristic trivalent ions, such as  $\text{La}^{3+}$  and  $\text{Ac}^{3+}$ .

**Difference:** Lanthanoids show a comparatively limited range of oxidation states, predominantly +3, with a few +2 and +4 cases. Actinoids exhibit a much wider range of oxidation states, especially among the earlier members. This happens because the energies of the  $5f$ ,  $6d$  and  $7s$  orbitals are close enough for different numbers of electrons to participate in bonding. For example, uranium can exhibit +3, +4, +5 and +6 states.

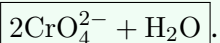
**Quick Tip to Solve:** For dichromate in an alkaline medium, write two chromate ions first, then add water and check both atoms and total ionic charge.

**Step 4: (III) Complete and check the ionic equation** Addition of hydroxide ions makes the medium alkaline and converts orange dichromate ions into yellow chromate ions:



There are two chromium atoms, nine oxygen atoms and two hydrogen atoms on each side. The total charge on the left is  $-2 - 2 = -4$ , equal to the charge of two chromate ions on the right. Chromium remains in the +6 oxidation state, so this is an acid-base equilibrium shift rather than a redox reaction.

**Step 5: Conclusion** Transition metals form alloys because their atomic sizes are similar;  $\text{Ce}^{4+}$  is strongly oxidising because it readily accepts an electron to form  $\text{Ce}^{3+}$ . Both lanthanoids and actinoids commonly show +3, but actinoids have a wider range of oxidation states. The missing products are



**Quick Tip to Solve:** For dichromate in an alkaline medium, write two chromate ions first, then add water and check both atoms and total ionic charge.

**35(a). (I) Give reasons:**

- (i) Aniline on nitration gives good amount of *m*-nitroaniline, though  $-\text{NH}_2$  group is *o/p* directing in electrophilic substitution reactions.
- (ii)  $(\text{CH}_3)_2\text{NH}$  is more basic than  $(\text{CH}_3)_3\text{N}$  in an aqueous solution.
- (iii) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

**(II) Write the reaction involved in the following:**

- (i) Carbylamine test
- (ii) Gabriel phthalimide synthesis

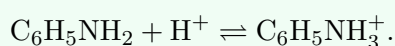
[5 marks]

**Solution:**

**Concept:**

- The directing effect of an amino group depends on whether its nitrogen lone pair is available. Neutral  $-\text{NH}_2$  activates the ortho and para positions, whereas protonated  $-\text{NH}_3^+$  is deactivating and meta directing.
- Basicity in water depends on electron donation to nitrogen, steric effects and hydration of the conjugate acid; the inductive effect alone does not determine the order.
- Primary amines undergo the carbylamine reaction. Gabriel synthesis uses an alkyl halide and a phthalimide anion to introduce one alkyl group, followed by hydrolysis to release a primary amine.

**Step 1: (I)(i) Explain the meta product during nitration of aniline** Nitration uses a strongly acidic mixture of concentrated nitric acid and sulphuric acid. In this medium, a substantial fraction of aniline is protonated:



The nitrogen in the anilinium ion has no lone pair available for donation into the ring. Its positively charged  $-\text{NH}_3^+$  group withdraws electron density and is meta directing. Nitration of this species therefore produces an appreciable amount of *m*-nitroaniline after work-up. The unprotonated

**Quick Tip to Solve:** For amine questions, check the medium first: acid protonates aniline, while water makes conjugate-acid hydration essential to the basicity order.

aniline can still give ortho and para products, so the normal directing effect of neutral  $-\text{NH}_2$  is not contradicted.

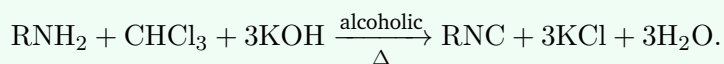
**Step 2: (I)(ii) Compare basicity in aqueous solution** Protonation produces  $(\text{CH}_3)_2\text{NH}_2^+$  from dimethylamine and  $(\text{CH}_3)_3\text{NH}^+$  from trimethylamine. The third methyl group enhances electron donation, but it also increases crowding around nitrogen and hinders hydration of the conjugate acid. The dimethylammonium ion is better solvated by water than the trimethylammonium ion. The combined inductive and solvation effects therefore favour protonation of dimethylamine more strongly in water, making  $(\text{CH}_3)_2\text{NH}$  more basic than  $(\text{CH}_3)_3\text{N}$ .

**Step 3: (I)(iii) Explain the limitation of ammonolysis** The primary amine formed by reaction of an alkyl halide with ammonia remains nucleophilic. It reacts further with the alkyl halide, forming a secondary amine, then a tertiary amine and eventually a quaternary ammonium salt:



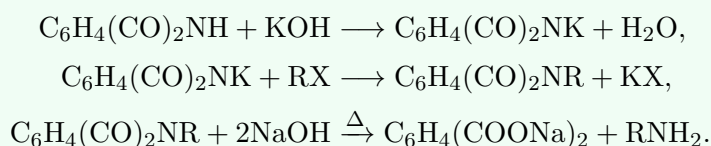
Each successive alkylation uses additional  $\text{RX}$ ; bases remove protons where necessary. Consequently, the product is a mixture that is difficult to separate into a pure primary amine. Excess ammonia favours the primary amine but does not make ammonolysis an ideal method for obtaining it pure.

**Step 4: (II)(i) Write the carbylamine reaction** Heating a primary amine with chloroform and alcoholic potassium hydroxide gives an offensive-smelling isocyanide (carbylamine):



Here R may be an alkyl or aryl group, and RNC denotes an isocyanide with the group attached to nitrogen. Both aliphatic and aromatic primary amines respond; secondary and tertiary amines do not give this test.

**Step 5: (II)(ii) Write Gabriel phthalimide synthesis** Phthalimide is treated with alcoholic potassium hydroxide to form potassium phthalimide. Its nitrogen then substitutes the halide of a primary alkyl halide. Hydrolysis of the resulting *N*-alkylphthalimide releases the primary amine:

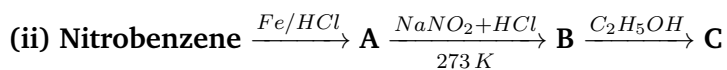
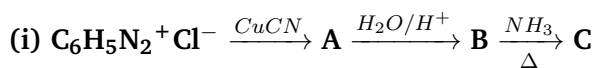


In these condensed structures,  $\text{C}_6\text{H}_4(\text{CO})_2$  is the cyclic phthalimide framework with adjacent carbonyl groups;  $\text{C}_6\text{H}_4(\text{COONa})_2$  is disodium phthalate. The method gives a primary aliphatic amine without successive alkylation. Aryl halides do not undergo the required substitution under these conditions, so it is not a method for preparing aniline.

**Step 6: Conclusion** The meta nitration product arises from protonated aniline; dimethylamine is more basic in water because its conjugate acid is better hydrated; repeated alkylation prevents pure primary-amine preparation by ammonolysis. The carbylamine test forms RNC, while Gabriel synthesis releases  $\text{RNH}_2$  by hydrolysis of *N*-alkylphthalimide.

**Quick Tip to Solve:** For amine questions, check the medium first: acid protonates aniline, while water makes conjugate-acid hydration essential to the basicity order.

35(b). (I) Write the structures of A, B and C in the following reactions:

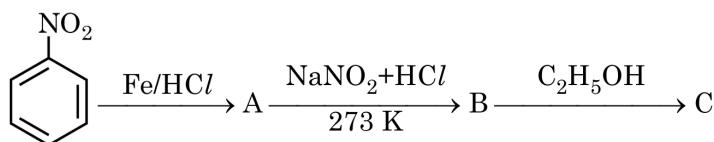
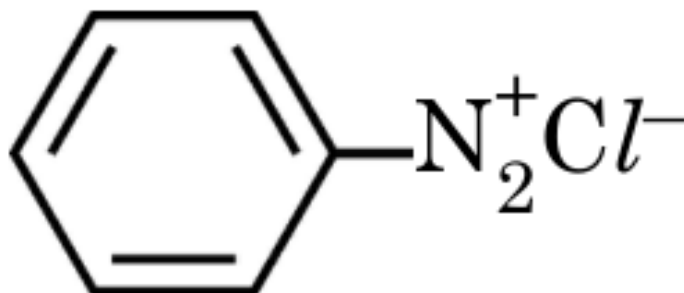


(II) Why aniline does not undergo Friedel-Crafts reaction?

(III) Arrange the following in increasing order of their boiling point:



[5 marks]



### Solution:

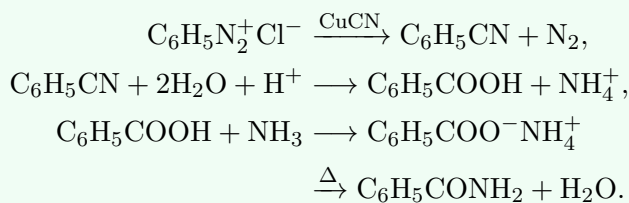
#### Concept:

- Sandmeyer cyanation replaces the diazonium group by  $-\text{CN}$ ; acid hydrolysis of a nitrile gives a carboxylic acid. Heating its ammonium salt gives the corresponding amide.
- Reduction converts  $-\text{NO}_2$  into  $-\text{NH}_2$ . Diazotisation with nitrous acid at 273 K produces an aromatic diazonium salt, which ethanol reduces to the arene.
- Aniline's nitrogen lone pair binds the Lewis acid catalyst used in Friedel-Crafts reactions. Boiling points depend on both hydrogen bonding and molecular size, hence on dispersion forces.

**Step 1: (I)(i) Identify the cyanation, hydrolysis and amidation products** Copper(I) cyanide replaces the diazonium group of benzenediazonium chloride by a nitrile group. Thus A is benzonitrile,  $\text{C}_6\text{H}_5 - \text{C} \equiv \text{N}$ . The nitrile carbon remains attached to the ring during acid hydrolysis, giving B, benzoic acid,  $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{OH}$ . Benzoic acid first forms ammonium benzoate with ammonia;

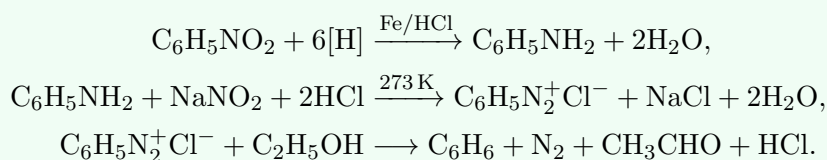
**Quick Tip to Solve:** Track the attached group at every arrow: diazonium to nitrile to acid to amide. Compare molecular size as well as hydrogen bonding when boiling-point candidates differ greatly in mass.

heating removes water to form C, benzamide,  $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH}_2$ .



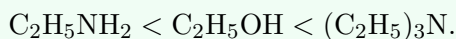
The last step gives an amide, since ammonia supplies nitrogen to the carboxyl group; it does not produce aniline.

**Step 2: (I)(ii) Identify the reduction and diazotisation products** Iron and hydrochloric acid reduce nitrobenzene to aniline, so A has structure  $\text{C}_6\text{H}_5 - \text{NH}_2$ . Sodium nitrite and hydrochloric acid generate nitrous acid in situ. At 273 K, aniline gives B, benzenediazonium chloride,  $\text{C}_6\text{H}_5 - \text{N} \equiv \text{N}^+\text{Cl}^-$ . Ethanol replaces the diazonium group by hydrogen, producing C, benzene,  $\text{C}_6\text{H}_6$ . Ethanol itself is oxidised to ethanal.



**Step 3: (II) Explain the failure of Friedel-Crafts reaction** The Lewis acid catalyst  $\text{AlCl}_3$  combines with the lone pair on aniline's nitrogen to form a salt-like Lewis acid-base complex, represented as  $\text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{AlCl}_3$ . This removes the availability of the lone pair for donation into the aromatic ring and gives the nitrogen electron-withdrawing character. The ring is strongly deactivated towards electrophilic substitution under these conditions. Hence aniline fails to undergo ordinary Friedel-Crafts alkylation or acylation.

**Step 4: (III) Compare hydrogen bonding and dispersion forces** Ethylamine and ethanol can form intermolecular hydrogen bonds, but the O – H hydrogen bonding of ethanol is stronger than the N – H hydrogen bonding of ethylamine. Thus ethanol boils above ethylamine. Triethylamine has no N – H bond, so its pure liquid does not form hydrogen bonds between its molecules. However, its substantially larger molecular size and electron cloud give stronger dispersion forces, raising its boiling point above ethanol. Therefore the increasing order is



**Step 5: Conclusion** (I)(i) A =  $\text{C}_6\text{H}_5\text{CN}$ , B =  $\text{C}_6\text{H}_5\text{COOH}$ , C =  $\text{C}_6\text{H}_5\text{CONH}_2$ ; (ii) A =  $\text{C}_6\text{H}_5\text{NH}_2$ , B =  $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ , C =  $\text{C}_6\text{H}_6$ . (II) Aniline forms a deactivating complex with  $\text{AlCl}_3$ . (III)  $\text{C}_2\text{H}_5\text{NH}_2 < \text{C}_2\text{H}_5\text{OH} < (\text{C}_2\text{H}_5)_3\text{N}$ .

**Quick Tip to Solve:** Track the attached group at every arrow: diazonium to nitrile to acid to amide. Compare molecular size as well as hydrogen bonding when boiling-point candidates differ greatly in mass.