

CBSE Class 12 Chemistry Question Paper 2026 with Solution PDF-Set 56-1-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)



Time Allowed: 3 hours

Maximum Marks: 70

General Instructions

- (i) This question paper contains **33** questions. **All** questions are **compulsory**.
- (ii) This question paper is divided into **five** sections – Section **A, B, C, D** and **E**.
- (iii) **Section A** – questions number **1** to **16** are multiple choice type questions. Each question carries **1** mark.
- (iv) **Section B** – questions number **17** to **21** are very short answer type questions. Each question carries **2** marks.
- (v) **Section C** – questions number **22** to **28** are short answer type questions. Each question carries **3** marks.
- (vi) **Section D** – questions number **29** and **30** are case-based questions. Each question carries **4** marks.
- (vii) **Section E** – questions number **31** to **33** are long answer type questions. Each question carries **5** marks.
- (viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the sections except Section –A.
- (ix) Kindly note that there is a separate question paper for Visually Impaired candidates.
- (x) Use of calculator is **NOT** allowed.

Section A (16 marks)

Questions No. 1 to 16 are Multiple Choice type questions carrying 1 mark each.

1. In the ring structure of fructose, the anomeric carbon is

[1 mark]

- (A) C-1
- (B) C-2
- (C) C-3
- (D) C-5

Correct Answer: (B) C-2

Solution:

Concept:

- The anomeric carbon is the former carbonyl carbon of the open-chain sugar.
- Fructose is a ketohexose: its ketone group occurs at C – 2.

Step 1: Locate the carbonyl carbon In open-chain fructose, C – 1 is a terminal CH₂OH carbon, while C – 2 carries the ketone group. On cyclisation, an internal hydroxyl group adds to this carbonyl carbon to form a cyclic hemiketal.

Step 2: Compare the positions The carbonyl carbon becomes bonded to two oxygen atoms and gives rise to the two anomeric configurations. Thus C – 1, C – 3 and C – 5 are not the anomeric carbon; participation of the hydroxyl on another carbon does not make that carbon anomeric.

Step 3: Conclusion The anomeric carbon is C – 2. Hence, the correct option is (B).

Quick Tip to Solve: Identify the original carbonyl carbon: C-1 in glucose, C-2 in fructose.

2. Which of the following is the correct expression of K_f which depends upon the nature of solvent?

[1 mark]

- (A) $K_f = \frac{M_1 T_f^2}{R \times 1000 \times \Delta_{\text{fus}} H}$
- (B) $K_f = \frac{R M_1 \Delta_{\text{fus}} H}{1000 T_f^2}$
- (C) $K_f = \frac{R T_f^2 \Delta_{\text{fus}} H}{1000 M_1}$
- (D) $K_f = \frac{R M_1 T_f^2}{1000 \Delta_{\text{fus}} H}$

Correct Answer: (D) $K_f = \frac{R M_1 T_f^2}{1000 \Delta_{\text{fus}} H}$

Solution:

Concept:

- The cryoscopic constant satisfies $\Delta T_f = K_f m$, where m is solute molality.

Quick Tip to Solve: Remember that K_f increases with the square of the solvent freezing temperature and decreases with its enthalpy of fusion.

- T_f is the freezing temperature of the pure solvent in kelvin, M_1 its molar mass in g mol^{-1} , and $\Delta_{\text{fus}}H$ its molar enthalpy of fusion.

Step 1: Use the solvent expression For a dilute ideal solution, freezing-point depression gives

$$K_f = \frac{RM_1T_f^2}{1000 \Delta_{\text{fus}}H}.$$

The factor 1000 converts the solvent molar mass from grams per mole to kilograms per mole. All the quantities on the right, apart from the universal gas constant R , characterise the solvent.

Step 2: Test the options Option (A) incorrectly places R in the denominator. Option (B) interchanges the positions of T_f^2 and the enthalpy of fusion. Option (C) places the solvent molar mass in the denominator and the enthalpy in the numerator. Only (D) has all these factors in the required positions.

Step 3: Conclusion $K_f = \frac{RM_1T_f^2}{1000 \Delta_{\text{fus}}H}$. Hence, the correct option is (D).

Quick Tip to Solve: Remember that K_f increases with the square of the solvent freezing temperature and decreases with its enthalpy of fusion.

3. Which of the following transition metals has lowest enthalpy of atomisation?

[1 mark]

- (A) Cr
- (B) V
- (C) Mn
- (D) Fe

Correct Answer: (C) Mn

Solution:

Concept:

- Enthalpy of atomisation is the energy needed to form gaseous atoms from the element in its standard state.
- Weaker metallic bonding gives a lower enthalpy of atomisation.

Step 1: Consider manganese Manganese has the configuration $[\text{Ar}] 3d^5 4s^2$. The stable half-filled $3d^5$ configuration is associated with comparatively weak metallic bonding in manganese, giving the conspicuously low atomisation enthalpy in this part of the first transition series.

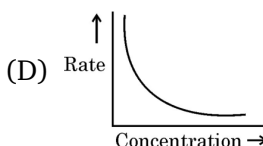
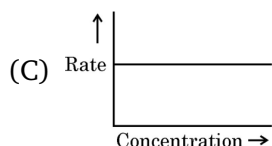
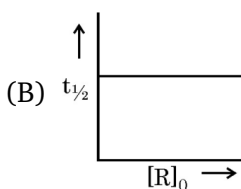
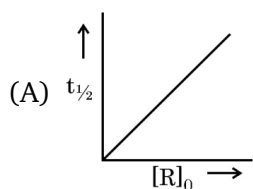
Step 2: Compare the listed metals The approximate atomisation enthalpies in kJ mol^{-1} are Mn: 281, Cr: 397, Fe: 416 and V: 515. Therefore chromium, vanadium and iron all require more energy for atomisation than manganese. Counting unpaired electrons alone would not explain this anomalously low value.

Step 3: Conclusion Mn has the lowest enthalpy of atomisation among these metals. Hence, the correct option is (C).

Quick Tip to Solve: Recall the manganese dip in the first transition-series atomisation enthalpy trend.

4. Which of the following curve represents the first order reaction?

[1 mark]



Correct Answer: (B)

Solution:

Concept:

- For a first-order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- The first-order half-life is independent of the initial reactant concentration $[R]_0$.

Step 1: Read the half-life graphs At fixed temperature, k is constant, so changing $[R]_0$ does not change $t_{1/2}$. A plot of half-life against initial concentration must therefore be a horizontal straight line. The rising half-life line in (A) instead shows a dependence on initial concentration.

Step 2: Read the rate graphs For first order, $\text{rate} = k[R]$, so a rate versus concentration graph rises linearly through the origin. The constant rate in (C) is characteristic of zero order, while the decreasing rate curve in (D) does not obey the first-order rate law. The axes must be checked before identifying a horizontal line.

Step 3: Conclusion The horizontal $t_{1/2}$ versus $[R]_0$ plot is the required curve. Hence, the correct option is (B).

Quick Tip to Solve: Check the vertical axis: first order has constant half-life, whereas zero order has constant rate.

5. Aniline on direct nitration yields

[1 mark]

- (A) 51%-ortho, 47%-para, 2%-meta derivatives
- (B) 51%-meta, 47%-ortho, 2%-para derivatives
- (C) 51%-para, 47%-meta, 2%-ortho derivatives
- (D) 51%-ortho, 47%-meta, 2%-para derivatives

Correct Answer: (C) 51%-para, 47%-meta, 2%-ortho derivatives

Solution:

Concept:

- Aniline is normally ortho- and para-directing because the $-\text{NH}_2$ group donates its lone pair.

Quick Tip to Solve: For direct aniline nitration, remember the substantial meta product caused by protonation in acid.

- In the strongly acidic nitrating mixture, aniline is protonated to the meta-directing anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$.

Step 1: Account for the acidic medium Direct nitration uses concentrated nitric and sulfuric acids. Protonation removes the availability of the nitrogen lone pair for ring donation, so a substantial amount of meta product forms through the anilinium ion. The unprotonated aniline present also accounts for ortho and para substitution.

Step 2: Match the distribution The standard product distribution for direct nitration is about 51 percent para, 47 percent meta and 2 percent ortho. Option (A) wrongly makes meta only 2 percent, while (B) and (D) both put para at only 2 percent. Steric hindrance makes the ortho proportion small compared with para.

Step 3: Conclusion The products are 51% para, 47% meta and 2% ortho derivatives. Hence, the correct option is (C).

Quick Tip to Solve: For direct aniline nitration, remember the substantial meta product caused by protonation in acid.

6. Which of the following is 'not' true about enantiomers?

[1 mark]

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

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

Solution:

Concept:

- Enantiomers are non-superimposable mirror images.
- In an achiral environment, they have identical ordinary physical properties but equal and opposite specific rotations.

Step 1: Compare optical rotation Under identical measurement conditions, one enantiomer rotates plane-polarised light clockwise and the other anticlockwise by an equal amount. If the specific rotation of one is $+a$, that of the other is $-a$. Their rotations have equal magnitudes, but their signed specific rotations are not the same.

Step 2: Check the remaining statements Enantiomers have the same melting point, boiling point and refractive index. They also have the same chemical reactivity towards achiral reagents, the ordinary comparison intended here. Their responses may differ with chiral reagents or biological systems, but this does not alter the distinguishing optical-rotation statement.

Step 3: Conclusion The statement that they have the same specific rotation is false. Hence, the correct option is (B).

Quick Tip to Solve: Distinguish equal magnitude of optical rotation from equal signed specific rotation.

7. The secondary valency of Co in $[\text{Co}(\text{en})_3]^{3+}$ is

[1 mark]

- (A) 4
- (B) 3
- (C) 5
- (D) 6

Correct Answer: (D) 6

Solution:

Concept:

- Werner's secondary valency equals the coordination number: the number of ligand donor atoms directly bonded to the metal.
- Ethylenediamine, en, is a bidentate ligand with two nitrogen donor atoms.

Step 1: Count the donor atoms The complex $[\text{Co}(\text{en})_3]^{3+}$ contains three en ligands. Each ligand coordinates through both nitrogen atoms, so the total number of direct cobalt–nitrogen coordinate bonds is

$$3 \times 2 = 6.$$

Counting ligand molecules alone would incorrectly give 3.

Step 2: Distinguish the two valencies Because en is neutral, the cobalt oxidation state is +3, corresponding to its primary valency. The charge 3+ does not give its secondary valency. Values 4 and 5 also fail to account for all six donor atoms supplied by the three complete chelating ligands.

Step 3: Conclusion The secondary valency of Co is $\boxed{6}$. Hence, the correct option is (D).

Quick Tip to Solve: For coordination number, multiply the number of each ligand by its denticity; do not count only ligand molecules.

8. At low temperature, phenol on reaction with Br_2 in CS_2 gives

[1 mark]

- (A) 2, 4, 6-Tribromophenol
- (B) a mixture of ortho- and para-bromophenol
- (C) ortho-bromophenol only
- (D) para-bromophenol only

Correct Answer: (B) a mixture of ortho- and para-bromophenol

Solution:

Concept:

- The hydroxyl group activates the benzene ring through resonance and directs electrophilic substitution to the ortho and para positions.
- Bromination in a nonpolar solvent such as CS_2 at low temperature gives controlled monosubstitution.

Step 1: Apply the stated reaction conditions In CS_2 , phenol reacts with bromine to give a mixture

Quick Tip to Solve: Check the solvent first: bromine water gives tribromination, while cold CS_2 gives monobromination.

of 2-bromophenol and 4-bromophenol. Both positions are activated by donation of an oxygen lone pair into the aromatic ring; the para product is generally the major product because it has less steric hindrance.

Step 2: Check the alternatives Option (A), 2,4,6-tribromophenol, is characteristic of bromine water, where extensive bromination occurs. Options (C) and (D) incorrectly exclude one of the two activated positions: these conditions do not give exclusively the ortho or exclusively the para isomer.

Step 3: Conclusion The products are a mixture of ortho- and para-bromophenol. Hence, the correct option is (B).

Quick Tip to Solve: Check the solvent first: bromine water gives tribromination, while cold CS₂ gives monobromination.

9. How the conductivity varies on decreasing concentration for both weak and strong electrolytes?

[1 mark]

- (A) It increases for weak electrolyte and decreases for strong electrolyte.
- (B) It decreases for weak electrolyte and increases for strong electrolyte.
- (C) It increases for both weak and strong electrolytes.
- (D) It decreases for both weak and strong electrolytes.

Correct Answer: (D) It decreases for both weak and strong electrolytes.

Solution:

Concept:

- Conductivity κ measures the conductance of a unit volume of solution and depends on the number of mobile ions per unit volume.
- Molar conductivity Λ_m is different from conductivity; for concentration c in mol L^{-1} , $\Lambda_m = 1000\kappa/c$.

Step 1: Consider dilution of either electrolyte Decreasing concentration by adding solvent decreases the number of ions present per unit volume. Thus conductivity decreases for both strong and weak electrolytes. Although a weak electrolyte ionises to a greater extent on dilution, this does not reverse the decrease in its conductivity.

Step 2: Distinguish the quantity in the question Molar conductivity increases on dilution for both types: ion mobility increases for strong electrolytes, and the degree of ionisation also increases for weak electrolytes. Options (A), (B) and (C) each claim that conductivity increases for at least one type and therefore confuse this behaviour with molar conductivity.

Step 3: Conclusion Conductivity decreases for both weak and strong electrolytes. Hence, the correct option is (D).

Quick Tip to Solve: Underline conductivity: ion count per unit volume decreases on dilution; molar conductivity instead increases.

10. $\text{CH}_3\text{-NH}_2$ on reaction with $(\text{CH}_3\text{CO})_2\text{O}$ gives

[1 mark]

- (A) CH_3CONH_2
- (B) $\text{CH}_3\text{COONHCH}_3$
- (C) $\text{CH}_3\text{-NH-CO-CH}_3$
- (D) $\text{CH}_3\text{-CO-CH}_2\text{-NH}_2$

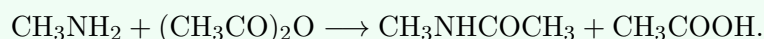
Correct Answer: (C) $\text{CH}_3\text{-NH-CO-CH}_3$

Solution:

Concept:

- Primary amines undergo acylation with acid anhydrides, replacing one hydrogen on nitrogen with an acyl group.
- Acetic anhydride transfers the acetyl group $\text{CH}_3\text{CO-}$; the original methyl group attached to nitrogen remains attached.

Step 1: Write the acylation reaction



The product is N-methylethanamide, also called N-methylacetamide. Nitrogen is bonded directly to the carbonyl carbon.

Step 2: Compare the product structures Option (C) retains the $\text{CH}_3\text{-N}$ bond and introduces -COCH_3 on nitrogen. Option (A) is ethanamide and loses the nitrogen-bound methyl group. Option (B) introduces an extra oxygen linkage, while option (D) gives an amino ketone rather than the amide formed by acylation.

Step 3: Conclusion The product is $\text{CH}_3\text{-NH-CO-CH}_3$. Hence, the correct option is (C).

Quick Tip to Solve: Keep the methyl group on nitrogen and replace one N-H hydrogen with the acetyl group $\text{CH}_3\text{CO-}$.

11. The activation energy of a reaction can be determined from the slope of which of the following curves? [1 mark]

- (A) $\ln k$ vs T
(B) $\ln k$ vs $\frac{1}{T}$
(C) $\ln \frac{k}{T}$ vs T
(D) $\frac{T}{\ln k}$ vs $\frac{1}{T}$

Correct Answer: (B) $\ln k$ vs $\frac{1}{T}$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the pre-exponential factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- A straight-line equation $y = mx + b$ identifies the slope m .

Step 1: Linearise the Arrhenius equation Taking natural logarithms gives

$$\ln k = \ln A - \frac{E_a}{R} \left(\frac{1}{T} \right).$$

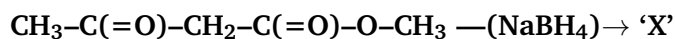
Thus, with $y = \ln k$ and $x = 1/T$, the slope is $m = -E_a/R$, so $E_a = -mR$.

Step 2: Test the remaining axes Option (A) uses T instead of its reciprocal and does not give this straight-line slope. Option (C), $\ln(k/T)$ versus T , adds a temperature-dependent logarithmic term. Option (D), $T/(\ln k)$ versus $1/T$, is also not the Arrhenius straight-line form; neither has slope $-E_a/R$.

Step 3: Conclusion Plot $\ln k$ against $1/T$. Hence, the correct option is (B).

Quick Tip to Solve: For natural logarithms, multiply the negative slope of $\ln k$ versus $1/T$ by R to obtain activation energy.

12. Identify 'X' in the following reaction :



'X' is

[1 mark]

- (A) $\text{CH}_3\text{--CH(OH)--CH}_2\text{--C(=O)--O--CH}_3$
(B) $\text{CH}_3\text{--C(=O)--CH}_2\text{--CH}_2\text{--OH}$
(C) $\text{CH}_3\text{--CH(OH)--CH}_2\text{--CH}_2\text{--OH}$
(D) $\text{CH}_3\text{--CH(OH)--CH}_2\text{--COOH}$

Correct Answer: (A) $\text{CH}_3\text{--CH(OH)--CH}_2\text{--C(=O)--O--CH}_3$

Solution:

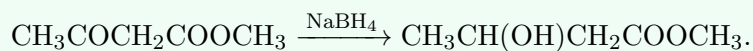
Concept:

- Sodium borohydride, NaBH_4 , reduces aldehydes and ketones to alcohols under ordinary conditions.

Quick Tip to Solve: With NaBH_4 , change the ketone C=O to CH(OH) and leave the methyl ester group intact.

- It does not normally reduce an ester group, so a molecule containing ketone and ester groups undergoes selective ketone reduction.

Step 1: Identify and reduce the ketone group The reactant $\text{CH}_3\text{COCH}_2\text{COOCH}_3$ contains a ketone carbonyl and a methyl ester group. The ketone carbonyl becomes $\text{CH}(\text{OH})$, while COOCH_3 remains unchanged:



Step 2: Eliminate the other structures Option (B) reduces the ester while leaving the ketone unchanged, the reverse of the reagent selectivity. Option (C) requires reduction of both groups to give a diol. Option (D) changes the methyl ester to a carboxylic acid, which requires hydrolysis and is not the stated reduction. Only option (A) preserves the ester and reduces the ketone.

Step 3: Conclusion X is $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOCH}_3$, methyl 3-hydroxybutanoate. Hence, the correct option is (A).

Quick Tip to Solve: With NaBH_4 , change the ketone $\text{C}=\text{O}$ to $\text{CH}(\text{OH})$ and leave the methyl ester group intact.

13. Assertion (A): The presence of $-\text{OH}$ group in phenols directs the incoming group at ortho- and para- positions.

Reason (R): $-\text{OH}$ group in phenols deactivates the aromatic ring.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

Solution:

Concept:

- In phenol, an oxygen lone pair is donated into the aromatic ring by resonance, producing a positive resonance effect.
- This donation increases electron density particularly at the ortho and para positions and activates electrophilic substitution.

Step 1: Judge the assertion The assertion is true. The hydroxyl group directs an incoming electrophile to the ortho and para positions because these positions have enhanced electron density and their substitution intermediates receive additional resonance stabilisation.

Step 2: Judge the reason The reason is false. Although oxygen exerts an electron-withdrawing inductive effect, its electron-donating resonance effect predominates in phenol. The net result is activation of the aromatic ring, not deactivation.

Quick Tip to Solve: For phenol, distinguish oxygen's withdrawing inductive effect from its stronger activating resonance donation.

Step 3: Check the explanatory relation A false reason cannot explain the true assertion. Both options (A) and (B) incorrectly treat the reason as true, while option (D) incorrectly treats the assertion as false. The valid explanation is resonance donation by the hydroxyl group.

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

Quick Tip to Solve: For phenol, distinguish oxygen's withdrawing inductive effect from its stronger activating resonance donation.

14. Assertion (A): Actinoids show irregularities in their electronic configurations.

Reason (R): Due to varying stabilities of f^0 , f^7 and f^{14} occupancies of the 5f orbitals.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

Solution:

Concept:

- Actinoids show irregular electronic configurations because the energies of the 5f, 6d and 7s orbitals are close.
- The relative stabilities of empty, half-filled and completely filled 5f subshells, represented by f^0 , f^7 and f^{14} , influence electron distribution.

Step 1: Judge the assertion The assertion is true. The actinoid series does not follow a perfectly regular filling pattern. Small energy differences between the available orbitals allow configurations that depart from a simple sequential filling of the 5f subshell.

Step 2: Judge the reason The reason is also true. The varying stability associated with $5f^0$, $5f^7$ and $5f^{14}$ occupancies affects which electronic arrangement is energetically preferred in an actinoid atom.

Step 3: Check whether the reason explains the assertion These stability differences help determine electron occupancy when orbital energies are comparable, and hence explain the observed irregularities. Option (B) incorrectly denies this connection; options (C) and (D) incorrectly classify one of the two true statements as false.

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

Quick Tip to Solve: For actinoid irregularities, connect the close orbital energies with the varying stability of 5f occupancies.

15. Assertion (A): The pentaacetate of glucose does not react with $\text{H}_2\text{N-OH}$.

Reason (R): It indicates the absence of free $-\text{CHO}$ group in glucose.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

Solution:

Concept:

- Hydroxylamine, NH_2OH , reacts with a free aldehyde or ketone carbonyl group to form an oxime.
- Glucose predominantly has a cyclic hemiacetal structure. Acetylation of all five hydroxyl groups gives glucose pentaacetate, with its anomeric oxygen acetylated.

Step 1: Judge Assertion (A) Glucose pentaacetate does not form an oxime with hydroxylamine. Its cyclic structure has no free aldehydic carbonyl group available for this reaction. Thus Assertion (A) is true.

Step 2: Judge Reason (R) The observation indicates the absence of a free $-\text{CHO}$ group in the cyclic structure of glucose retained in its pentaacetate. Thus Reason (R) is true in the structural sense intended here. Glucose itself can react through the small open-chain fraction in equilibrium; the statement does not mean that free glucose can never show aldehyde reactions.

Step 3: Decide whether the reason explains the assertion Oxime formation requires an available carbonyl group. The absence of that free group in the pentaacetate directly explains its failure to react with NH_2OH . Therefore the explanation relationship holds; (B) wrongly denies it, while (C) and (D) wrongly declare one statement false.

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

Quick Tip to Solve: For glucose pentaacetate, check whether the anomeric centre can expose a free carbonyl before predicting an oxime test.

16. Assertion (A): It is not possible to separate the components of an azeotrope by fractional distillation.

Reason (R): Minimum boiling azeotrope is formed by the solutions showing large positive deviation from Raoult's law.

Select the correct answer from the codes (A), (B), (C) and (D).

[1 mark]

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

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

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

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

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

Solution:

Concept:

- An azeotrope is a constant-boiling mixture whose vapour and liquid have the same composition at the azeotropic composition.
- Fractional distillation separates components by enriching the vapour in a more volatile component. A large positive deviation from Raoult's law can produce a minimum-boiling azeotrope.

Step 1: Judge Assertion (A) At the azeotropic composition, vaporisation does not change composition: the condensed vapour has the same proportions as the original liquid. Repeated vaporisation and condensation therefore cannot separate its components by fractional distillation. Assertion (A) is true.

Step 2: Judge Reason (R) A solution showing sufficiently large positive deviation has a vapour pressure higher than expected for ideal mixing. The corresponding boiling temperature is lower and a minimum-boiling azeotrope may form. Reason (R), which states this relation, is true.

Step 3: Test the explanatory link The reason describes how a minimum-boiling azeotrope is formed; it does not state the equal liquid and vapour compositions responsible for failed separation. Maximum-boiling azeotropes also resist fractional distillation at their azeotropic composition. Thus R does not explain A. Option (A) wrongly assigns the explanation; (C) and (D) wrongly treat one statement as false.

Step 4: Conclusion Both A and R are true, but R is not the correct explanation of A. Hence, the correct option is (B).

Quick Tip to Solve: For an azeotrope separation question, use equal liquid and vapour compositions; the sign of deviation only identifies its boiling type.

Section B (10 marks)

17. What type of deviation is shown by a mixture of chloroform and acetone from Raoult's law? Give reason. What will happen to the boiling point of the solution on mixing chloroform and acetone?

[2 marks]

Solution:

Concept:

- For an ideal solution, Raoult's law gives $p_i = x_i p_i^\circ$, where p_i is component vapour pressure, x_i its liquid mole fraction and p_i° its pure vapour pressure.
- Stronger attractions between unlike molecules reduce their escape into the vapour and produce negative deviation. A liquid boils when its vapour pressure equals the external pressure.

Step 1: Identify the deviation and explain its molecular origin Chloroform and acetone show negative deviation from Raoult's law. The hydrogen atom of chloroform, CHCl_3 , forms a hydrogen bond with the oxygen atom of the carbonyl group in acetone, $(\text{CH}_3)_2\text{CO}$. These chloroform–acetone attractions are stronger than the corresponding attractions in the unmixed liquids. Molecules are retained more strongly in the liquid, so their escaping tendency decreases and the vapour pressure lies below the ideal value.

Step 2: Relate the reduced vapour pressure to boiling At a given temperature, this stronger inter-molecular attraction lowers the solution vapour pressure relative to the ideal mixture. A higher temperature is therefore needed to bring the vapour pressure up to the same external pressure. Consequently mixing produces an increase in boiling point relative to ideal mixing; sufficiently large negative deviation can lead to a maximum-boiling azeotrope.

Step 3: Conclusion The mixture shows negative deviation due to hydrogen bonding between chloroform and acetone; its boiling point increases relative to the ideal mixture.

Quick Tip to Solve: Look for the chloroform H and acetone carbonyl O: their hydrogen bonding lowers vapour pressure and raises the boiling temperature.

18. Following reaction takes place in one step:



How will the rate of above reaction change if the volume of the reaction vessel is decreased to one third of its original volume? Will there be any change in the order of reaction with the reduced volume?

[2 marks]

Solution:

Concept:

- For an elementary reaction occurring in one step, the stoichiometric coefficients of the reactants give their powers in the rate law.
- Concentration is n/V , where n is the amount of substance and V the vessel volume. At fixed temperature the rate constant k remains unchanged.

Step 1: Write the rate law for the one-step reaction For the elementary reaction $2A + B \rightarrow 2C$, the

Quick Tip to Solve: When all reactant concentrations triple, multiply the rate by $3^{\text{overall order}}$; here use $3^3 = 27$.

rate is

$$r = k[A]^2[B].$$

The reaction has order two with respect to A and order one with respect to B. Its overall order is therefore $2 + 1 = 3$. The one-step condition is essential: reaction coefficients alone do not generally give the rate law for a multistep reaction.

Step 2: Calculate the effect of reducing the vessel volume Let the original concentrations be $[A]$ and $[B]$. Immediately after compression, the amounts of both reactants remain the same. With $V_{\text{new}} = V/3$, each concentration triples:

$$[A]_{\text{new}} = 3[A], \quad [B]_{\text{new}} = 3[B].$$

At the same temperature,

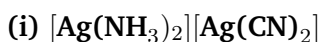
$$r_{\text{new}} = k(3[A])^2(3[B]) = 27k[A]^2[B] = 27r.$$

Compression changes concentrations, but it does not change the exponents in the rate law or the elementary reaction mechanism.

Step 3: Conclusion The rate becomes 27 times its original value. The overall order remains 3; reducing volume does not change the reaction order.

Quick Tip to Solve: When all reactant concentrations triple, multiply the rate by $3^{\text{overall order}}$; here use $3^3 = 27$.

19(a). Write IUPAC names of the following coordination compounds:



[2 marks]

Solution:

Concept:

- Name the cation before the anion. Ligand names precede the metal name; show the metal oxidation state in Roman numerals.
- NH_3 is the neutral ligand ammine, CN^- is cyanido, and $\text{C}_2\text{O}_4^{2-}$ is oxalato. An anionic complex uses an -ate metal name.

Step 1: Name the silver complex salt In $[\text{Ag}(\text{NH}_3)_2][\text{Ag}(\text{CN})_2]$, the complex cation is $[\text{Ag}(\text{NH}_3)_2]^+$. Since ammonia is neutral, silver is in oxidation state +1, giving diamminesilver(I). In the complex anion $[\text{Ag}(\text{CN})_2]^-$, let the silver oxidation state be x . Then $x + 2(-1) = -1$, so $x = +1$. The anion is dicyanidoargentate(I), using argentate for silver in an anionic complex. Combine the cation and anion names in that order.

Step 2: Name the potassium oxalato complex In $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$, three potassium cations require the complex anion to have charge -3 . Each oxalato ligand has charge -2 , hence

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

Quick Tip to Solve: First balance ligand charges to find the metal oxidation state; use argentate and ferrate only for the anionic complexes.

The three oxalato ligands are indicated by tris(oxalato), and the anionic iron complex takes the metal name ferrate(III). The counter-ion is named potassium first.

Step 3: Conclusion (i) Diamminesilver(I) dicyanidoargentate(I).
(ii) Potassium tris(oxalato)ferrate(III).

Quick Tip to Solve: First balance ligand charges to find the metal oxidation state; use argentate and ferrate only for the anionic complexes.

OR

19(b). (i) Give a chemical test to show that $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ are ionisation isomers.

(ii) What is meant by the 'Chelate effect'? Give an example.

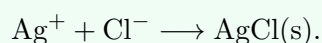
[2 marks]

Solution:

Concept:

- Ionisation isomers exchange a ligand within the coordination sphere with a counter-ion outside it; only the free counter-ion gives the immediate precipitation test.
- The chelate effect is the enhanced stability of a complex with chelating multidentate ligands compared with a comparable complex containing monodentate ligands.

Step 1: (i) Test the free counter-ions Dissolve the compounds separately in water and add aqueous silver nitrate. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$ releases free Cl^- , so it gives a white precipitate of AgCl :



The chloride ligand in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$ lies inside the coordination sphere and does not give this immediate chloride test. Alternatively, aqueous barium chloride gives a white BaSO_4 precipitate with the second compound because its sulphate ion is free; the first compound has coordinated sulphate. These different ions released in solution establish ionisation isomerism.

Step 2: (ii) Explain the chelate effect with an example A multidentate ligand binds the same metal ion through two or more donor atoms, forming one or more rings. Such chelated complexes are more stable than analogous complexes with monodentate ligands. For example, $[\text{Ni}(\text{en})_3]^{2+}$, where en is bidentate ethane-1,2-diamine, is more stable than $[\text{Ni}(\text{NH}_3)_6]^{2+}$; each en ligand forms a chelate ring with nickel.

Step 3: Conclusion (i) The first complex gives the free-chloride test with AgNO_3 ; the second gives the free-sulphate test with BaCl_2 . (ii) Chelation enhances complex stability, as illustrated by $[\text{Ni}(\text{en})_3]^{2+}$.

Quick Tip to Solve: For an ionisation-isomer test, first identify the ion written outside the square brackets.

20. Differentiate between the following:

(i) Fibrous protein and Globular protein

(ii) Peptide linkage and Phosphodiester linkage

[2 marks]

Solution:

Concept:

- Protein shape depends on how polypeptide chains fold and associate; shape is linked to solubility and biological role.
- A peptide bond joins amino-acid residues, whereas a phosphodiester bond joins nucleotide sugar units through phosphate.

Step 1: (i) Fibrous and globular proteins Fibrous proteins have polypeptide chains arranged mainly in elongated, fibre-like structures, often held together by hydrogen bonds and disulphide bonds. They are generally insoluble in water and perform structural roles; keratin and myosin are examples. Globular proteins have chains folded into compact, approximately spherical shapes. They are generally water-soluble and commonly perform metabolic or transport functions; insulin and albumin are examples. Thus shape and usual water solubility provide two clear points of distinction.

Step 2: (ii) Peptide and phosphodiester linkages A peptide linkage is the amide group $-\text{CO}-\text{NH}-$, formed between the carboxyl group of one amino acid and the amino group of another with elimination of water. It builds the polypeptide backbone of proteins. A phosphodiester linkage has a phosphate group esterified to two sugar hydroxyl groups; in nucleic acids it connects the 3' position of one sugar to the 5' position of the next. It builds the sugar-phosphate backbone of DNA and RNA, rather than joining amino acids.

Step 3: Conclusion Fibrous proteins are elongated and generally water-insoluble; globular proteins are compact and generally water-soluble. Peptide linkages join amino acids in proteins, while 3'-5' phosphodiester linkages join nucleotides in nucleic acids.

Quick Tip to Solve: Remember the backbone: proteins contain amide bonds; DNA and RNA contain sugar-phosphate bonds.

21. Why are haloarenes less reactive towards nucleophilic substitution reaction? Give two reasons.

[2 marks]

Solution:

Concept:

- Ordinary nucleophilic substitution requires cleavage of the carbon-halogen bond.
- In a haloarene, the halogen is bonded directly to an sp^2 -hybridised aromatic carbon, and its lone pair interacts with the ring.

Step 1: 1. Resonance strengthens the carbon-halogen bond A lone pair on the halogen overlaps with the aromatic π system. Resonance therefore gives the aryl carbon-halogen bond partial double-bond character. This bond is shorter and stronger than the corresponding single bond in a haloalkane, so its cleavage during nucleophilic substitution is difficult. For example, the carbon-chlorine bond in

Quick Tip to Solve: For two reasons, state resonance first and greater s-character of the bonded aromatic carbon second.

chlorobenzene is strengthened by this delocalisation; the halogen is consequently less easily displaced by a nucleophile.

Step 2: 2. The bonded carbon is sp^2 -hybridised The aromatic carbon attached to the halogen is sp^2 -hybridised, whereas the corresponding carbon in a haloalkane is sp^3 -hybridised. An sp^2 orbital has greater s-character and holds its bonding electron pair closer to the carbon nucleus. The aryl carbon-halogen bond is therefore shorter and more strongly held, making its rupture harder. Together these two bond-strengthening effects explain the lower reactivity of haloarenes under ordinary nucleophilic substitution conditions.

Step 3: Conclusion Haloarenes are less reactive because resonance gives the carbon-halogen bond partial double-bond character, and bonding to an sp^2 carbon further makes that bond shorter and stronger.

Quick Tip to Solve: For two reasons, state resonance first and greater s-character of the bonded aromatic carbon second.

Section C (21 marks)

22. Calculate the boiling point of a solution containing 0.61 g of benzoic acid (Molar mass = 122 g mol^{-1}) in 5 g of CS_2 in which it dimerises to the extent of 88%. The boiling point and K_b of CS_2 are 46.2°C and $2.3 \text{ K kg mol}^{-1}$ respectively. [3 marks]

Solution:

Concept:

- Boiling-point elevation is $\Delta T_b = iK_b m$, where i is the van't Hoff factor, K_b the ebullioscopic constant and m the molality calculated before association.
- For dimerisation with associated fraction α , two monomers form one particle, so $i = 1 - \alpha/2$.

Step 1: Calculate the initial molality The amount of benzoic acid added is

$$n = \frac{0.61 \text{ g}}{122 \text{ g mol}^{-1}} = 0.005 \text{ mol.}$$

The solvent mass is $5 \text{ g} = 0.005 \text{ kg}$. Hence the molality based on the added monomer is

$$m = \frac{0.005 \text{ mol}}{0.005 \text{ kg}} = 1.00 \text{ mol kg}^{-1}.$$

Use solvent mass here, rather than the mass of the solution.

Step 2: Account for dimer formation Benzoic acid associates according to $2\text{C}_6\text{H}_5\text{COOH} \rightleftharpoons (\text{C}_6\text{H}_5\text{COOH})_2$. With $\alpha = 0.88$, an initial amount n leaves $n(1 - \alpha)$ moles of monomer and produces $n\alpha/2$ moles of dimer. Thus the final number of solute particles relative to the initial number is

$$i = \frac{n(1 - \alpha) + n\alpha/2}{n} = 1 - \frac{0.88}{2} = 0.56.$$

This factor is below unity because association reduces the particle count.

Quick Tip to Solve: For dimerisation use half the associated fraction: 88 percent association gives $i = 0.56$, not 0.12.

Step 3: Find the elevation and add it to the solvent boiling point Substitute the corrected particle factor into the colligative-property relation:

$$\begin{aligned}\Delta T_b &= iK_b m \\ &= 0.56 \times 2.3 \text{ K kg mol}^{-1} \times 1.00 \text{ mol kg}^{-1} \\ &= 1.288 \text{ K}.\end{aligned}$$

A temperature difference of 1.288 K equals 1.288 °C. Therefore

$$T_b = 46.2 + 1.288 = 47.488 \text{ °C}.$$

The rise is smaller than that for an unassociated solute of the same initial molality, as expected.

Step 4: Conclusion The boiling point of the solution is $47.488 \text{ °C} \approx 47.49 \text{ °C}$.

Quick Tip to Solve: For dimerisation use half the associated fraction: 88 percent association gives $i = 0.56$, not 0.12.

23. Write the reaction involved in the following:

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedal-Crafts acylation of anisole

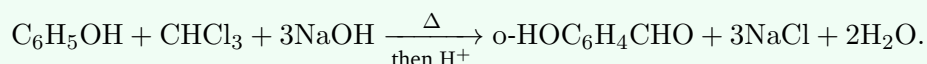
[3 marks]

Solution:

Concept:

- Phenol activates its ring towards electrophilic substitution at the ortho and para positions. Reimer-Tiemann formylation and Kolbe carboxylation normally yield the ortho product as the principal product.
- The methoxy group of anisole is an ortho- and para-directing activating group. Friedel-Crafts acylation introduces an acyl group into its benzene ring.

Step 1: (a) Reimer-Tiemann reaction Phenol is treated with chloroform and aqueous sodium hydroxide on heating, followed by acidification. The principal product is 2-hydroxybenzaldehyde (salicylaldehyde):

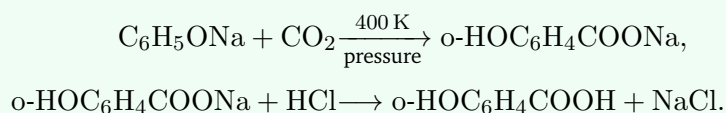


The aldehyde group is introduced adjacent to the hydroxyl group. A small amount of the para isomer also forms.

Step 2: (b) Kolbe's reaction Sodium phenoxide reacts with carbon dioxide under pressure at about

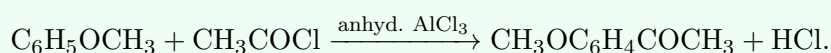
Quick Tip to Solve: Distinguish the phenol reactions by the group introduced: chloroform gives $-\text{CHO}$, while carbon dioxide gives $-\text{COOH}$ after acidification.

400 K. Acidification of the sodium salicylate obtained gives salicylic acid:



The carboxyl group is introduced at the ortho position relative to the hydroxyl group.

Step 3: (c) Friedel-Crafts acylation of anisole Anisole reacts with acetyl chloride in the presence of anhydrous aluminium chloride. Each substitution can be represented by



The products have $-\text{OCH}_3$ and $-\text{COCH}_3$ in the ortho or para arrangement: ortho- and para-methoxyacetophenone. The para isomer predominates owing to less steric hindrance.

Step 4: Conclusion Reimer-Tiemann reaction gives salicylaldehyde; Kolbe's reaction gives salicylic acid after acidification; acylation of anisole gives ortho- and predominantly para-methoxyacetophenone.

Quick Tip to Solve: Distinguish the phenol reactions by the group introduced: chloroform gives $-\text{CHO}$, while carbon dioxide gives $-\text{COOH}$ after acidification.

24. Give reasons for the following:

- (a) Carboxylic acids have higher boiling point than alcohols of comparable molecular masses.
 - (b) Alpha (α) hydrogens of aldehydes and ketones are acidic in nature.
 - (c) Nucleophilic addition of ammonia and its derivatives does not occur with carbonyl group in strongly acidic medium.
- [3 marks]

Solution:

Concept:

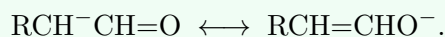
- Boiling requires overcoming intermolecular attractions. Stronger hydrogen bonding and molecular association increase the energy required for vaporisation.
- Acidity depends on the stability of the conjugate base. Resonance stabilisation of an enolate favours removal of an alpha hydrogen from a carbonyl compound.
- Ammonia and its derivatives attack a carbonyl carbon using the nitrogen lone pair. Protonation of this lone pair reduces their nucleophilicity.

Step 1: (a) Compare intermolecular association A carboxylic acid has both a hydrogen-bond donor (the hydroxyl group) and a strong acceptor (the carbonyl oxygen). Two acid molecules form a cyclic dimer held together by two intermolecular hydrogen bonds. Such dimers persist even in the vapour phase to an appreciable extent. Alcohols also form hydrogen bonds, but carboxylic acids have stronger intermolecular association. More energy is therefore needed to separate acid molecules during boiling, so acids have higher boiling points than alcohols of comparable molecular masses.

Step 2: (b) Explain the stability of the conjugate base An alpha hydrogen is bonded to the carbon directly adjacent to the carbonyl group. Removal of this hydrogen as a proton gives an enolate ion.

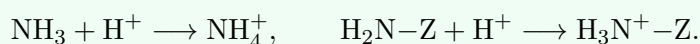
Quick Tip to Solve: For carbonyl condensation, distinguish protonation of oxygen (activation) from protonation of the nitrogen nucleophile (inhibition in excess acid).

For an aldehyde, its resonance forms are



The negative charge is delocalised between the alpha carbon and the more electronegative oxygen atom. The electron-withdrawing effect of the carbonyl group also assists proton removal. Aldehydes and ketones therefore possess acidic alpha hydrogens; an analogous enolate is formed from a ketone.

Step 3: (c) Account for inhibition in strongly acidic medium In a strongly acidic medium, ammonia and its derivatives are predominantly protonated:



Protonation uses the nitrogen lone pair, so the protonated species cannot effectively attack the electrophilic carbonyl carbon. The concentration of free nucleophile becomes too low for addition. Mild acidity can activate the carbonyl group, but strong acidity inhibits the reaction by protonating the nucleophile.

Step 4: Conclusion The reasons are strong hydrogen-bonded dimerisation of carboxylic acids, resonance stabilisation of enolate ions, and loss of nucleophilicity through protonation of ammonia or its derivatives.

Quick Tip to Solve: For carbonyl condensation, distinguish protonation of oxygen (activation) from protonation of the nitrogen nucleophile (inhibition in excess acid).

25. For the first order thermal decomposition reaction, following data was obtained:



Calculate rate constant. [Given: $\log 3 = 0.48$]

[3 marks]

S. No.	Time(s)	Total Pressure (atm)
1	0	0.30
2	30	0.50

Solution:

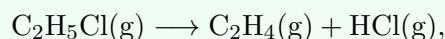
Concept:

- At constant temperature and volume, gas partial pressure is proportional to the amount of that gas. Total pressure includes both unreacted reactant and products.
- For a first-order reaction, $k = \frac{2.303}{t} \log \frac{p_0}{p_A}$, where p_0 is the initial reactant pressure and p_A its partial pressure after time t .

Step 1: Find the pressure of unreacted ethyl chloride Initially only ethyl chloride is present, so its initial pressure is $p_0 = 0.30$ atm. Let x be the pressure corresponding to the amount of ethyl chloride

Quick Tip to Solve: For one gaseous reactant producing two gaseous molecules, first calculate its remaining partial pressure as $2P_0 - P_t$; then use that value in the first-order equation.

decomposed after 30 s. From the stoichiometry



the reactant pressure becomes $p_0 - x$, while each product has pressure x . Consequently,

$$P_t = (p_0 - x) + x + x = p_0 + x.$$

The measured total pressure is 0.50 atm, giving

$$\begin{aligned}x &= 0.50 - 0.30 = 0.20 \text{ atm}, \\p_A &= 0.30 - 0.20 = 0.10 \text{ atm}.\end{aligned}$$

Equivalently, $p_A = 2p_0 - P_t$. The total pressure must not be substituted for the remaining reactant pressure.

Step 2: Apply the integrated first-order rate equation Using the partial pressures, the initial-to-final reactant ratio is $0.30/0.10 = 3$. Thus, with the supplied value $\log 3 = 0.48$,

$$\begin{aligned}k &= \frac{2.303}{30} \log \frac{0.30}{0.10} \\&= \frac{2.303 \times 0.48}{30} \\&= 0.036848 \text{ s}^{-1}.\end{aligned}$$

The pressure ratio is dimensionless, and the unit of the first-order rate constant is inverse time. Both pressures can therefore remain in atmospheres without conversion.

Step 3: Conclusion The rate constant is $k \approx 3.68 \times 10^{-2} \text{ s}^{-1}$, using the given logarithm value.

Quick Tip to Solve: For one gaseous reactant producing two gaseous molecules, first calculate its remaining partial pressure as $2P_0 - P_t$; then use that value in the first-order equation.

26. How do you explain the presence of following in open structure of glucose?

- (a) all the six carbon atoms are in a straight chain.
- (b) five -OH groups which are attached to different carbon atoms.
- (c) an aldehyde group.

[3 marks]

Solution:

Concept:

- Characteristic reactions establish the carbon skeleton and functional groups of glucose.
- Exhaustive reduction reveals the carbon chain, acetylation counts alcoholic hydroxyl groups, and mild oxidation distinguishes an aldehyde from a ketone.

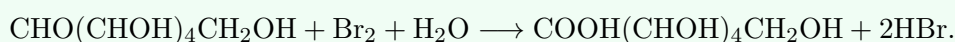
Step 1: Establish the straight chain of six carbon atoms On prolonged heating with hydrogen iodide, glucose gives *n*-hexane, $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$. This product has six carbon atoms in one unbranched chain.

Quick Tip to Solve: Match each feature to its test: HI reveals the carbon skeleton, acetylation counts hydroxyl groups, and bromine water identifies the aldehyde.

Since this conversion removes the oxygen-containing groups without changing the carbon skeleton, it shows that all six carbon atoms in glucose are connected in a straight chain.

Step 2: Establish five hydroxyl groups on different carbon atoms Glucose reacts with acetic anhydride to form glucose pentaacetate. Formation of five acetate ester groups demonstrates the presence of five alcoholic -OH groups. The pentaacetate is stable; this supports the attachment of the five hydroxyl groups to different carbon atoms, rather than two hydroxyl groups being attached to the same carbon atom.

Step 3: Establish the aldehyde group Glucose reacts with hydroxylamine to form an oxime, showing the presence of a carbonyl group. It is oxidised by the mild oxidising agent bromine water to gluconic acid, retaining all six carbon atoms. Bromine water oxidises an aldehyde under these conditions but does not ordinarily oxidise a ketone. Thus the carbonyl group is an aldehyde group, -CHO , at the end of the chain:



Step 4: Conclusion Formation of *n*-hexane establishes the straight six-carbon chain; glucose pentaacetate establishes five hydroxyl groups on different carbons; bromine-water oxidation to gluconic acid establishes the aldehyde group.

Quick Tip to Solve: Match each feature to its test: HI reveals the carbon skeleton, acetylation counts hydroxyl groups, and bromine water identifies the aldehyde.

27. Compound 'X' with molecular formula $\text{C}_4\text{H}_9\text{Br}$ reacts with aqueous KOH to give an alcohol. The rate of this reaction depends only on the concentration of the compound 'X'. When an optically active isomer 'Y' of the compound 'X' was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound 'Y' and aqueous KOH both.

(a) Write down the structural formula of both 'X' and 'Y'.

(b) Out of 'X' and 'Y', which one will undergo racemisation and why?

(c) Out of 'X' and 'Y', which one will form product with inversion of configuration and why? [3 marks]

Solution:

Concept:

- An $\text{S}_{\text{N}}1$ reaction has rate $k[\text{X}]$; slow ionisation forms a carbocation before nucleophilic attack.
- An $\text{S}_{\text{N}}2$ reaction has rate $k[\text{Y}][\text{OH}^-]$; concerted backside attack causes inversion at a stereogenic carbon.
- Racemisation requires a chiral reactant or product: a planar carbocation alone does not make an achiral molecule racemise.

Step 1: (a) Identify X and Y from the rate laws The first-order rate law identifies X as the tertiary bromide 2-bromo-2-methylpropane, $(\text{CH}_3)_3\text{CBr}$, which readily forms a tertiary carbocation. Its aqueous-KOH product is $(\text{CH}_3)_3\text{COH}$. The optically active isomer Y is 2-bromobutane, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$. Its second carbon carries four different groups: H, Br, methyl and ethyl. The given second-order rate

Quick Tip to Solve: Use the rate law to identify the mechanism, then check for four different groups before claiming racemisation; tert-butyl bromide is achiral.

law specifies its S_N2 reaction to form butan-2-ol.

Step 2: (b) Assess the racemisation demand The usual stereochemical feature of an S_N1 reaction is racemisation when an optically active substrate forms a planar carbocation that can be attacked from both faces. Here X follows S_N1 , but its three methyl groups are identical: both X and its alcohol product are achiral. Therefore X cannot actually undergo racemisation. The given Y follows S_N2 , so it undergoes inversion rather than racemisation. Thus neither compound literally racemises under the specified reactions; X is the compound associated with the mechanism normally responsible for racemisation.

Step 3: (c) Explain inversion for Y In Y , OH^- approaches the stereogenic carbon from the side opposite the C–Br bond. Formation of the C–OH bond and cleavage of the C–Br bond occur together through a single transition state. This backside displacement reverses the spatial arrangement at that carbon (Walden inversion), producing butan-2-ol with inverted configuration. There is no freely planar carbocation in this mechanism.

Step 4: Conclusion $X = (\text{CH}_3)_3\text{CBr}$ and $Y = \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$. X follows S_N1 , the usual racemisation mechanism, but is achiral and cannot itself racemise. Y forms butan-2-ol with inversion by S_N2 .

Quick Tip to Solve: Use the rate law to identify the mechanism, then check for four different groups before claiming racemisation; tert-butyl bromide is achiral.

28(a). Answer the following:

- (i) Why is the Equilibrium Constant (K_c) related to E_{cell}° and not to E_{cell} ?
- (ii) Two metals 'A' and 'B' have standard electrode potential values of -0.24 V and $+0.80 \text{ V}$ respectively. Which of these will liberate hydrogen gas from dil. H_2SO_4 ?
- (iii) Write the cell reaction which occurs in lead storage battery when it is in charging. [3 marks]

Solution:

Concept:

- Standard Gibbs energy links the equilibrium constant and standard cell potential: $\Delta G^\circ = -RT \ln K_c = -nFE_{\text{cell}}^\circ$.
- A metal displaces hydrogen when oxidation of that metal coupled to reduction of H^+ gives a positive cell potential.
- Charging a rechargeable battery reverses its discharge reaction using an external electrical source.

Step 1: (i) Relate equilibrium constant to standard potential At a specified temperature, K_c is related to the standard Gibbs energy change, so

$$\ln K_c = \frac{nFE_{\text{cell}}^\circ}{RT}.$$

Here n is the number of transferred electrons, F the Faraday constant, R the gas constant and T the absolute temperature. The actual potential E_{cell} depends on concentrations through the reaction

Quick Tip to Solve: At equilibrium the actual emf is zero; compare metal reduction potentials with zero for hydrogen, and reverse the lead-battery discharge equation for charging.

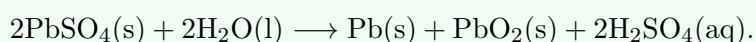
quotient Q :

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q.$$

At equilibrium $Q = K_c$ and $E_{\text{cell}} = 0$; therefore the equilibrium relation contains E_{cell}° , rather than the concentration-dependent actual potential.

Step 2: (ii) Decide which metal liberates hydrogen Treat the given electrode potentials as standard reduction potentials. For $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, $E^{\circ} = 0\text{ V}$. Pairing hydrogen-ion reduction with metal oxidation gives $E_{\text{cell}}^{\circ} = 0 - E_{\text{metal}}^{\circ}$. For A this is $+0.24\text{ V}$, whereas for B it is -0.80 V . Hence A liberates hydrogen from dilute sulphuric acid, while B does not.

Step 3: (iii) Write the charging reaction During discharge, both electrodes become lead sulphate and sulphuric acid is consumed. On charging, an external source regenerates lead at the negative electrode and lead dioxide at the positive electrode, while sulphuric acid concentration increases. The overall reaction is



The atoms are balanced and this reaction is the reverse of the discharge reaction.

Step 4: Conclusion (i) K_c is linked to E_{cell}° through ΔG° . (ii) Metal A liberates hydrogen. (iii) Charging: $2\text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4$.

Quick Tip to Solve: At equilibrium the actual emf is zero; compare metal reduction potentials with zero for hydrogen, and reverse the lead-battery discharge equation for charging.

OR

28(b). What type of battery is Mercury cell? Why it is more advantageous than dry cell? Write overall reaction taking place in Mercury cell. [3 marks]

Solution:

Concept:

- A primary cell supplies electrical energy by a spontaneous chemical reaction and is not designed to be recharged.
- A mercury cell uses zinc amalgam as the anode, mercury(II) oxide as the cathode and an alkaline electrolyte containing KOH and ZnO.
- Cell potential remains nearly constant when the overall discharge reaction does not change the electrolyte concentration.

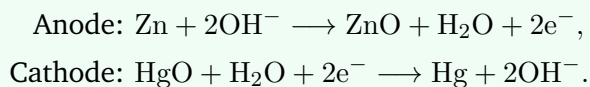
Step 1: Identify the type of battery A mercury cell is a primary battery. During discharge, zinc is oxidised and mercury(II) oxide is reduced. The reactants are consumed, so it is not a rechargeable storage battery.

Step 2: Explain its advantage over a dry cell Its main advantage is its nearly constant potential of about 1.35 V throughout its useful life. In the mercury cell, the overall reaction involves no ions in solution, so the electrolyte composition remains essentially unchanged. In an ordinary dry cell,

Quick Tip to Solve: Add the alkaline half-reactions and cancel hydroxide ions to explain why the mercury-cell voltage stays steady.

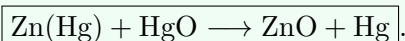
changes in reactant concentrations and polarisation cause its voltage to fall during use. Thus a mercury cell supplies a steadier voltage, useful in devices requiring a stable small current.

Step 3: Combine the electrode reactions The alkaline half-reactions are



Adding them cancels the electrons, water and hydroxide ions. Zinc oxide and mercury are the discharge products; hydroxide is regenerated, explaining the stable electrolyte concentration.

Step 4: Conclusion The mercury cell is a primary battery with nearly constant voltage. Its overall discharge reaction is



Here Zn(Hg) denotes zinc amalgam.

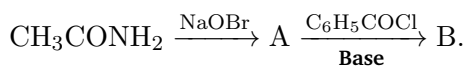
Quick Tip to Solve: Add the alkaline half-reactions and cancel hydroxide ions to explain why the mercury-cell voltage stays steady.

Section D (8 marks)

The following questions are case-based questions. Each question has an internal choice and carries 4(2 + 1 + 1) marks each. Read the passage carefully and answer the questions that follow.

29(a). (i) Why is CH_3NH_2 a stronger base than $(\text{CH}_3)_3\text{N}$ in aqueous solution?

(ii) Write structural formulae of the compounds A and B:



[2 marks]

Solution:

Concept:

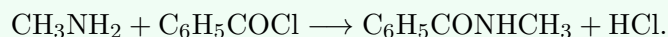
- In water, amine basicity depends on both the electron-releasing effect of alkyl groups and stabilisation of the conjugate acid by hydration.
- Hofmann bromamide degradation converts an amide into a primary amine containing one carbon atom less.
- A primary amine reacts with benzoyl chloride in base to form an N-substituted benzamide.

Step 1: (i) Compare hydration in aqueous solution Methylamine accepts a proton to give CH_3NH_3^+ , whereas trimethylamine gives $(\text{CH}_3)_3\text{NH}^+$. The methylammonium ion has three N–H bonds and less steric crowding, so it is more effectively hydrated through hydrogen bonding than trimethylammonium. Although three methyl groups exert a stronger electron-releasing effect, the poorer hydration and greater crowding of the trimethylammonium ion outweigh that advantage here. Hence methylamine is the stronger base in aqueous solution.

Quick Tip to Solve: Remove the amide carbonyl carbon in the NaOBr step, then attach a benzoyl group to the amine nitrogen.

Step 2: (ii) Identify A from the first reaction The starting amide is ethanamide, CH_3CONH_2 . Sodium hypobromite causes Hofmann degradation: the carbonyl carbon is lost and the remaining methyl group becomes attached to the amino group. Thus A has the structure $\text{CH}_3 - \text{NH}_2$, methylamine.

Step 3: (ii) Identify B from benzoylation The nitrogen of methylamine attacks benzoyl chloride, replacing its chlorine by $-\text{NHCH}_3$. The base removes the HCl formed:



Thus B is N-methylbenzamide with structural formula $\text{C}_6\text{H}_5 - \text{C}(=\text{O}) - \text{NH} - \text{CH}_3$.

Step 4: Conclusion (i) Greater hydration of CH_3NH_3^+ makes methylamine more basic in water. (ii) $\boxed{\text{A} = \text{CH}_3\text{NH}_2}$ and $\boxed{\text{B} = \text{C}_6\text{H}_5\text{CONHCH}_3}$.

Quick Tip to Solve: Remove the amide carbonyl carbon in the NaOBr step, then attach a benzoyl group to the amine nitrogen.

29(b). A compound 'X' with molecular formula $\text{C}_3\text{H}_9\text{N}$ reacts with Hinsberg reagent to give a product insoluble in alkali. Identify 'X'. [1 mark]

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$.
- A secondary amine forms an N,N-disubstituted sulphonamide with no acidic N-H proton, making it insoluble in alkali.

Step 1: Use the observed Hinsberg reaction X reacts with Hinsberg reagent, excluding a tertiary amine under the usual test conditions. Its sulphonamide product is insoluble in alkali, so X is secondary: the product has no N-H proton that could be removed by hydroxide. A primary amine would give a sulphonamide with an acidic N-H bond and therefore an alkali-soluble product.

Step 2: Apply the molecular formula A secondary amine has two alkyl groups attached to nitrogen. With a total of three carbon atoms, these groups must be methyl and ethyl. The structure is therefore $\text{CH}_3 - \text{NH} - \text{CH}_2\text{CH}_3$; its formula is $\text{C}_3\text{H}_9\text{N}$. Its reaction produces $\text{C}_6\text{H}_5\text{SO}_2\text{N}(\text{CH}_3)(\text{C}_2\text{H}_5)$, which contains no N-H bond.

Step 3: Conclusion $\boxed{\text{X} = \text{CH}_3\text{NHCH}_2\text{CH}_3}$, N-methylethanamine (ethylmethylamine).

Quick Tip to Solve: An alkali-insoluble Hinsberg product identifies a secondary amine; split the three carbons into methyl and ethyl groups.

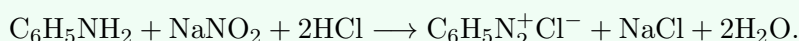
29(b). How can you convert aniline to benzonitrile?

[1 mark]

Solution:**Concept:**

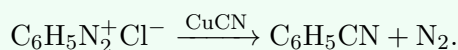
- Aniline undergoes diazotisation with nitrous acid generated from sodium nitrite and hydrochloric acid at 273–278 K.
- In the Sandmeyer reaction, CuCN replaces the diazonium group by a cyano group with liberation of nitrogen.

Step 1: Prepare benzenediazonium chloride Treat aniline with NaNO_2/HCl while keeping the mixture at 273–278 K. Nitrous acid is formed in situ and converts $-\text{NH}_2$ into the diazonium group:



The low temperature prevents premature decomposition of the diazonium salt.

Step 2: Replace the diazonium group by cyanide Treat the benzenediazonium chloride with cuprous cyanide, CuCN, in the Sandmeyer reaction:



The new carbon atom belongs to the cyano group attached to the benzene ring.

Step 3: Conclusion $\text{C}_6\text{H}_5\text{NH}_2 \xrightarrow[273-278\text{ K}]{\text{NaNO}_2/\text{HCl}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- \xrightarrow{\text{CuCN}} \text{C}_6\text{H}_5\text{CN}$. The final product is benzonitrile.

Quick Tip to Solve: For aromatic amino-to-cyano conversion, first diazotise cold and then use CuCN in the Sandmeyer step.

29(c). Why is $-\text{NH}_2$ group of aniline acetylated before carrying out nitration?

[1 mark]

Solution:**Concept:**

- The free $-\text{NH}_2$ group strongly activates the benzene ring and can undergo oxidation under direct nitration conditions.
- Acetylation converts aniline into acetanilide, containing $-\text{NHCOCH}_3$, which is less activating but still ortho/para directing.

Step 1: Explain the difficulty with direct nitration The strongly acidic nitrating mixture protonates aniline to the anilinium ion, $\text{C}_6\text{H}_5\text{NH}_3^+$, which directs substitution towards the meta position. Direct nitration therefore gives an unwanted mixture; the unprotected amino group is also susceptible to oxidation in the harsh medium.

Step 2: Explain the protective role of acetylation Acetylating $-\text{NH}_2$ forms acetanilide. The nitrogen

Quick Tip to Solve: Protect aniline as acetanilide before nitration, then hydrolyse the acetyl group after introducing the nitro group.

lone pair is shared with the carbonyl group, moderating ring activation and protecting the amino group from oxidation. Nitration consequently gives mainly para-nitroacetanilide, which can be hydrolysed to obtain para-nitroaniline.

Step 3: Conclusion The amino group is acetylated to protect it from oxidation and control its activating effect, enabling nitration mainly at the para position.

Quick Tip to Solve: Protect aniline as acetanilide before nitration, then hydrolyse the acetyl group after introducing the nitro group.

30(a). In octahedral crystal field, energies of which d-orbitals will be raised when ligands approach the central metal atom/ion? Give reason in support of your answer. [2 marks]

Solution:

Concept:

- In an octahedral field, six ligands approach along the positive and negative x , y and z axes. Their electron pairs repel the electrons in the metal d-orbitals.
- The d-orbitals split into the higher-energy e_g set and the lower-energy t_{2g} set, according to their orientations relative to the ligands.

Step 1: Identify the orbitals facing the ligands The lobes of $d_{x^2-y^2}$ point along the x and y axes, while the principal lobes of d_{z^2} point along the z axis. These two orbitals therefore face the ligands directly and form the e_g set.

Step 2: Explain their energy increase Electrons in these orbitals experience greater electrostatic repulsion than those in d_{xy} , d_{yz} and d_{xz} , whose lobes lie between the axes. Relative to the barycentre, e_g rises by $\frac{3}{5}\Delta_o$ and t_{2g} falls by $\frac{2}{5}\Delta_o$, where Δ_o is the octahedral splitting energy.

Step 3: Conclusion The energies of $d_{x^2-y^2}$ and d_{z^2} are raised because their lobes point directly towards the ligands, causing greater electrostatic repulsion.

Quick Tip to Solve: Place octahedral ligands on the axes first: the orbitals pointing along those axes form the raised e_g set.

30(b). Using crystal field theory, write the electronic configuration of central metal atom/ion of the following:

(i) $[\text{CoF}_6]^{3-}$

(ii) $[\text{Co}(\text{NH}_3)_6]^{3+}$ [At. No.: Co = 27]

[1 mark]

Solution:

Concept:

- Both complexes contain Co^{3+} , with configuration $[\text{Ar}]3d^6$. In an octahedral field, t_{2g} is lower in energy than e_g .
- A weak ligand field gives high spin when $\Delta_o < P$; a strong field gives low spin when $\Delta_o > P$,

Quick Tip to Solve: Count cobalt as d-six in both ions before applying the weak-field versus strong-field filling rule.

where P is electron-pairing energy.

Step 1: Fill orbitals for the fluoride complex For $[\text{CoF}_6]^{3-}$, $x + 6(-1) = -3$ gives $x = +3$. The weak-field ligand F^- favours maximum unpaired electrons, giving $t_{2g}^4 e_g^2$ for the six d-electrons.

Step 2: Fill orbitals for the ammine complex In $[\text{Co}(\text{NH}_3)_6]^{3+}$, neutral ammonia makes cobalt again $+3$. For this cobalt(III) complex the ligand field is sufficiently strong to pair all six electrons in t_{2g} , giving $t_{2g}^6 e_g^0$.

Step 3: Conclusion (i) $[\text{CoF}_6]^{3-} : t_{2g}^4 e_g^2$; (ii) $[\text{Co}(\text{NH}_3)_6]^{3+} : t_{2g}^6 e_g^0$.

Quick Tip to Solve: Count cobalt as d-six in both ions before applying the weak-field versus strong-field filling rule.

30(c). $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{Ni}(\text{CO})_4]$ is diamagnetic though both are tetrahedral. Why? [Atomic No.: Ni = 28] [1 mark]

Solution:

Concept:

- Paramagnetism requires unpaired electrons, while a species with all electrons paired is diamagnetic.
- Find the metal oxidation state before counting d-electrons; identical tetrahedral geometry does not imply identical electron configurations.

Step 1: Count electrons in the chloride complex In $[\text{NiCl}_4]^{2-}$, $x - 4 = -2$, so nickel is Ni^{2+} with $3d^8$. Chloride gives a weak tetrahedral field. Its configuration is $e^4 t_2^4$, with two unpaired electrons in the upper t_2 set.

Step 2: Count electrons in nickel tetracarbonyl In $[\text{Ni}(\text{CO})_4]$, carbon monoxide is neutral, so nickel has oxidation state zero. In this complex the metal has a filled $3d^{10}$ configuration, with all d-electrons paired; its tetrahedral configuration is $e^4 t_2^6$.

Step 3: Conclusion $[\text{NiCl}_4]^{2-}$ is paramagnetic because it has two unpaired electrons; $[\text{Ni}(\text{CO})_4]$ is diamagnetic because all electrons are paired.

Quick Tip to Solve: Check ligand charges first: chloride gives nickel(II), whereas neutral CO gives nickel(0).

OR

30(c). Write hybridization and magnetic behaviour of the complex $[\text{Fe}(\text{CN})_6]^{3-}$. [Atomic No.: Fe = 26] [1 mark]

Solution:

Concept:

- In $[\text{Fe}(\text{CN})_6]^{3-}$, iron is $+3$ because $x + 6(-1) = -3$. Thus Fe^{3+} has the configuration $[\text{Ar}]3d^5$.
- CN^- is a strong-field ligand and favours pairing in the lower octahedral t_{2g} orbitals.

Quick Tip to Solve: A strong field pairs d-five into two pairs and one single electron; low spin here still means paramagnetic.

Step 1: Determine the electronic arrangement The five d-electrons occupy the lower t_{2g} set as two pairs and one single electron, giving the low-spin configuration $t_{2g}^5 e_g^0$. Two inner 3d orbitals are consequently vacant.

Step 2: Determine hybridisation and magnetism The two vacant 3d orbitals combine with one 4s and three 4p orbitals to give six d^2sp^3 hybrid orbitals in an octahedral arrangement. The remaining single unpaired electron produces paramagnetic behaviour.

Step 3: Conclusion $[\text{Fe}(\text{CN})_6]^{3-}$ has d^2sp^3 hybridisation and is paramagnetic, with one unpaired electron.

Quick Tip to Solve: A strong field pairs d-five into two pairs and one single electron; low spin here still means paramagnetic.

Section E (15 marks)

31(a). (i) From the given data of E° values, answer the following questions:

(I) Why $E_{M^{2+}/M}^\circ$ show irregular trend in the above values?

(II) Why is $E_{\text{Cu}^{2+}/\text{Cu}}^\circ$ value exceptionally positive?

(III) Why $E_{\text{Mn}^{2+}/\text{Mn}}^\circ$ value is highly negative?

(ii) Write the ionic equations for the oxidising action of potassium permanganate for its reaction with I^- in both acidic and alkaline solutions. [5 marks]

$E_{M^{2+}/M}^\circ$	V	Cr	Mn	Fe	Co	Ni	Cu
	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Solution:

Concept:

- The standard reduction potential $E_{M^{2+}/M}^\circ$ measures the tendency of $M^{2+}(aq)$ to gain two electrons and form $M(s)$. Its value depends on the overall free-energy change, not on electronic configuration alone.
- Conversion of a metal to its aqueous divalent ion involves atomisation, the first two ionisations and hydration of M^{2+} . The competing energy contributions vary across the series.
- Permanganate is reduced to Mn^{2+} in acidic medium and to MnO_2 in neutral or alkaline medium; the oxidation product of iodide also depends on the medium.

Step 1: (i)(I) Explain the irregular trend For the oxidation process $M(s) \rightarrow M^{2+}(aq) + 2e^-$, atomisation and ionisation require energy, while hydration releases energy. The enthalpies of atomisation, the sum of the first and second ionisation enthalpies, and the hydration enthalpies do not vary regularly across the 3d series. Their combined effect therefore produces an irregular trend in the reverse reduction potentials. The extra stability of particular d-electron configurations also affects these contributions; counting d electrons alone cannot predict the tabulated potentials.

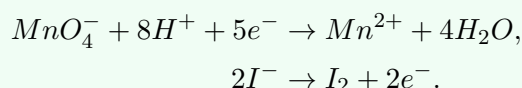
Step 2: (i)(II) Explain the positive copper potential Copper has a high energy requirement for atomisation and ionisation to Cu^{2+} . The hydration enthalpy of Cu^{2+} does not compensate for this

Quick Tip to Solve: Before balancing permanganate with iodide, choose both products: acid gives Mn^{2+} and I_2 , while alkali gives MnO_2 and IO_3^- .

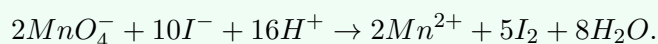
requirement. Hence oxidation of copper metal to aqueous Cu^{2+} is unfavourable under standard conditions, whereas the reverse reduction is favourable. This accounts for the exceptionally positive value $E_{Cu^{2+}/Cu}^{\circ} = +0.34\text{ V}$.

Step 3: (i)(III) Explain the negative manganese potential The ion Mn^{2+} has the particularly stable half-filled configuration $[Ar]3d^5$. Formation of this stable aqueous divalent ion is favoured, and its reduction back to manganese metal is relatively difficult. Thus $E_{Mn^{2+}/Mn}^{\circ}$ is highly negative, with the given value -1.18 V . The sign describes the reduction tendency of the ion, not the oxidation tendency of the metal.

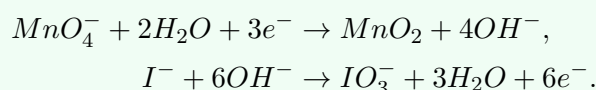
Step 4: (ii) Write the equation in acidic solution Iodide is oxidised to iodine while permanganate is reduced to Mn^{2+} . The half-reactions are



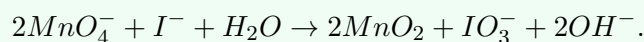
Multiplying the first by two and the second by five cancels ten electrons, giving



Step 5: (ii) Write the equation in alkaline solution In alkaline solution, iodide is oxidised to iodate, IO_3^- , and permanganate forms manganese dioxide. The half-reactions are



Doubling the first equation and adding gives



Both equations conserve atoms and total charge. In the alkaline equation each of the two manganese atoms gains three electrons, matching the six electrons lost by iodine.

Step 6: Conclusion The irregular potentials arise from competing atomisation, ionisation and hydration contributions. Copper has a positive potential because its oxidation energy is not compensated by hydration; manganese has a negative potential because Mn^{2+} is stabilised by $3d^5$. Permanganate converts iodide to I_2 in acid and IO_3^- in alkaline solution, according to the balanced equations above.

Quick Tip to Solve: Before balancing permanganate with iodide, choose both products: acid gives Mn^{2+} and I_2 , while alkali gives MnO_2 and IO_3^- .

31(b). Answer the following questions:

(i) Name a member of the lanthanoid series

(I) which exhibits +4 oxidation state

(II) which exhibits +2 oxidation state.

(ii) Why transition metals act as good catalyst?

(iii) Why Cr has higher melting point than Mn?

(iv) What happens when acidic solution of potassium permanganate is allowed to stand for sometime? Give the equation involved. What is this type of reaction called?

[5 marks]

Solution:

Concept:

- Lanthanoids mainly exhibit the +3 oxidation state. Additional states can be stabilised by empty, half-filled or completely filled $4f$ subshells.
- Transition metals catalyse reactions through variable oxidation states, intermediate formation and adsorption of reactants on metal surfaces.
- Metallic bond strength depends on the participation of valence electrons in bonding. Melting points reflect this bonding strength.
- In a redox reaction oxidation numbers increase and decrease. Disproportionation requires the same element in one initial oxidation state to undergo both oxidation and reduction.

Step 1: (i) Identify the lanthanoids and their stable configurations (I) Cerium, Ce , exhibits the +4 oxidation state. The ion Ce^{4+} has the stable configuration $[Xe]4f^0$, with an empty $4f$ subshell.

(II) Europium, Eu , exhibits the +2 oxidation state. Its ion Eu^{2+} has the stable half-filled configuration $[Xe]4f^7$. Thus cerium and europium provide the required examples for +4 and +2, respectively.

Step 2: (ii) Explain transition-metal catalysis Transition metals can adopt more than one oxidation state because the energies of their ns and $(n-1)d$ electrons are comparable. They can therefore form intermediate compounds with reactants and participate in successive electron-transfer steps, returning to their original state at the end of the catalytic cycle. This supplies an alternative reaction pathway with a lower activation energy.

In heterogeneous catalysis, their surfaces also adsorb reactant molecules. Adsorption brings reactants close together and weakens bonds that must break, making reaction easier. These variable oxidation states and surface interactions account for their effectiveness as catalysts.

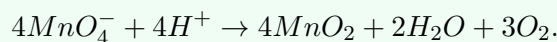
Step 3: (iii) Compare the melting points of chromium and manganese Chromium has the electronic configuration $[Ar]3d^54s^1$, whereas manganese has $[Ar]3d^54s^2$. Chromium has six unpaired valence electrons, while manganese has five and a paired $4s$ subshell. Chromium consequently has stronger metallic bonding through greater participation of its unpaired valence electrons.

Manganese has unusually weak metallic bonding relative to chromium because its stable half-filled $3d^5$ configuration restricts the participation of these electrons in bonding. More energy is needed to overcome the metallic bonding in chromium, so its melting point is higher than that of manganese.

Step 4: (iv) Describe the change on standing and write the equation On standing, an acidic solution

Quick Tip to Solve: For the standing acidic permanganate solution, track both Mn and O oxidation numbers: different elements change, so classify it as internal redox decomposition.

of potassium permanganate slowly decomposes: brown manganese dioxide is formed and oxygen gas is liberated. The purple permanganate colour fades as MnO_4^- is consumed. The balanced ionic equation is



There are four manganese atoms, sixteen oxygen atoms and four hydrogen atoms on each side, and the net charge is zero on both sides. The potassium ions are spectators and do not appear in the net ionic equation.

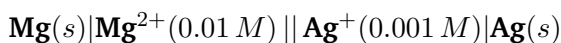
Step 5: (iv) Classify the reaction using oxidation numbers Manganese changes from +7 in permanganate to +4 in MnO_2 , so it is reduced. Oxygen changes from -2 to 0 in the liberated O_2 , so it is oxidised. Four manganese atoms gain a total of twelve electrons, matching the twelve electrons lost in forming three oxygen molecules. The reaction is therefore a redox decomposition, also called self-oxidation-reduction or an internal redox reaction.

It is not disproportionation: manganese is only reduced, and the element oxidised is oxygen. Disproportionation would require the same element to form products both above and below its original oxidation state.

Step 6: Conclusion (i) *Ce* exhibits +4, and *Eu* exhibits +2. (ii) Variable oxidation states, intermediate formation and adsorption explain transition-metal catalysis. (iii) Stronger metallic bonding gives chromium a higher melting point than manganese. (iv) Acidic permanganate slowly yields MnO_2 and O_2 through the redox decomposition $4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 2H_2O + 3O_2$.

Quick Tip to Solve: For the standing acidic permanganate solution, track both Mn and O oxidation numbers: different elements change, so classify it as internal redox decomposition.

32(a). Calculate emf and ΔG for the following cell at 298 K:



Given: $E_{Mg^{2+}/Mg}^\circ = -2.37 V$, $E_{Ag^+/Ag}^\circ = +0.80 V$

[1 F = 96500 C mol⁻¹, log 10 = 1]

[5 marks]

Solution:

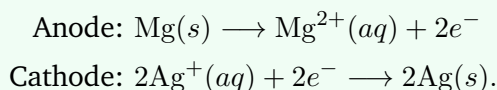
Concept:

- The standard cell potential is $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$, where both tabulated values are reduction potentials. The electrode with the higher reduction potential undergoes reduction.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E_{\text{cell}}^\circ - (0.0591/n) \log Q$, where n is the number of electrons transferred and Q is the reaction quotient. Pure solids have unit activity.
- The Gibbs energy change for the reaction under the stated conditions is $\Delta G = -nFE_{\text{cell}}$, with $F = 96500 \text{ C mol}^{-1}$. Use the actual emf here because the ion concentrations are not standard.

Step 1: Identify the electrodes and balance the cell reaction Silver has the more positive reduction

Quick Tip to Solve: Balance the silver half-reaction first: it fixes both $n = 2$ and the square on the silver-ion concentration in Q .

potential and is the cathode. Magnesium is oxidised at the anode. The two half-reactions are



Adding them gives $\text{Mg}(s) + 2\text{Ag}^{+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + 2\text{Ag}(s)$. Thus $n = 2$; multiplying the silver half-reaction by two balances electrons but does not multiply its electrode potential.

Step 2: Calculate the standard potential and reaction quotient Using the supplied reduction potentials,

$$E_{\text{cell}}^{\circ} = 0.80 - (-2.37) = 3.17 \text{ V}.$$

Concentrations enter with powers equal to their coefficients in the balanced equation. Therefore

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Ag}^{+}]^2} = \frac{0.01}{(0.001)^2} = 10^4, \quad \log Q = 4.$$

Neither solid metal appears in this quotient. In particular, the silver concentration must be squared, since two silver ions are consumed per magnesium atom.

Step 3: Apply the Nernst equation at the stated concentrations Substituting $n = 2$ and $\log Q = 4$,

$$\begin{aligned}E_{\text{cell}} &= 3.17 - \frac{0.0591}{2}(4) \\ &= 3.17 - 0.1182 = 3.0518 \text{ V}.\end{aligned}$$

Since $Q > 1$, the logarithmic correction lowers the potential from its standard value. This agrees with the very small silver-ion concentration, which reduces the tendency for cathodic reduction relative to standard conditions.

Step 4: Obtain the Gibbs energy change The reaction transfers two moles of electrons per mole of reaction as written. Hence

$$\begin{aligned}\Delta G &= -2(96500)(3.0518) \\ &= -589,997.4 \text{ J mol}^{-1} \\ &\simeq -590.0 \text{ kJ mol}^{-1}.\end{aligned}$$

The negative sign follows from the positive cell potential and indicates that the forward cell reaction is spontaneous under the supplied conditions. Using E° instead would give ΔG° , which is a different quantity.

Step 5: Conclusion At 298 K, the results for the balanced reaction are

$$\boxed{E_{\text{cell}} \simeq 3.052 \text{ V}}, \quad \boxed{\Delta G \simeq -590.0 \text{ kJ mol}^{-1}}.$$

Quick Tip to Solve: Balance the silver half-reaction first: it fixes both $n = 2$ and the square on the silver-ion concentration in Q .

32(b). For the reaction:



Calculate emf of the cell at 25 °C.

Given: $\Delta G^\circ = -43500 \text{ J mol}^{-1}$

[log 10 = 1, 1 F = 96500 C mol⁻¹]

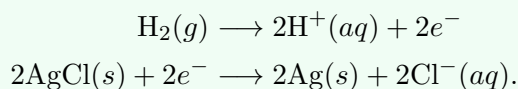
[5 marks]

Solution:

Concept:

- Standard Gibbs energy and standard cell potential are related by $\Delta G^\circ = -nFE_{\text{cell}}^\circ$, where n is the number of electrons transferred per reaction as written and F is the Faraday constant.
- For a reaction at 25 °C, $E_{\text{cell}} = E_{\text{cell}}^\circ - (0.0591/n) \log Q$. The reaction quotient includes dissolved ions and gas pressure, each raised to its stoichiometric coefficient; pure solids have unit activity.
- In the usual dilute-solution approximation, ion activities are represented by their molar concentrations divided by the standard concentration, and gas activity by pressure divided by the standard pressure used for the supplied data.

Step 1: Determine the number of transferred electrons Hydrogen is oxidised, while silver in silver chloride is reduced to metallic silver. The half-reactions are



Their sum is the reaction printed in the question, so $n = 2$. Each silver atom accepts one electron, and there are two silver atoms in the balanced overall equation. This electron count must match the reaction to which the supplied ΔG° refers.

Step 2: Calculate the standard cell potential Rearrange the thermodynamic relation and substitute the supplied values:

$$\begin{aligned}E_{\text{cell}}^\circ &= -\frac{\Delta G^\circ}{nF} \\ &= -\frac{-43500}{2(96500)} \\ &= 0.22539 \text{ V}.\end{aligned}$$

The negative standard Gibbs energy thus gives a positive standard potential. This potential applies to standard activities; the stated concentrations and hydrogen pressure require a Nernst correction before obtaining the requested emf.

Step 3: Form the quotient for the printed forward reaction Silver chloride and metallic silver are pure solids and are omitted from Q . Hydrogen is a reactant, so its pressure appears in the denominator.

Quick Tip to Solve: Omit both solids from Q , square each product-ion concentration, and divide by hydrogen pressure before taking the logarithm.

Both hydrogen-ion and chloride-ion concentrations are squared:

$$\begin{aligned} Q &= \frac{[\text{H}^+]^2[\text{Cl}^-]^2}{p_{\text{H}_2}} \\ &= \frac{(0.1)^2(0.2)^2}{0.4} \\ &= \frac{0.0004}{0.4} = 0.001 = 10^{-3}. \end{aligned}$$

Here the numerical pressure is relative to 1 atm, consistent with the pressure given in the question. Thus $\log Q = -3$, directly using $\log 10 = 1$; no logarithm of 2 is required.

Step 4: Calculate the emf at the given conditions At 25 °C, substitution into the Nernst equation gives

$$\begin{aligned} E_{\text{cell}} &= 0.22539 - \frac{0.0591}{2}(-3) \\ &= 0.22539 + 0.08865 \\ &= 0.31404 \text{ V}. \end{aligned}$$

Since $Q < 1$, the logarithm is negative and the correction increases the emf above its standard value. The relatively low activities of the ionic products favour the forward reaction, which is consistent with this increase and provides a useful sign check.

Step 5: Conclusion The emf of the cell at 25 °C under the stated conditions is $E_{\text{cell}} \simeq 0.314 \text{ V}$.

Quick Tip to Solve: Omit both solids from Q , square each product-ion concentration, and divide by hydrogen pressure before taking the logarithm.

33(a). (i) An organic compound (X) has the molecular formula $\text{C}_5\text{H}_{10}\text{O}$. Draw structures for (X) if it:

(I) does not give Tollen's test but gives a positive iodoform test.

(II) does not give Tollen's test and iodoform test but undergoes Aldol condensation.

(III) undergoes Cannizzaro's reaction.

(ii) Show how each of the following compounds can be converted to benzoic acid:

(I) Acetophenone (II) Ethyl benzene

[5 marks]

Solution:

Concept:

- Tollens' reagent oxidises aldehydes, giving a silver mirror; ordinary ketones do not respond. The iodoform test identifies the methyl ketone group, $\text{CH}_3\text{CO}-$.
- Aldol condensation requires at least one hydrogen on a carbon adjacent to the carbonyl carbon (an α -hydrogen). An aldehyde lacking α -hydrogens undergoes Cannizzaro disproportionation in concentrated alkali.
- A methyl ketone gives a carboxylate in the haloform reaction. An alkylbenzene with a benzylic hydrogen gives benzoate on strong oxidation; acidification gives benzoic acid.

Step 1: (i)(I) Identify the methyl ketones Absence of Tollens' reaction excludes an aldehyde, while the

Quick Tip to Solve: Locate the carbon directly beside the carbonyl: a methyl there gives iodoform, a hydrogen there permits aldol, and no hydrogen there allows an aldehyde to undergo Cannizzaro reaction.

positive iodoform test requires $\text{CH}_3\text{CO}-\text{R}$. For $\text{C}_5\text{H}_{10}\text{O}$, the remaining group R is C_3H_7 , which can be straight or branched. Thus both pentan-2-one, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_3$, and 3-methylbutan-2-one, $\text{CH}_3\text{COCH}(\text{CH}_3)_2$, meet the conditions. Each contains the methyl ketone group and gives yellow CHI_3 with iodine and alkali.

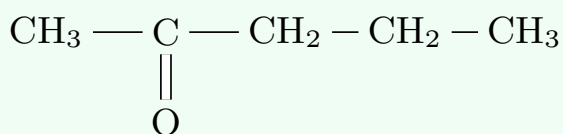
Step 2: (i)(II) Identify a non-methyl ketone with alpha-hydrogens Pentan-3-one, $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$, is a ketone, so it gives no silver mirror. Neither group directly bonded to the carbonyl carbon is a methyl group, so the iodoform test is negative. Both adjacent CH_2 groups carry α -hydrogens, enabling enolate formation and hence aldol condensation. The distinction is the group directly attached to CO , not the presence of terminal methyl groups elsewhere in the molecule.

Step 3: (i)(III) Identify an aldehyde without alpha-hydrogens Choose 2,2-dimethylpropanal, $(\text{CH}_3)_3\text{CCHO}$. Its carbon adjacent to CHO is bonded to three methyl groups and the aldehyde carbon; it has no hydrogen. Consequently it undergoes Cannizzaro reaction rather than aldol condensation:

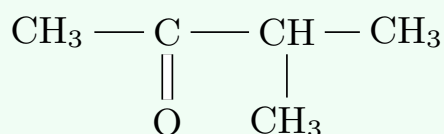


One aldehyde molecule is reduced to the alcohol while the other is oxidised to the carboxylate. The formula contains five carbons, ten hydrogens and one oxygen as required.

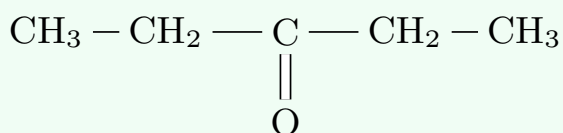
(I) Pentan-2-one



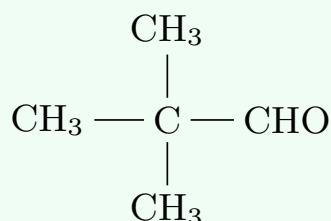
(I) 3-Methylbutan-2-one



(II) Pentan-3-one

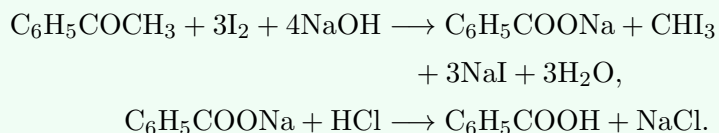


(III) 2,2-Dimethylpropanal



Structural formulae satisfying the three sets of tests; both alternatives in (I) are valid.

Step 4: (ii)(I) Convert acetophenone by the haloform reaction Treat acetophenone with iodine in aqueous sodium hydroxide, then acidify the sodium benzoate formed with dilute hydrochloric acid:

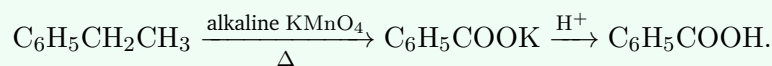


The methyl carbon leaves as iodoform, and the carbonyl carbon becomes the carboxyl carbon of benzoic acid.

Step 5: (ii)(II) Oxidise the ethyl side chain Heat ethylbenzene with alkaline potassium permanganate

Quick Tip to Solve: Locate the carbon directly beside the carbonyl: a methyl there gives iodoform, a hydrogen there permits aldol, and no hydrogen there allows an aldehyde to undergo Cannizzaro reaction.

and then acidify. The benzylic CH_2 group has hydrogens, allowing oxidation of the side chain to the benzoate group. The second side-chain carbon is removed during strong oxidation:



Step 6: Conclusion (i) (I) Pentan-2-one or 3-methylbutan-2-one; (II) pentan-3-one; (III) 2,2-dimethylpropanal. (ii) Acetophenone gives benzoic acid by I_2/NaOH followed by acidification; ethylbenzene gives it by hot alkaline KMnO_4 followed by acidification.

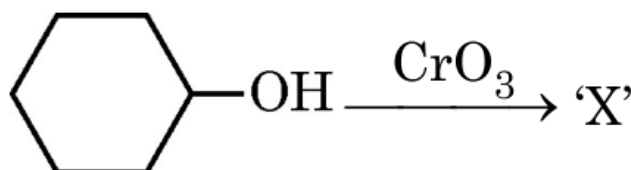
Quick Tip to Solve: Locate the carbon directly beside the carbonyl: a methyl there gives iodoform, a hydrogen there permits aldol, and no hydrogen there allows an aldehyde to undergo Cannizzaro reaction.

OR

33(b). Answer the following questions:

- Draw structure of the 2,4-dinitrophenyl hydrazone derivative of benzaldehyde.
- Arrange the following in increasing order of their reactivity towards HCN : Di-tert. butyl ketone, Acetaldehyde, Acetone.
- Give a simple chemical test to distinguish between benzoic acid and ethyl benzoate.
- Write the name of the reagent to convert Ethanenitrile to Ethanal.
- Draw the structure of 'X' in the following reaction:

[5 marks]



Solution:

Concept:

- Aldehydes and ketones condense with 2,4-dinitrophenylhydrazine to give hydrazones: the carbonyl oxygen is replaced by $=\text{N}-\text{NH}-\text{Ar}$, where Ar is the 2,4-dinitrophenyl group.
- Nucleophilic addition to a carbonyl group is favoured by low steric hindrance and a strongly electrophilic carbonyl carbon. Alkyl groups reduce electrophilicity through their electron-releasing effect.
- Carboxylic acids liberate carbon dioxide from aqueous sodium hydrogen carbonate; esters do not. Controlled reduction of a nitrile followed by hydrolysis gives an aldehyde, while oxidation of a secondary alcohol gives a ketone.

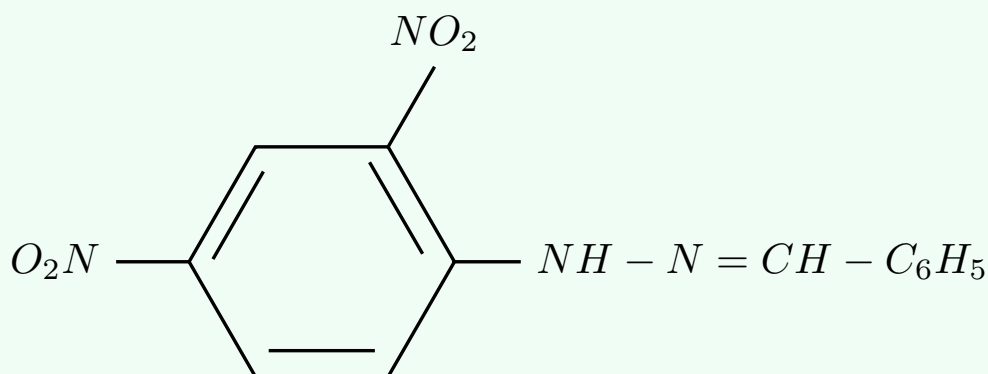
Step 1: (i) Form the benzaldehyde hydrazone Benzaldehyde, $\text{C}_6\text{H}_5\text{CHO}$, reacts with the terminal $-\text{NH}_2$ group of 2,4-dinitrophenylhydrazine. Condensation eliminates one molecule of water and

Quick Tip to Solve: In a hydrazone, keep the linkage in the order $\text{C}=\text{N}-\text{NH}-\text{Ar}$; for HCN addition, compare both the size and the number of alkyl groups attached to the carbonyl carbon.

gives



On the dinitrophenyl ring, the nitro groups occupy positions 2 and 4 relative to the carbon attached to $-NH-$. The required structure is shown below; C_6H_5 denotes the phenyl group of benzaldehyde.

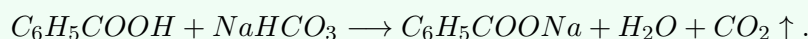


Benzaldehyde 2,4-dinitrophenylhydrazone

Step 2: (ii) Compare reactivity towards HCN The nucleophile CN^- attacks the carbonyl carbon. Di-tert-butyl ketone has two bulky tert-butyl groups that hinder attack and also donate electron density. Acetone has smaller methyl groups and is therefore more reactive. Acetaldehyde has only one alkyl group and one hydrogen, so it has the least steric hindrance and greater carbonyl electrophilicity. Thus the increasing order is

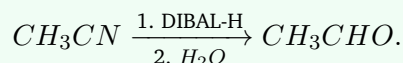


Step 3: (iii) Use the sodium hydrogen carbonate test Add aqueous $NaHCO_3$ separately to the two compounds. Benzoic acid gives brisk effervescence of CO_2 , which turns limewater milky. The reaction is



Ethyl benzoate gives no effervescence under these test conditions because it is an ester and does not possess the acidic carboxyl hydrogen.

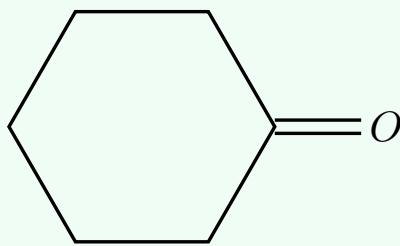
Step 4: (iv) Reduce ethanenitrile selectively Use diisobutylaluminium hydride (DIBAL-H), followed by hydrolysis. Controlled reduction of the nitrile group and subsequent hydrolysis produce ethanal:



Stephen reduction using stannous chloride and hydrochloric acid, followed by hydrolysis, is also a suitable conversion. A strong reducing agent such as $LiAlH_4$ would instead reduce the nitrile to a primary amine.

Step 5: (v) Identify the oxidation product The printed starting compound is cyclohexanol, a secondary alcohol. Chromium trioxide, CrO_3 , oxidises its $-CH(OH)-$ group to $>C=O$ without changing the six-membered carbon skeleton. Therefore X is cyclohexanone, whose structure is shown below. The carbonyl carbon is itself one of the six ring atoms; the oxygen is outside the ring.

Quick Tip to Solve: In a hydrazone, keep the linkage in the order $C=N-NH-Ar$; for HCN addition, compare both the size and the number of alkyl groups attached to the carbonyl carbon.



Cyclohexanone, the product X

Step 6: Conclusion (i) Benzaldehyde 2,4-dinitrophenylhydrazone: $C_6H_5CH = N - NH - C_6H_3(NO_2)_2$, with nitro groups at positions 2 and 4. (ii) Di-tert-butyl ketone < acetone < acetaldehyde. (iii) Aqueous $NaHCO_3$ gives CO_2 effervescence with benzoic acid only. (iv) DIBAL-H followed by hydrolysis. (v) *X* is cyclohexanone.

Quick Tip to Solve: In a hydrazone, keep the linkage in the order $C=N-NH-Ar$; for HCN addition, compare both the size and the number of alkyl groups attached to the carbonyl carbon.