

CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-5-3

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) Question paper is divided into **FIVE** sections – **Section A, B, C, D and E**.
- (iii) **Section A** – question number **1 to 16** are multiple choice type questions. Each question carries **1** mark.
- (iv) **Section B** – question number **17 to 21** are very short answer type questions. Each question carries **2** marks.
- (v) **Section C** – question number **22 to 28** are short answer type questions. Each question carries **3** marks.
- (vi) **Section D** – question number **29 and 30** are case-based questions. Each question carries **4** marks.
- (vii) **Section E** – question 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)

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

1. Van't Hoff factor for K_2SO_4 solution, assuming complete ionization is

[1 mark]

- (A) 1
- (B) 3
- (C) 13
- (D) 2

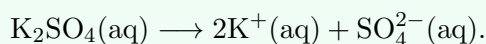
Correct Answer: (B) 3

Solution:

Concept:

- The van't Hoff factor i is the ratio of the number of solute particles after dissociation to the number of formula units initially dissolved.
- Complete ionisation means all ions in the dissociation equation contribute independently to the particle count.

Step 1: Write the dissociation equation Potassium sulphate dissociates completely in water as



One formula unit supplies two potassium ions and one sulphate ion.

Step 2: Count particles and compare options The particle count is therefore $2 + 1 = 3$, so $i = 3/1 = 3$. Option (A), 1, would describe an undissociated solute. Option (D), 2, counts ionic species instead of the total ions. Option (C), 13, has no basis in the dissociation stoichiometry; the ionic charges are not added to obtain i .

Step 3: Conclusion The van't Hoff factor is $i = 3$. Hence, the correct option is (B).

Quick Tip to Solve: Count the coefficients of all product ions, not the number of different ionic species.

2. Dilution affects both conductivity as well as molar conductivity. Effect of dilution on both is as follows:

[1 mark]

- (A) both increase with dilution.
- (B) both decrease with dilution.
- (C) conductivity increases whereas molar conductivity decreases on dilution.
- (D) conductivity decreases whereas molar conductivity increases on dilution.

Correct Answer: (D) conductivity decreases whereas molar conductivity increases on dilution.

Solution:

Concept:

- Conductivity κ measures the conductance of a solution of unit dimensions; it depends on the concentration of charge carriers per unit volume.

Quick Tip to Solve: For dilution, separate ions per unit volume from the conducting ability of one mole.

- Molar conductivity is $\Lambda_m = 1000\kappa/c$ when c is in mol L^{-1} ; it measures conducting ability per mole of electrolyte.

Step 1: Consider conductivity on dilution Adding water lowers the number of ions per unit volume. Consequently the conductivity κ decreases even though ionic movement becomes easier.

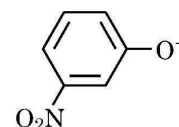
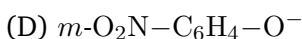
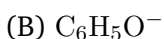
Step 2: Consider molar conductivity and eliminate options On dilution, interionic attractions weaken and ionic mobility increases; for weak electrolytes, the degree of ionisation also increases. Thus Λ_m increases. Options (A) and (C) wrongly predict increasing conductivity, while option (B) wrongly predicts decreasing molar conductivity. These quantities have different concentration dependences.

Step 3: Conclusion Conductivity decreases whereas molar conductivity increases on dilution. Hence, the correct option is (D).

Quick Tip to Solve: For dilution, separate ions per unit volume from the conducting ability of one mole.

3. Which of the following species can act as the strongest base?

[1 mark]



Correct Answer: (C) RO^-

Solution:

Concept:

- A base accepts a proton. A negative charge that is less stabilised is generally more available for proton acceptance.
- Alkyl groups exert a positive inductive effect, whereas resonance delocalisation and electron-withdrawing groups stabilise an anion and reduce its basicity.

Step 1: Compare alkoxide with hydroxide In RO^- , the electron-releasing alkyl group increases electron density on oxygen relative to OH^- . Alkoxide therefore has a greater tendency to accept H^+ and is the stronger base in the standard comparison.

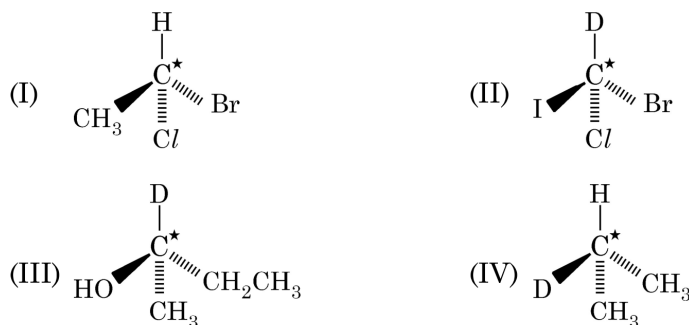
Step 2: Compare the aromatic anions In phenoxide, $\text{C}_6\text{H}_5\text{O}^-$, the negative charge is delocalised into the aromatic ring, stabilising the anion and decreasing its proton affinity. In the printed meta-nitrophenoxide, the nitro group withdraws electrons through its negative inductive effect and further lowers basicity. Thus neither option (B) nor (D) exceeds alkoxide; hydroxide in option (A) lacks the alkyl group's electron-releasing effect.

Step 3: Conclusion RO^- is the strongest base among these species. Hence, the correct option is (C).

Quick Tip to Solve: Look for electron donation to the charged oxygen; resonance stabilisation of an anion weakens its basicity.

4. In which of the following molecules, C atom marked with asterisk is chiral?

[1 mark]



- (A) I, II, III
(B) I, II, III, IV
(C) II, III, IV
(D) I, III, IV

Correct Answer: (A) I, II, III

Solution:

Concept:

- A tetrahedral carbon is a chiral centre when it is bonded to four different substituents.
- Isotopes count as different substituents: hydrogen H and deuterium D differ, but two identical methyl groups do not.

Step 1: Check structures I, II and III In I, the marked carbon is attached to H, CH₃, Br, Cl, all different. In II its groups are D, I, Br, Cl, also all different. In III the groups are D, OH, CH₃, CH₂CH₃; methyl and ethyl are different, so this carbon is chiral as well.

Step 2: Check structure IV and the combinations In IV, the carbon is attached to H, D, CH₃, CH₃. Although H and D differ, the two methyl groups are identical, so this centre is not chiral. Every combination in options (B), (C) and (D) contains IV and is therefore incorrect. Only option (A) contains all three chiral structures and excludes IV.

Step 3: Conclusion The marked carbon is chiral in I, II, III. Hence, the correct option is (A).

Quick Tip to Solve: List all four attached groups explicitly; two identical groups rule out chirality even when H and D differ.

5. The rate of a reaction increases sixteen times when the concentration of the reactant increases four times. The order of the reaction is [1 mark]

- (A) 2.5
- (B) 2.0
- (C) 1.5
- (D) 0.5

Correct Answer: (B) 2.0

Solution:

Concept:

- For a reaction with one varying reactant, $r = k[A]^n$, where n is the reaction order and k is constant at a fixed temperature.
- Taking a ratio of rates eliminates k : $r_2/r_1 = ([A]_2/[A]_1)^n$.

Step 1: Use the given rate and concentration ratios The concentration becomes four times its original value while the rate becomes sixteen times its original value. Therefore

$$16 = 4^n.$$

Since $16 = 4^2$, the exponent required by the experimental change is $n = 2$.

Step 2: Check the alternative orders For $n = 2.5$, the predicted rate multiplier is $4^{2.5} = 32$. For $n = 1.5$, it is $4^{1.5} = 8$, and for $n = 0.5$, it is $4^{0.5} = 2$. None matches sixteen. The order 2.0 alone gives $4^2 = 16$.

Step 3: Conclusion The reaction is second order: $n = 2.0$. Hence, the correct option is (B).

Quick Tip to Solve: Express the rate multiplier as a power of the concentration multiplier; that exponent is the order.

6. Which of the following cell is used in hearing aids? [1 mark]

- (A) Mercury cell
- (B) $H_2 - O_2$ fuel cell
- (C) Dry cell
- (D) Ni-Cd cell

Correct Answer: (A) Mercury cell

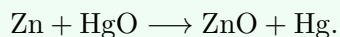
Solution:

Concept:

- A mercury cell is a compact primary cell that supplies an approximately constant potential of 1.35 V.
- Its electrode materials are zinc amalgam at the anode and mercuric oxide mixed with carbon at the cathode, with an alkaline electrolyte.

Quick Tip to Solve: Remember the association: small hearing aids require the compact mercury cell with nearly constant voltage.

Step 1: Identify the cell suited to the device Hearing aids need a small cell providing a steady potential. The mercury cell meets these requirements and is the standard cell associated with hearing aids in this question. Its overall reaction is



The overall reaction has no ions whose changing concentration would significantly alter the cell potential.

Step 2: Compare the other choices The hydrogen-oxygen fuel cell requires a continuous supply of gaseous reactants and is not the compact button-cell answer. A dry cell is conventionally used in devices such as torches, while the nickel-cadmium cell is a rechargeable secondary cell. Neither is the standard hearing-aid cell identified here.

Step 3: Conclusion The cell used in hearing aids is the mercury cell. Hence, the correct option is (A).

Quick Tip to Solve: Remember the association: small hearing aids require the compact mercury cell with nearly constant voltage.

7. Isotonic solutions have the same

[1 mark]

- (A) density
- (B) refractive index
- (C) osmotic pressure
- (D) volume

Correct Answer: (C) osmotic pressure

Solution:

Concept:

- Isotonic solutions have equal osmotic pressures at the same temperature. Osmotic pressure is the pressure needed to stop osmosis through a semipermeable membrane.
- For a dilute solution, $\pi = iCRT$, where i is the van't Hoff factor, C is molar concentration, R is the gas constant and T is absolute temperature.

Step 1: Apply the definition Two solutions are isotonic when their osmotic pressures are equal at the same temperature. A semipermeable membrane separating them therefore shows no net solvent transfer due to an osmotic-pressure difference.

Step 2: Check the alternatives Density and refractive index depend on the nature of the substances, so equality of osmotic pressure does not require equal values of either property. Volume is an extensive quantity and can be varied without changing the osmotic pressure of a solution of fixed concentration.

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

Quick Tip to Solve: Use the definition of isotonic: compare osmotic pressure at the same temperature, not solution volume.

8. Transition metals are known to make interstitial compounds. Formation of interstitial compounds makes the transition metal [1 mark]

- (A) more hard
- (B) more soft
- (C) more ductile
- (D) more metallic

Correct Answer: (A) more hard

Solution:

Concept:

- Interstitial compounds form when small atoms such as hydrogen, carbon or nitrogen occupy spaces between metal atoms in a crystal lattice.
- These compounds retain metallic conductivity but are generally harder and less ductile than the parent metal.

Step 1: Relate the structure to hardness Small atoms in the interstitial spaces restrict the movement of layers of metal atoms and hinder deformation of the lattice. The resulting material resists scratching and deformation more strongly than the pure metal.

Step 2: Eliminate the other properties The increased resistance to deformation means greater hardness, rather than greater softness or ductility. Metallic character is retained, but formation of an interstitial compound is not described as making the metal more metallic.

Step 3: Conclusion Formation of interstitial compounds makes the transition metal more hard. Hence, the correct option is (A).

Quick Tip to Solve: When small atoms enter metal-lattice gaps, connect restricted layer movement with increased hardness.

9. Auto-oxidation of chloroform in air and light produces a poisonous gas known as [1 mark]

- (A) Phosphine
- (B) Mustard gas
- (C) Phosgene
- (D) Tear gas

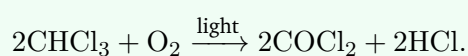
Correct Answer: (C) Phosgene

Solution:

Concept:

- Chloroform, CHCl_3 , is slowly oxidised by atmospheric oxygen in the presence of light.
- The toxic oxidation product is carbonyl chloride, COCl_2 , whose common name is phosgene.

Step 1: Write the oxidation reaction The balanced reaction is



Quick Tip to Solve: Remember the chloroform oxidation product as carbonyl chloride: its common name is phosgene.

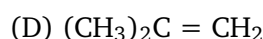
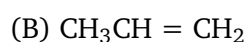
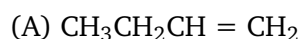
The carbonyl chloride formed in this reaction is the poisonous gas named in the question.

Step 2: Identify the gas among the options Phosphine is PH_3 , so it is unrelated to this oxidation. Mustard gas is a different sulfur-containing compound. Tear gas describes lachrymatory agents rather than the carbonyl chloride produced here.

Step 3: Conclusion The poisonous gas is phosgene, COCl_2 . Hence, the correct option is (C).

Quick Tip to Solve: Remember the chloroform oxidation product as carbonyl chloride: its common name is phosgene.

10. Out of the following alkenes, the one which will produce tertiary butyl alcohol on acid catalysed hydration is [1 mark]



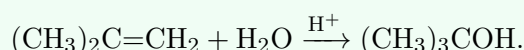
Correct Answer: (D) $(\text{CH}_3)_2\text{C}=\text{CH}_2$

Solution:

Concept:

- Acid-catalysed hydration adds hydrogen and hydroxyl across an alkene double bond according to Markovnikov's rule.
- Tertiary butyl alcohol is 2-methylpropan-2-ol, $(\text{CH}_3)_3\text{COH}$; its hydroxyl-bearing carbon is bonded to three carbon atoms.

Step 1: Hydrate the branched alkene For 2-methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, protonation occurs at the terminal carbon to give the tertiary carbocation $(\text{CH}_3)_3\text{C}^+$. Water attacks this carbocation, and loss of a proton gives



Step 2: Test the remaining alkenes But-1-ene in (A) and but-2-ene in (C) yield butan-2-ol under ordinary acid-catalysed hydration. Propene in (B) yields propan-2-ol and has only three carbon atoms. These products are secondary alcohols, whereas the branched alkene in (D) gives the required tertiary alcohol.

Step 3: Conclusion The required alkene is $(\text{CH}_3)_2\text{C}=\text{CH}_2$, 2-methylpropene. Hence, the correct option is (D).

Quick Tip to Solve: Work backwards from tert-butyl alcohol: remove OH and a hydrogen to recover 2-methylpropene.

11. The correct name of the given reaction is



[1 mark]

- (A) Sandmeyer's reaction
- (B) Gabriel Phthalimide synthesis
- (C) Carbyl amine reaction
- (D) Hoffmann bromamide degradation reaction

Correct Answer: (A) Sandmeyer's reaction

Solution:

Concept:

- In the Sandmeyer reaction, an aromatic diazonium group is replaced by chloride, bromide or cyanide using the appropriate copper(I) salt.
- The diazonium group leaves as nitrogen gas; Ar represents an aryl group.

Step 1: Identify the functional-group replacement The given reaction replaces $-\text{N}_2^+$ of an aryl diazonium salt with $-\text{CN}$, using CuCN/KCN , and releases N_2 . Copper(I) cyanide-mediated replacement of the diazonium group is characteristic of the Sandmeyer reaction.

Step 2: Distinguish the other named reactions Gabriel phthalimide synthesis prepares primary amines from suitable alkyl halides. The carbylamine reaction converts primary amines into isocyanides. Hofmann bromamide degradation converts an amide into an amine with one fewer carbon atom. None describes the diazonium-to-nitrile conversion shown.

Step 3: Conclusion The given reaction is Sandmeyer's reaction. Hence, the correct option is (A).

Quick Tip to Solve: Spot a diazonium salt with a copper(I) reagent: replacement by CN, Cl or Br identifies Sandmeyer.

12. The specific sequence in which amino acids are arranged in a protein is called its

[1 mark]

- (A) Primary structure
- (B) Secondary structure
- (C) Tertiary structure
- (D) Quaternary structure

Correct Answer: (A) Primary structure

Solution:

Concept:

- The primary structure of a protein is the specific linear sequence of amino-acid residues joined by peptide bonds.
- Secondary, tertiary and quaternary structures describe progressively larger aspects of folding and

Quick Tip to Solve: Sequence means primary structure; local folding, overall folding and subunit assembly name the higher levels.

subunit arrangement.

Step 1: Identify the level described The question asks for the order in which amino acids occur in a protein chain. This is the amino-acid sequence, which defines its primary structure; changing the order changes the primary structure even if the amino-acid composition is unchanged.

Step 2: Compare the other structural levels Secondary structure refers to local folding patterns such as an alpha helix or beta-pleated sheet. Tertiary structure is the overall three-dimensional folding of one polypeptide chain. Quaternary structure describes the arrangement of multiple polypeptide subunits. These describe spatial organisation rather than the residue sequence.

Step 3: Conclusion The specific amino-acid sequence is the primary structure. Hence, the correct option is (A).

Quick Tip to Solve: Sequence means primary structure; local folding, overall folding and subunit assembly name the higher levels.

13. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): The units of rate constant of a zero order reaction and rate of reaction are the same.

Reason (R): In zero order reaction, the rate of reaction is independent of the concentration of reactants. [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 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:

- The rate law is $r = k[A]^n$, where r is the reaction rate, k is the rate constant and n is the reaction order.
- A zero order reaction has $n = 0$, so its rate is independent of reactant concentration.

Step 1: Judge the Assertion For zero order, $r = k[A]^0 = k$. Rate has units of concentration per unit time, conventionally $\text{mol L}^{-1} \text{s}^{-1}$. Since rate equals the rate constant, k has exactly the same units. Assertion (A) is true.

Step 2: Judge the Reason The zero exponent makes the concentration factor unity. Thus changing $[A]$ does not change the rate within the conditions where the zero order law applies. Reason (R) is true.

Step 3: Connect the statements The concentration independence expressed by R gives $r = k$, which directly establishes equal units. Therefore R explains A; the option claiming no explanatory connection is incorrect, and options calling either statement false are also incorrect.

Quick Tip to Solve: For units of a zero order rate constant, first write $r = k$; no concentration factor remains.

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 units of a zero order rate constant, first write $r = k$; no concentration factor remains.

14. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): Zr and Hf are of almost similar atomic radii.

Reason (R): This is due to the Lanthanoid contraction.

[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 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:

- Lanthanoid contraction is the gradual decrease in atomic and ionic size across the lanthanoids as nuclear charge increases.
- The $4f$ electrons shield nuclear charge poorly, increasing the effective attraction experienced by outer electrons.

Step 1: Judge the Assertion Zirconium (Zr) and hafnium (Hf) are members of the same group in the $4d$ and $5d$ series respectively. Their atomic radii are almost equal despite Hf having an additional principal shell. Hence Assertion (A) is true.

Step 2: Judge the Reason The lanthanoids occur before Hf. Across these elements, the added $4f$ electrons do not adequately screen the increasing nuclear charge, causing contraction. This contraction also influences the size of Hf. Thus Reason (R) is true.

Step 3: Check the explanation The contraction offsets the size increase expected on moving from Zr to Hf down the group. It therefore accounts for their nearly identical radii. Option (B) incorrectly denies this explanation; (C) and (D) incorrectly assign a false truth value to one statement.

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

Quick Tip to Solve: When comparing a $4d$ element with its $5d$ partner, check whether lanthanoid contraction offsets the extra shell.

15. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): *p*-methoxyphenol is a stronger acid than *m*-methoxyphenol.

Reason (R): Methoxy group exerts +R effect at both ortho and para position.

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

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

Solution:

Concept:

- Phenol acidity depends on the stability of the phenoxide ion formed by loss of H^+ .
- The methoxy group has an electron-withdrawing inductive effect ($-I$) and an electron-donating resonance effect ($+R$).

Step 1: Judge the Assertion At the para position, the methoxy group donates electron density by resonance into the phenoxide system. This destabilises the negatively charged conjugate base and reduces acidity. At meta, this direct resonance interaction with the phenoxide charge is absent, while the withdrawing inductive effect operates. Thus *p*-methoxyphenol is weaker, not stronger, than *m*-methoxyphenol. A is false.

Step 2: Judge the Reason The oxygen lone pair of $-OCH_3$ can donate into the aromatic ring. Its resonance donation increases electron density at the ortho and para positions. The statement about the $+R$ effect is therefore true.

Step 3: Select the truth combination The correct combination is false Assertion and true Reason. Options (A) and (B) require a true Assertion, while (C) additionally calls the true Reason false, so none of these fits.

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

Quick Tip to Solve: For methoxyphenols, compare conjugate-base stability: para resonance donation opposes acidity, while meta mainly shows induction.

16. Two statements are given – Assertion (A) and Reason (R). Select the correct option:

Assertion (A): Inversion of configuration is observed when 1-Bromobutane is hydrolysed.

Reason (R): The reaction is S_N2 and proceeds with the formation of transition state. [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 Assertion (A).
- (C) Assertion (A) is true, but Reason (R) is false.
- (D) Assertion (A) is false, but Reason (R) is true.

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

Solution:

Concept:

- An S_N2 substitution proceeds by backside attack in a single step through a transition state.
- An observable inversion of stereochemical configuration requires a stereogenic reacting carbon with distinguishable substituents.

Step 1: Judge the Assertion for the named substrate 1-Bromobutane is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$. The carbon bearing bromine is attached to two identical hydrogen atoms, so it is not a stereogenic centre. Hydrolysis gives $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, also with two hydrogens on that carbon. Consequently, no inversion of a distinguishable stereochemical configuration can be observed for this substrate. Assertion (A), as printed, is false.

Step 2: Judge the Reason For the primary haloalkane reacting with aqueous hydroxide, nucleophilic attack and loss of bromide occur together by S_N2 . Its transition state has partial bonds to the incoming hydroxide and departing bromide. Thus Reason (R) is true.

Step 3: Distinguish attack geometry from observable configuration Backside attack reverses the local arrangement, but the two identical hydrogens prevent this from being an observable configurational inversion. Applying the inversion rule for a chiral substrate to 1-bromobutane would incorrectly make A true. Options (A), (B) and (C) all require A to be true.

Step 4: Conclusion For the stated achiral 1-bromobutane, A is false and R is true. Hence, the correct option is (D).

Quick Tip to Solve: Before claiming observable inversion, inspect the reacting carbon: two identical hydrogens mean there is no stereogenic centre.

Section B (10 marks)

17(a)(i). Carry out the following conversions:

Nitrobenzene to Aniline

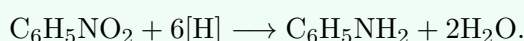
[1 mark]

Solution:

Concept:

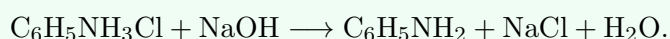
- An aromatic nitro group can be reduced to an amino group using tin and hydrochloric acid.
- In an acidic reduction mixture, aniline exists as its anilinium salt; alkali liberates the free amine.

Step 1: Reduce the nitro group Treat nitrobenzene with Sn/HCl and heat. The nitro group is reduced without changing the benzene ring. The overall reduction can be represented as



Here $[\text{H}]$ represents reducing equivalents supplied by the metal-acid system.

Step 2: Liberate aniline from the acidic mixture Because hydrochloric acid protonates the amino group, the initial product in the reaction mixture is anilinium chloride. Add aqueous NaOH after reduction to obtain free aniline:



This alkaline work-up is necessary when reporting the isolated free amine rather than its salt.

Step 3: Conclusion Convert nitrobenzene to aniline with Sn/HCl , followed by aqueous NaOH .

Quick Tip to Solve: For a metal-acid reduction of nitrobenzene, include alkaline work-up to release aniline from its ammonium salt.

17(a)(ii). Carry out the following conversions:

Aniline to Phenol

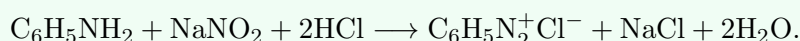
[1 mark]

Solution:

Concept:

- A primary aromatic amine undergoes diazotisation with nitrous acid generated in situ from NaNO_2/HCl .
- An aromatic diazonium salt gives phenol on warming with water, releasing nitrogen gas.

Step 1: Prepare benzene diazonium chloride Treat aniline with sodium nitrite and dilute hydrochloric acid at 273–278 K. The low temperature preserves the diazonium salt:

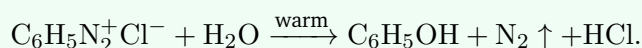


Nitrous acid is prepared in the reaction mixture because it is unstable.

Step 2: Hydrolyse the diazonium salt Warm the aqueous diazonium salt solution. The diazonium

Quick Tip to Solve: Keep diazotisation cold, then warm with water only after the diazonium salt has formed to obtain phenol.

group is replaced by hydroxyl, producing phenol:



Nitrogen gas evolves during this step. Direct treatment of aniline with water does not accomplish the conversion; diazotisation creates the group that can be replaced.

Step 3: Conclusion Aniline $\xrightarrow[273-278\text{ K}]{\text{NaNO}_2/\text{HCl}}$ benzene diazonium chloride $\xrightarrow{\text{H}_2\text{O, warm}}$ phenol.

Quick Tip to Solve: Keep diazotisation cold, then warm with water only after the diazonium salt has formed to obtain phenol.

OR

17(b)(i). Write a chemical test to distinguish between Dimethyl amine and Ethanamine. [1 mark]

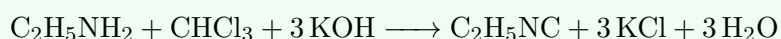
Solution:

Concept:

- The carbylamine test is given only by primary amines, which form foul-smelling isocyanides on heating with chloroform and alcoholic potassium hydroxide.
- Ethanamine, $\text{C}_2\text{H}_5\text{NH}_2$, is a primary amine; dimethylamine, $(\text{CH}_3)_2\text{NH}$, is a secondary amine.

Step 1: Identify the amine classes In ethanamine, one ethyl group is attached to nitrogen, whereas in dimethylamine two methyl groups are attached. Thus only ethanamine has the primary amino group required for the carbylamine reaction.

Step 2: Apply the carbylamine test Heat each sample separately with CHCl_3 and alcoholic KOH. Ethanamine produces a foul-smelling ethyl isocyanide, but dimethylamine gives no carbylamine reaction.



Step 3: Conclusion Ethanamine gives a positive carbylamine test (foul-smelling ethyl isocyanide); dimethylamine gives a negative test.

Quick Tip to Solve: Count the carbon groups attached to nitrogen: the carbylamine test distinguishes the primary ethanamine from secondary dimethylamine.

17(b)(ii). Write the product formed when benzene diazonium chloride is treated with KI. [1 mark]

Solution:

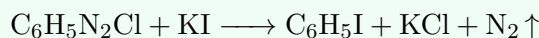
Concept:

- An aromatic diazonium group can be replaced by iodide when the diazonium salt is treated with potassium iodide.
- The stable nitrogen molecule, N_2 , is expelled during replacement of the diazonium group.

Quick Tip to Solve: For a diazonium salt treated with KI, replace the diazonium group by I and show nitrogen gas as a by-product.

Step 1: Replace the diazonium group Benzene diazonium chloride contains the group $-\text{N}_2^+$ attached to the benzene ring. On treatment with KI, this group is replaced by iodine, preserving the benzene ring.

Step 2: Write the reaction The substitution liberates nitrogen gas and produces potassium chloride as the accompanying salt:



This preparation of the iodo compound does not require a copper(I) salt.

Step 3: Conclusion The organic product is iodobenzene, $\text{C}_6\text{H}_5\text{I}$.

Quick Tip to Solve: For a diazonium salt treated with KI, replace the diazonium group by I and show nitrogen gas as a by-product.

18. Define the following terms:

(a) Limiting molar conductivity (Λ_m°)

(b) Fuel cell

[2 marks]

Solution:

Concept:

- Molar conductivity measures the conducting ability of the ions produced by one mole of electrolyte in solution.
- A galvanic cell converts the chemical energy of a spontaneous redox reaction directly into electrical energy.

Step 1: Define limiting molar conductivity Limiting molar conductivity, Λ_m° , is the molar conductivity of an electrolyte at infinite dilution, that is, as its concentration approaches zero:

$$\Lambda_m^\circ = \lim_{c \rightarrow 0} \Lambda_m.$$

At this limit, interactions between ions become negligible and each ion contributes independently to conduction. Its commonly used unit is $\text{S cm}^2 \text{mol}^{-1}$.

Step 2: Define a fuel cell A fuel cell is a galvanic cell in which the energy released by the continuous reaction of a supplied fuel and oxidant is converted directly into electrical energy. The reactants are fed continuously to the electrodes, allowing the cell to operate while the supply lasts. For example, a hydrogen-oxygen fuel cell uses H_2 and O_2 and forms water.

Step 3: Conclusion Λ_m° is molar conductivity at infinite dilution; a fuel cell converts the chemical energy of continuously supplied fuel and oxidant directly into electricity.

Quick Tip to Solve: Include both the infinite-dilution limit in the first definition and continuous reactant supply in the fuel-cell definition.

19. Classify the following sugars into monosaccharides and disaccharides:

Sucrose, Lactose, Glucose, Fructose

[2 marks]

Solution:

Concept:

- Monosaccharides are the simplest carbohydrates and cannot be hydrolysed to smaller carbohydrate units.
- Disaccharides contain two monosaccharide units joined by a glycosidic bond and yield those units on hydrolysis.

Step 1: Identify the monosaccharides Glucose and fructose each consist of a single sugar unit. They cannot be broken down into simpler carbohydrates by hydrolysis, so both are monosaccharides. Glucose is an aldohexose and fructose is a ketohexose; this functional-group difference does not change their classification as single sugar units.

Step 2: Identify the disaccharides Sucrose and lactose each contain two monosaccharide units joined by a glycosidic linkage. Hydrolysis of sucrose gives glucose and fructose, while hydrolysis of lactose gives glucose and galactose. Therefore, both are disaccharides. Classification here depends on the number of sugar units, rather than whether a sugar is reducing.

Step 3: Conclusion Monosaccharides: glucose and fructose. Disaccharides: sucrose and lactose.

Quick Tip to Solve: Recall the hydrolysis pairs: sucrose gives glucose plus fructose, and lactose gives glucose plus galactose; each pair identifies a disaccharide.

20. Resistance of a conductivity cell filled with 0.2 mol L^{-1} KCl solution is 200Ω . If the resistance of the same cell when filled with 0.05 mol L^{-1} KCl solution is 620Ω , calculate the conductivity and molar conductivity of 0.05 mol L^{-1} KCl solution. The conductivity of 0.2 mol L^{-1} KCl solution is 0.0248 S cm^{-1} .

[2 marks]

Solution:

Concept:

- Conductivity and resistance are related by $\kappa = K_{\text{cell}}/R$, where $K_{\text{cell}} = l/A$ is the cell constant.
- For κ in S cm^{-1} and concentration c in mol L^{-1} , molar conductivity is $\Lambda_m = 1000\kappa/c$.

Step 1: Determine the cell constant Using the known conductivity and resistance of the 0.2 mol L^{-1} solution,

$$K_{\text{cell}} = \kappa R = 0.0248 \times 200 = 4.96 \text{ cm}^{-1}.$$

The geometry is unchanged when the same cell is refilled, so this constant also applies to the dilute solution.

Step 2: Calculate conductivity of the dilute solution For the 0.05 mol L^{-1} solution, its measured resistance is 620Ω . Therefore,

$$\kappa = \frac{4.96}{620} = 0.00800 \text{ S cm}^{-1}.$$

The higher resistance is consistent with a lower conductivity.

Quick Tip to Solve: First find the fixed cell constant from the reference solution; retain the factor 1000 when concentration is in mol per litre.

Step 3: Calculate molar conductivity Convert the concentration from moles per litre to moles per cubic centimetre through the factor 1000:

$$\Lambda_m = \frac{1000 \times 0.00800}{0.05} = 160 \text{ S cm}^2 \text{ mol}^{-1}.$$

This quantity describes conduction per mole rather than conduction per unit volume.

Step 4: Conclusion The conductivity is $0.00800 \text{ S cm}^{-1}$, and the molar conductivity is $160 \text{ S cm}^2 \text{ mol}^{-1}$.

Quick Tip to Solve: First find the fixed cell constant from the reference solution; retain the factor 1000 when concentration is in mol per litre.

21. A first order reaction takes 40 min for 75% decomposition. Calculate rate constant.

[Given: $\log 2 = 0.30$, $\log 4 = 0.60$]

[2 marks]

Solution:

Concept:

- For a first order reaction, the rate is proportional to the concentration remaining: $-d[A]/dt = k[A]$, where k is the rate constant.
- The integrated rate equation is $k = (2.303/t) \log([A]_0/[A]_t)$, where $[A]_0$ and $[A]_t$ are initial and remaining concentrations.

Step 1: Find the fraction remaining Decomposition of 75% means that 25% of the original reactant remains after 40 min. If the initial concentration is a , the remaining concentration is $0.25a$. Hence $[A]_0/[A]_t = a/(0.25a) = 4$. The initial concentration cancels, so its numerical value is unnecessary. The integrated equation uses the reactant remaining, not the amount decomposed.

Step 2: Calculate the rate constant Using the given value $\log 4 = 0.60$,

$$k = \frac{2.303}{40} \log 4 = \frac{2.303 \times 0.60}{40} = 0.034545 \text{ min}^{-1}.$$

Since time is expressed in minutes, the unit of the first order rate constant is inverse minutes. It does not include a concentration unit.

Step 3: Conclusion The rate constant is $k = 3.45 \times 10^{-2} \text{ min}^{-1}$.

Quick Tip to Solve: Convert percentage decomposition to percentage remaining before using the integrated first order equation.

Section C (21 marks)

22. A compound 'X' with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify 'X' and give the IUPAC name of the product. Write the reaction involved. [3 marks]

Solution:

Concept:

- Hinsberg reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It distinguishes primary, secondary and tertiary amines by their sulphonamide formation and solubility in alkali.
- A secondary amine forms a sulphonamide with no nitrogen-bound hydrogen; this product cannot form a salt with alkali and is insoluble in it.

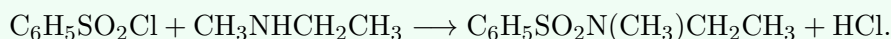
Step 1: Identify the class of amine The compound reacts with Hinsberg reagent to form a solid sulphonamide, so it cannot be a tertiary amine, which has no N-H bond and does not form this product. A primary amine gives a sulphonamide retaining an N-H bond. That hydrogen is acidic because of the electron-withdrawing sulphonyl group, and the product dissolves in alkali by forming a salt. Here the product is insoluble in alkali, identifying X as a secondary amine.

Step 2: Use the molecular formula The printed formula is C_3H_9N . A secondary amine has two alkyl groups attached to nitrogen. Distributing three carbon atoms between these groups gives one methyl and one ethyl group:



Its IUPAC name is N-methylethanamine. The two primary isomers, propan-1-amine and propan-2-amine, would give alkali-soluble sulphonamides; trimethylamine is tertiary and does not give the stated sulphonamide.

Step 3: Write the reaction and name the product The N-H hydrogen is replaced by the benzene-sulphonyl group:



The product is N-ethyl-N-methylbenzenesulphonamide. Nitrogen is bonded to the sulphonyl group, methyl group and ethyl group, so it has no N-H hydrogen available for salt formation in alkali.

Step 4: Conclusion $X = CH_3NHCH_2CH_3$, N-methylethanamine; the product is N-ethyl-N-methylbenzenesulphonamide, insoluble in alkali.

Quick Tip to Solve: In the Hinsberg test, an alkali-insoluble sulphonamide identifies a secondary amine: check whether the product retains an N-H bond.

23. Account for the following:

(a) Haloalkanes react with AgCN to form isocyanide as main product.

(b) Allyl chloride shows high reactivity towards S_N1 reaction.

(c) Haloarenes are extremely less reactive towards nucleophilic substitution reactions.

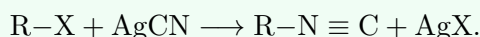
[3 marks]

Solution:

Concept:

- An ambident nucleophile has two possible attacking atoms. Cyanide can bond through carbon or nitrogen, depending on the reagent.
- In an S_N1 reaction, ionisation to a carbocation is rate determining; resonance stabilisation promotes this step.
- Aryl carbon-halogen bonds have partial double-bond character and are attached to sp^2 -hybridised carbon, making ordinary nucleophilic substitution difficult.

Step 1: (a) Why AgCN gives isocyanide AgCN is predominantly covalent, with the carbon end of cyanide bonded to silver. The nitrogen end is available to attack the haloalkane. Therefore the new bond forms between the alkyl carbon and nitrogen, giving an isocyanide as the main product:



In contrast, ionic KCN supplies free cyanide ions, whose carbon end mainly attacks to form nitriles.

Step 2: (b) Why allyl chloride reacts readily by S_N1 Loss of chloride from allyl chloride forms an allylic carbocation. Its positive charge is delocalised over the two terminal carbon atoms by resonance:



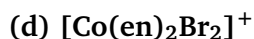
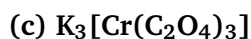
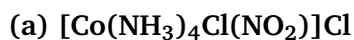
This stabilisation facilitates the rate-determining ionisation step. Consequently allyl chloride has high reactivity towards the S_N1 mechanism compared with an ordinary primary alkyl chloride.

Step 3: (c) Why haloarenes resist substitution The halogen lone pair is conjugated with the aromatic ring, giving the carbon-halogen bond partial double-bond character. The bond is therefore shorter and stronger than in haloalkanes. The carbon bonded to halogen is also sp^2 -hybridised and holds the bond electrons more tightly. For an S_N1 pathway, breaking the bond would form a highly unstable phenyl cation. For an S_N2 pathway, the aromatic ring obstructs the required backside attack. These factors make haloarenes much less reactive under ordinary conditions.

Step 4: Conclusion AgCN favours nitrogen attack and isocyanide formation; allyl chloride ionises readily because its carbocation is resonance stabilised; haloarenes resist substitution because of their strong aryl-halogen bond and unfavourable substitution pathways.

Quick Tip to Solve: For these explanations, identify the attacking atom, the stability of the intermediate, and the nature of the carbon-halogen bond respectively.

24. Write the IUPAC names of the following coordination compounds (any three):



[3 marks]

Solution:

Concept:

- Name ligands alphabetically, ignoring multiplicative prefixes, followed by the metal and its oxidation state in Roman numerals. Neutral ligands NH_3 and en contribute zero charge; Cl^- , Br^- and NO_2^- contribute -1 , and oxalato contributes -2 .
- Name the cation before the anion. An anionic coordination entity uses a metal name ending in “ate”, whereas a cationic entity retains the metal name. Use bis or tris with compound ligand names.

Step 1: Name the cobalt complex in (a) The outside Cl^- makes the complex cation singly charged. If cobalt has oxidation state x , then $x - 1 - 1 = +1$, giving $x = +3$. There are four ammine ligands, one chlorido ligand and one N-bound nitrito ligand, written NO_2 . Alphabetical order gives ammine, chlorido, then nitrito-N. Thus (a) is tetraamminechloridonitrito-N-cobalt(III) chloride. The outer chloride is a counter-ion and is named separately.

Step 2: Name the nickel complex in (b) The two outer chloride ions have total charge -2 ; hence $[\text{Ni}(\text{NH}_3)_6]^{2+}$ has charge $+2$. Because all six ammonia ligands are neutral, nickel is in oxidation state $+2$. The name is hexaamminenickel(II) chloride. “Ammine” has two m letters when ammonia is a ligand.

Step 3: Name the chromium complex in (c) Three potassium ions require the complex ion to have charge -3 . For three oxalato ligands, $x + 3(-2) = -3$, so chromium has oxidation state $+3$. Since the complex is anionic, use chromate rather than chromium. The name is potassium tris(oxalato)chromate(III).

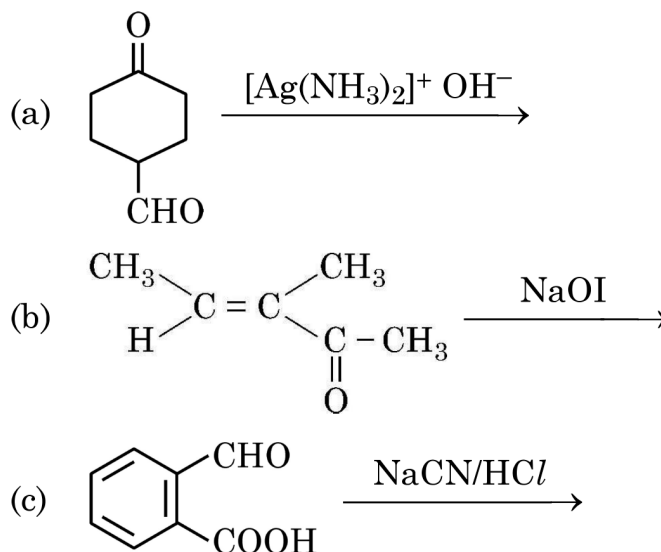
Step 4: Name the cobalt complex ion in (d) Each en ligand is neutral ethane-1,2-diamine, and the two bromido ligands have total charge -2 . Thus $x - 2 = +1$, giving cobalt(III). Bromido precedes ethane-1,2-diamine alphabetically; bis encloses the compound ligand name. The ion is dibromidobis(ethane-1,2-diamine)cobalt(III). No counter-ion is supplied, so none is added to its name.

Step 5: Conclusion (a) Tetraamminechloridonitrito-N-cobalt(III) chloride; (b) hexaamminenickel(II) chloride; (c) potassium tris(oxalato)chromate(III); (d) dibromidobis(ethane-1,2-diamine)cobalt(III). Any three of these satisfy the question.

Quick Tip to Solve: Determine the charge inside the square brackets from the outside ions before calculating the metal oxidation state; use “ate” only for an anionic complex.

25. Draw the structures of major product(s) in each of the following reactions:

[3 marks]



Solution:

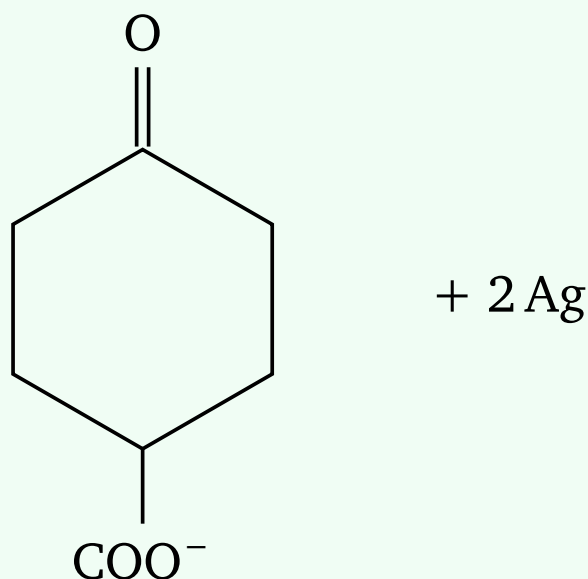
Concept:

- Tollens' reagent oxidises an aldehyde group to a carboxylate ion in alkaline medium while depositing silver. An ordinary ketone group is unchanged.
- A methyl ketone RCOCH_3 undergoes the iodoform reaction with sodium hypoiodite, giving RCOONa and yellow CHI_3 . The remainder of the carbon skeleton is retained.
- NaCN/HCl generates HCN . Cyanide adds to the electrophilic aldehyde carbonyl carbon, and protonation of the resulting alkoxide gives a cyanohydrin, $\text{RCH}(\text{OH})\text{CN}$.

Step 1: Oxidise the formyl group in (a) The substrate contains both a cyclohexanone carbonyl and a $-\text{CHO}$ group at the opposite ring carbon. Tollens' reagent reacts with the aldehyde, not the ring ketone. Since the medium contains OH^- , show the oxidised group as $-\text{COO}^-$; the ring $\text{C}=\text{O}$ remains intact. Silver metal is the other product. The organic product is 4-oxocyclohexane-1-carboxylate. Acidification, if subsequently performed, would give the corresponding carboxylic acid, but no acid work-up is indicated here.



Quick Tip to Solve: Circle the reacting group before drawing: Tollens changes only CHO , NaOI cleaves only the methyl-ketone end, and HCN adds OH and CN to the same aldehyde carbon.

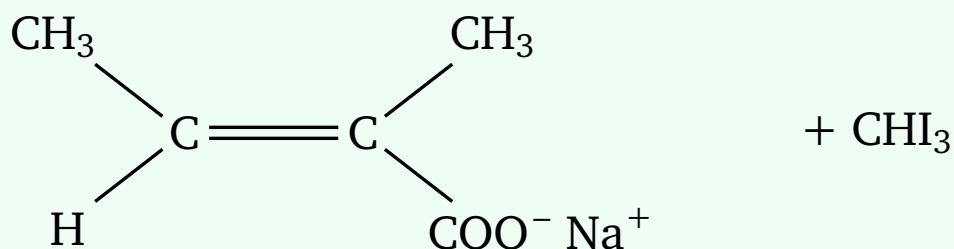


Product (a): ring ketone retained; aldehyde oxidised to carboxylate.

Step 2: Apply the iodoform reaction in (b) The printed substrate is $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COCH}_3$. Its terminal $-\text{COCH}_3$ group is the methyl-ketone unit. Replace this unit by $-\text{COO}^- \text{Na}^+$; the terminal methyl carbon becomes CHI_3 . Thus the products are sodium 2-methylbut-2-enoate and iodoform. Preserve the printed alkene arrangement in the carboxylate structure: the two methyl substituents remain on the same side. Do not remove the methyl substituent attached directly to the alkene carbon.



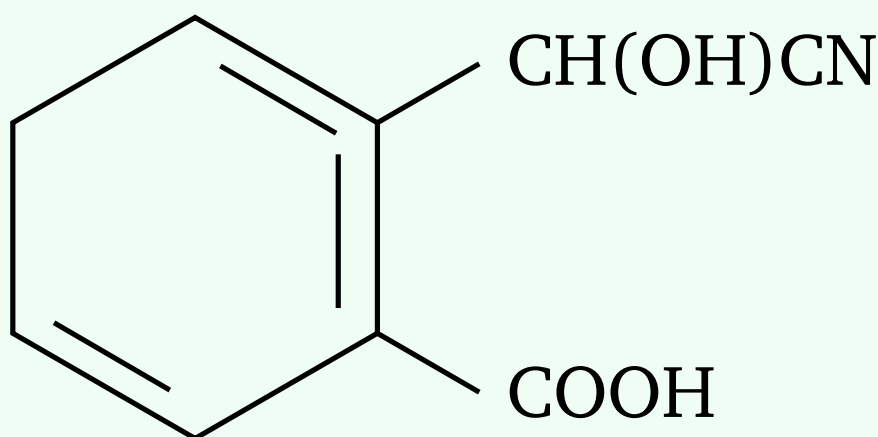
Here R denotes $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)-$.



Products (b): sodium carboxylate and iodoform.

Step 3: Form the cyanohydrin in (c) The aldehyde group on the benzene ring undergoes nucleophilic addition of HCN . Its carbonyl oxygen becomes $-\text{OH}$, and $-\text{CN}$ bonds to that same carbon, which still carries its original hydrogen. The neighbouring $-\text{COOH}$ group remains unchanged. The product is $\text{o-HOOC}-\text{C}_6\text{H}_4-\text{CH}(\text{OH})\text{CN}$; the two substituents retain their ortho positions. Attack on either face of the planar aldehyde gives a racemic cyanohydrin, so an ordinary structural formula is sufficient.

Quick Tip to Solve: Circle the reacting group before drawing: Tollens changes only CHO , NaOI cleaves only the methyl-ketone end, and HCN adds OH and CN to the same aldehyde carbon.

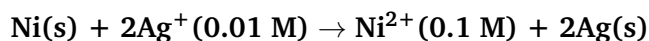


Product (c): cyanohydrin with the carboxylic acid group ortho to it.

Step 4: Conclusion The major organic products are (a) 4-oxocyclohexane-1-carboxylate, with silver deposition; (b) $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COONa}$ and CHI_3 ; (c) $\text{o-HOOC-C}_6\text{H}_4\text{-CH(OH)CN}$. Their structures are shown with the respective working.

Quick Tip to Solve: Circle the reacting group before drawing: Tollens changes only CHO, NaOI cleaves only the methyl-ketone end, and HCN adds OH and CN to the same aldehyde carbon.

26. Calculate the emf of the following cell:



Given that $E^\circ_{\text{cell}} = 1.05 \text{ V}$, $\log 10 = 1$

[3 marks]

Solution:

Concept:

- At 298 K, the Nernst equation is $E = E^\circ - \frac{0.0591}{n} \log Q$, where n counts transferred electrons and Q is the reaction quotient.
- Pure solids have unit activity. Only dissolved ions enter the reaction quotient, raised to their stoichiometric powers.

Step 1: Obtain the electron count and reaction quotient Oxidation is $\text{Ni(s)} \rightarrow \text{Ni}^{2+}(\text{aq}) + 2\text{e}^-$, while reduction is $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Ag(s)}$. Therefore $n = 2$, not one; the two silver ions together accept the two electrons released by one nickel atom. For the reaction as written,

$$Q = \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2} = \frac{0.1}{(0.01)^2} = 1000 = 10^3.$$

Neither nickel nor silver metal appears in this expression. The silver-ion concentration is squared because its coefficient in the balanced reaction is two.

Step 2: Calculate the emf Taking the usual room temperature 298 K, and using $\log 10 = 1$, gives

Quick Tip to Solve: Count electrons from the half-reactions, and square the silver-ion concentration before taking the logarithm.

$\log Q = 3$. Therefore,

$$\begin{aligned}E_{\text{cell}} &= 1.05 - \frac{0.0591}{2} \times 3 \\&= 1.05 - 0.08865 \\&= 0.96135 \text{ V.}\end{aligned}$$

The sign of the correction is negative because $Q > 1$. Thus these ionic concentrations give an emf smaller than the standard cell emf, as expected when the concentration of the reactant silver ions is low.

Step 3: Conclusion The cell emf at 298 K is $E_{\text{cell}} \simeq 0.961 \text{ V}$.

Quick Tip to Solve: Count electrons from the half-reactions, and square the silver-ion concentration before taking the logarithm.

27. Give the structure of the major product expected from the following reactions:

(a) Reaction of propanal with methyl magnesium bromide followed by hydrolysis.

(b) Reaction of phenol with Br_2 in CS_2 .

(c) Reaction of propene with diborane followed by oxidation.

[3 marks]

Solution:

Concept:

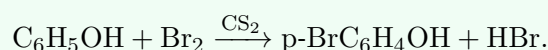
- Grignard reagents add their alkyl group to the carbonyl carbon; hydrolysis of the magnesium alkoxide then gives an alcohol.
- The hydroxyl group activates the phenol ring and directs bromination to ortho and para positions. In nonpolar CS_2 , monobromination occurs, with the para product predominant.
- Hydroboration followed by oxidation converts an alkene into an alcohol with anti-Markovnikov placement of the hydroxyl group.

Step 1: (a) Add methyl to propanal and hydrolyse The methyl group from CH_3MgBr attaches to the carbonyl carbon of $\text{CH}_3\text{CH}_2\text{CHO}$. Hydrolysis replaces the oxygen-magnesium bond by an oxygen-hydrogen bond:



The product has four carbons and is a secondary alcohol: butan-2-ol.

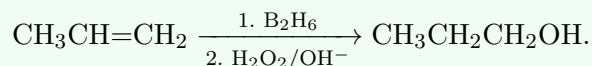
Step 2: (b) Brominate phenol in carbon disulphide Phenol undergoes electrophilic substitution at the ortho and para positions. In CS_2 , the principal product is para-bromophenol:



Here OH occupies carbon 1 and Br carbon 4 on the benzene ring. Ortho-bromophenol is a minor product; para substitution is favoured by less steric crowding. The aqueous-bromine product, 2,4,6-tribromophenol, is not the major product under these conditions.

Quick Tip to Solve: Track the added methyl carbon in (a), the nonpolar bromination solvent in (b), and the terminal hydroxyl group in (c).

Step 3: (c) Carry out hydroboration and oxidation Diborane supplies borane, which adds to propene with boron at the less substituted terminal carbon. Oxidation with alkaline hydrogen peroxide replaces the carbon-boron bond by a carbon-oxygen bond:



Hence the hydroxyl group is on carbon 1, giving propan-1-ol rather than propan-2-ol.

Step 4: Conclusion The major products are (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$, butan-2-ol; (b) $\text{p-BrC}_6\text{H}_4\text{OH}$, 4-bromophenol; and (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$, propan-1-ol.

Quick Tip to Solve: Track the added methyl carbon in (a), the nonpolar bromination solvent in (b), and the terminal hydroxyl group in (c).

28. The rate constant of a reaction quadruples when the temperature changes from 700 K to 720 K. Calculate the activation energy for this reaction.

[$\log 2 = 0.30$, $\log 4 = 0.60$, $2.303 R = 19.15 \text{ J K}^{-1} \text{ mol}^{-1}$]

[3 marks]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, R is the gas constant and T is absolute temperature.
- For two temperatures, assuming the pre-exponential factor A remains constant, $\log(k_2/k_1) = \frac{E_a}{2.303R}(1/T_1 - 1/T_2)$.

Step 1: Set up the two-temperature relation The initial and final temperatures are $T_1 = 700 \text{ K}$ and $T_2 = 720 \text{ K}$. Quadrupling means $k_2/k_1 = 4$, so the given common logarithm is $\log(k_2/k_1) = \log 4 = 0.60$. Taking the ratio of the two Arrhenius expressions eliminates the unknown factor A . Thus,

$$0.60 = \frac{E_a}{19.15} \left(\frac{1}{700} - \frac{1}{720} \right).$$

The reciprocal-temperature difference is positive because the higher rate constant corresponds to the higher temperature.

Step 2: Evaluate the activation energy with units Rearranging before substitution avoids losing the small difference between the two reciprocal temperatures:

$$\begin{aligned} E_a &= (2.303R) \log 4 \frac{T_1 T_2}{T_2 - T_1} \\ &= 19.15 \times 0.60 \times \frac{700 \times 720}{20} \\ &= 289548 \text{ J mol}^{-1} \\ &= 289.548 \text{ kJ mol}^{-1}. \end{aligned}$$

The temperature factor has units of kelvin, cancelling the kelvin in $2.303R$; the result is therefore

Quick Tip to Solve: Use the ratio 4 directly and combine reciprocal temperatures as $(T_2 - T_1)/(T_1 T_2)$ before substitution.

energy per mole. Division by 1000 converts joules into kilojoules. The positive activation energy agrees with an increasing rate constant as the temperature rises.

Step 3: Conclusion Using the supplied numerical constants, $E_a \simeq 289.55 \text{ kJ mol}^{-1}$.

Quick Tip to Solve: Use the ratio 4 directly and combine reciprocal temperatures as $(T_2 - T_1)/(T_1 T_2)$ before substitution.

Section D (8 marks)

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

29(a). Case: The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Similarly the charge on the complex is the sum of the charges of the constituent parts i.e. the sum of the charges on the central metal ion and its surrounding ligands. Based on this, the complex is called neutral if the sum of the charges of the constituents is equal to zero. However, for an anion or cationic complex, the sum of the charges of the constituents is equal to the charge on the coordination sphere.

(a) What is the secondary valence of Co in $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$?

[1 mark]

Solution:

Concept:

- Werner's secondary valence is the coordination number: the number of ligand donor atoms directly bonded to the central metal.
- Both ammonia, NH_3 , and chloride, Cl^- , are monodentate ligands; each contributes one donor atom.

Step 1: Identify the coordinated ligands In $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, all four ammonia molecules and both chloride ions lie inside the square brackets. They therefore belong to the coordination sphere and bond directly to cobalt.

Step 2: Count the donor atoms The four ammonia ligands donate through four nitrogen atoms, while the two chloride ligands donate through two chlorine atoms. Thus the coordination number is $4 + 2 = 6$. The overall charge +1 is not the secondary valence; it is used to determine the oxidation state.

Step 3: Conclusion The secondary valence of cobalt is $\boxed{6}$.

Quick Tip to Solve: For secondary valence, count donor atoms inside the brackets rather than using the ionic charge.

29(b). What type of isomerism is shown by the complex $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$?

[1 mark]

Solution:

Concept:

- Solvate isomerism occurs when solvent molecules exchange positions between the coordination sphere and the crystal lattice.
- When the solvent is water, solvate isomerism is specifically called hydrate isomerism.

Step 1: Compare the water molecules In $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, all six water molecules are directly coordinated to chromium. In $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, five waters are coordinated and one water is outside the coordination sphere as water of crystallisation.

Step 2: Identify the positional exchange A coordinated water molecule is replaced by a chloride ion, and the displaced water appears in the crystal lattice. Both compounds retain the same overall composition but differ in which species are directly attached to chromium. This is the defining change for hydrate isomers.

Step 3: Conclusion The complexes exhibit hydrate (solvate) isomerism.

Quick Tip to Solve: Compare water inside and outside the brackets; movement of water into the lattice identifies hydrate isomerism.

29(c). Write the electronic configuration of d^4 ion on the basis of crystal field theory when

(i) $\Delta_o < P$

(ii) $\Delta_o > P$

[2 marks]

Solution:

Concept:

- In an octahedral field, the five d orbitals split into lower-energy t_{2g} and higher-energy e_g sets, separated by Δ_o .
- The pairing energy P is the energy needed to pair two electrons in one orbital. Electrons choose promotion or pairing according to the relative sizes of Δ_o and P .

Step 1: Case (i): weak field When $\Delta_o < P$, promotion to the higher e_g level costs less energy than pairing in t_{2g} . The first three electrons occupy the three t_{2g} orbitals singly, following Hund's rule, and the fourth occupies an e_g orbital. This gives $t_{2g}^3 e_g^1$, a high-spin arrangement with four unpaired electrons.

Step 2: Case (ii): strong field When $\Delta_o > P$, pairing in a lower t_{2g} orbital costs less than promoting the fourth electron to e_g . After three singly occupied t_{2g} orbitals form, the fourth electron pairs in one of them. The result is $t_{2g}^4 e_g^0$, a low-spin arrangement with two unpaired electrons. In each case the superscripts add to four, matching the stated d^4 ion.

Step 3: Conclusion (i) $t_{2g}^3 e_g^1$; (ii) $t_{2g}^4 e_g^0$.

Quick Tip to Solve: For a d^4 ion, place the first three electrons in t_{2g} , then compare splitting energy with pairing energy for the fourth.

29(c). Find the oxidation state and coordination number of the central metal ion in $[\text{Co}(\text{H}_2\text{O})(\text{CN})(\text{en})_2]^{2+}$.

[2 marks]

Solution:

Concept:

- The sum of the oxidation state of the metal and the charges on its ligands equals the charge of the complex ion.
- Coordination number counts donor atoms, not ligand molecules. Ethane-1,2-diamine, en, is a neutral bidentate ligand with two nitrogen donors.

Step 1: Calculate the oxidation state Let the oxidation state of cobalt be x . Water is neutral, cyanide has charge -1 , and each en ligand is neutral. The coordination sphere carries charge $+2$, so

$$x + 0 + (-1) + 2(0) = +2.$$

Solving this charge balance gives $x = +3$. The two en molecules change the number of donor atoms but do not contribute any ionic charge.

Step 2: Count donor atoms The single water ligand provides one oxygen donor and the single cyanide ligand provides one donor atom. Each of the two en ligands provides two nitrogen donors because it is bidentate. Hence the total number of metal-donor bonds is

$$1 + 1 + 2 \times 2 = 6.$$

Counting only four ligand molecules would miss the second donor of each en ligand.

Step 3: Conclusion The oxidation state is $+3$ and the coordination number is 6 .

Quick Tip to Solve: Use ligand charges for oxidation state, but use ligand denticity for coordination number; each en contributes two donors.

30(a). Certain organic compounds are required in small amounts in our diet but their deficiency causes specific disease. These compounds are called vitamins. Most of the vitamins cannot be synthesized in our body but plants can synthesize almost all of them. So they are considered as essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. The term 'vitamin' was coined from the words vital + amine, since the earlier identified compounds had amino group. Vitamins are classified into two groups depending upon their solubility in water or fat namely-fat soluble vitamins and water soluble vitamins.

(a) What is the other name of Vitamin B₆?

[1 mark]

Solution:

Concept:

- The B-group vitamins are water-soluble vitamins, and their numerical labels correspond to specific chemical names.
- Vitamin B₆ is known as pyridoxine in the standard vitamin classification.

Step 1: Read the vitamin identifier The question specifies vitamin B₆. Its subscript identifies the particular member of the B-group whose common chemical name must be recalled. The question asks for that name and does not require a source or a deficiency disease.

Step 2: Match the standard name The standard correspondence is vitamin B₆: pyridoxine. For comparison, thiamine belongs to vitamin B₁ and riboflavin to vitamin B₂, so neither is the requested name. Reading the subscript carefully avoids confusing these members of the B-group.

Step 3: Conclusion The other name of vitamin B₆ is pyridoxine.

Quick Tip to Solve: Associate B1 with thiamine, B2 with riboflavin and B6 with pyridoxine before choosing the requested vitamin name.

30(b). Name the vitamin whose deficiency causes increased blood clotting time.

[1 mark]

Solution:

Concept:

- Vitamin K is a fat-soluble vitamin essential for normal blood coagulation.
- A vitamin deficiency can impair a specific physiological function; a longer clotting time indicates impaired coagulation.

Step 1: Identify the function affected Increased blood clotting time means that blood takes longer than normal to form a clot. The vitamin associated with the normal formation and functioning of blood-clotting factors is vitamin K.

Step 2: Connect the deficiency with the symptom When vitamin K is deficient, the synthesis of functional clotting factors is impaired. Coagulation becomes slower, which accounts for the increased clotting time described in the question.

Step 3: Conclusion The vitamin is vitamin K.

Quick Tip to Solve: Associate vitamin K with coagulation: deficiency delays blood clotting.

30(c). Xerophthalmia is caused by the deficiency of which vitamin? Give two sources of this vitamin.

[2 marks]

Solution:

Concept:

- Vitamin A is a fat-soluble vitamin needed for normal vision and maintenance of epithelial tissues.
- Xerophthalmia is an eye disorder associated with vitamin A deficiency; food sources supply vitamin A or its precursors.

Step 1: Identify the deficient vitamin Xerophthalmia is caused by deficiency of vitamin A. The deficiency affects the normal maintenance of the surface of the eye, leading to dryness of the conjunctiva and cornea. Thus, the reference to xerophthalmia identifies vitamin A rather than vitamin C or vitamin K.

Step 2: Give two dietary sources Two sources of vitamin A are carrots and fish-liver oil. Carrots contain carotenoids, including beta-carotene, which the body can convert into vitamin A. Fish-liver oil supplies preformed vitamin A. Either source therefore helps provide the vitamin associated with healthy eyes.

Step 3: Conclusion Xerophthalmia is caused by vitamin A deficiency. Two sources are carrots and fish-liver oil.

Quick Tip to Solve: For vitamin A questions, pair the eye disorder xerophthalmia with carrots and fish-liver oil.

OR

30(c). Why can't vitamin C be stored in our body? Name the disease caused by the deficiency of this vitamin.

[2 marks]

Solution:

Concept:

- Vitamin C, also called ascorbic acid, is a water-soluble vitamin.
- Water-soluble vitamins are generally not retained in substantial body stores; excess vitamin C is excreted in urine.
- Vitamin C deficiency causes scurvy, which is associated with bleeding gums and impaired wound healing.

Step 1: Explain why vitamin C is not stored Vitamin C dissolves in water and belongs to the water-soluble group of vitamins. Excess vitamin C is eliminated from the body through urine rather than accumulating in fat stores. Consequently, the body does not maintain substantial reserves of it, and a regular dietary supply is needed.

Step 2: Identify the deficiency disease Deficiency of vitamin C causes scurvy. Vitamin C is needed for normal collagen formation; its deficiency weakens supporting tissues and can produce bleeding gums and poor wound healing. These characteristic symptoms distinguish scurvy from the eye disorder caused by vitamin A deficiency.

Quick Tip to Solve: Remember the linked facts for vitamin C: water-soluble, excreted in urine, and deficiency causes scurvy.

Step 3: Conclusion Vitamin C is water-soluble and its excess is excreted in urine, so it cannot be stored in substantial amounts. Its deficiency causes scurvy.

Quick Tip to Solve: Remember the linked facts for vitamin C: water-soluble, excreted in urine, and deficiency causes scurvy.

Section E (15 marks)

31(a)(i). Ishan's automobile radiator is filled with 1.0 kg of water. How many grams of ethylene glycol (molar mass = 62 g mol^{-1}) must Ishan add to get the freezing point of the solution lowered to -2.8°C ? K_f for water is $1.86 \text{ K kg mol}^{-1}$. [3 marks]

Solution:

Concept:

- For a dilute solution, freezing-point depression is $\Delta T_f = iK_fm$, where K_f is the cryoscopic constant and m is molality.
- Molality is the amount of solute in moles divided by the mass of solvent in kilograms.
- Ethylene glycol is a non-electrolyte, so it neither dissociates nor associates in the usual dilute-solution treatment and $i = 1$.

Step 1: Calculate the required freezing-point depression Pure water freezes at 0°C . The desired solution freezes at -2.8°C , so the positive depression is

$$\Delta T_f = 0 - (-2.8) = 2.8 \text{ K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius. The solvent mass is already given in kilograms, 1.0 kg.

Step 2: Determine molality and amount of ethylene glycol Use $i = 1$ and $K_f = 1.86 \text{ K kg mol}^{-1}$:

$$m = \frac{\Delta T_f}{K_f} = \frac{2.8}{1.86} = 1.5054 \text{ mol kg}^{-1},$$
$$n = m \times (1.0 \text{ kg}) = 1.5054 \text{ mol}.$$

The kilogram in molality refers to the mass of water, not the total mass of solution.

Step 3: Convert the amount into mass With molar mass $M = 62 \text{ g mol}^{-1}$,

$$w = nM = 1.5054 \times 62 = 93.33 \text{ g}.$$

As a check, $93.33/62$ moles in 1.0 kg of water gives $1.86 \times (93.33/62) \approx 2.8 \text{ K}$ freezing-point depression. The sign of the final freezing temperature is negative, while the depression used in the formula is positive.

Step 4: Conclusion Ishan must add approximately 93.3 g of ethylene glycol.

Quick Tip to Solve: Use the solvent mass in kilograms and take freezing-point depression as the positive difference from pure water.

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

Solution:

Concept:

- Raoult's law for an ideal binary solution is $p_A = x_A p_A^0$ and $p_B = x_B p_B^0$, where x denotes mole fraction and p^0 the vapour pressure of the pure component.
- Positive deviation occurs when attractions between unlike molecules in the mixture are weaker than the attractions in the pure liquids, allowing molecules to escape more readily into the vapour phase.

Step 1: Compare the intermolecular attractions Pure ethanol molecules are associated through intermolecular hydrogen bonding involving their $-\text{OH}$ groups. On adding acetone, acetone molecules come between ethanol molecules and disrupt some of this hydrogen-bonded association. The resulting ethanol-acetone interactions are weaker overall than the interactions responsible for association in pure ethanol.

Step 2: Relate the disruption to vapour pressure With weaker effective attractions in the mixed liquid, molecules have a greater tendency to escape. Thus the partial vapour pressures, and consequently the total vapour pressure, are higher than the values predicted by Raoult's law at the same temperature and composition. This is the criterion for a positive deviation; stronger unlike interactions would instead give a negative deviation.

Step 3: Conclusion The ethanol-acetone mixture shows positive deviation from Raoult's law, because acetone disrupts ethanol's hydrogen bonding and weakens the effective intermolecular attractions in the mixture.

Quick Tip to Solve: For ethanol mixed with acetone, link disruption of ethanol hydrogen bonding to easier escape and hence higher vapour pressure.

OR

31(b). (i) Boiling point of water at 750 mm Hg pressure is 99.68°C . How much sucrose (Molar mass = 342 g mol^{-1}) is to be added to 500 g of water such that it boils at 100°C ? (K_b for water = $0.52\text{ K kg mol}^{-1}$)

(ii) State Henry's law and write its any one application. [5 marks]

Solution:

Concept:

- A non-volatile solute elevates the boiling point: $\Delta T_b = K_b m$, where K_b is the solvent's ebullioscopic constant and m is the solute molality in mol kg^{-1} .
- Sucrose does not dissociate in water, so its van't Hoff factor is $i = 1$. Molality is moles of sucrose divided by the mass of water in kilograms.
- Henry's law relates the partial pressure p of a gas above a solution to its mole fraction x in the solution at a fixed temperature: $p = K_H x$.

Quick Tip to Solve: Use 99.68 degrees Celsius as the initial boiling point at 750 mm Hg, and 0.500 kg of solvent in molality.

Step 1: (i) Find the required boiling-point elevation The boiling point of pure water must be taken at the given pressure of 750 mm Hg. Therefore, the initial boiling point is 99.68 °C, and the required solution boiling point is 100 °C at this same pressure. The required elevation is

$$\Delta T_b = 100 - 99.68 = 0.32 \text{ K.}$$

The mass of solvent is 500 g = 0.500 kg.

Step 2: (i) Calculate the sucrose mass Let w be the mass of sucrose in grams. Using its molar mass 342 g mol⁻¹, the number of moles is $w/342$. Hence

$$m = \frac{\Delta T_b}{K_b} = \frac{0.32}{0.52} = 0.61538 \text{ mol kg}^{-1}.$$

The moles needed in 0.500 kg of water are

$$n = m(0.500) = 0.30769 \text{ mol,} \quad w = nM = 0.30769 \times 342 = 105.23 \text{ g.}$$

Use solvent mass, not solution mass, for molality.

Step 3: (ii) State Henry's law and give an application At a constant temperature, the partial pressure of a gas in the vapour phase above a solution is directly proportional to the mole fraction of that gas dissolved in the solution:

$$p = K_H x.$$

Here K_H is Henry's law constant. In carbonating soft drinks, carbon dioxide is dissolved under high pressure. A greater gas pressure increases its dissolved mole fraction. Opening the bottle lowers the pressure, releasing carbon dioxide bubbles.

Step 4: Conclusion (i) The required sucrose mass is 105.23 g, approximately 105 g. (ii) Henry's law is $p = K_H x$ at constant temperature; it is applied in carbonating soft drinks under high carbon dioxide pressure.

Quick Tip to Solve: Use 99.68 degrees Celsius as the initial boiling point at 750 mm Hg, and 0.500 kg of solvent in molality.

32(a). An organic compound (A) with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Fehling solution and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzene dicarboxylic acid.

(i) Identify the compound (A) and write its IUPAC name.

(ii) Write the reaction of compound (A) with

(1) 2,4-Dinitrophenyl hydrazine and

(2) Fehling solution

(iii) Write the equation of compound (A) when it undergoes Cannizzaro reaction.

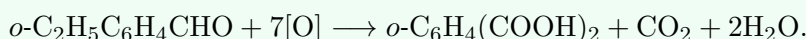
[5 marks]

Solution:

Concept:

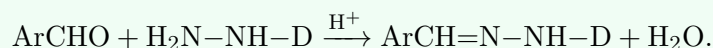
- Formation of a 2,4-dinitrophenylhydrazone establishes the presence of an aldehyde or ketone carbonyl group. Cannizzaro reaction is characteristic of aldehydes without an α -hydrogen.
- Vigorous oxidation converts an alkyl side chain bearing a benzylic hydrogen into a carboxyl group. Formation of benzene-1,2-dicarboxylic acid locates the two oxidisable substituents at adjacent positions.
- Ordinary aromatic aldehydes do not reduce Fehling solution. Consequently, the printed positive Fehling test is inconsistent with the structure indicated by the other observations.

Step 1: (i) Determine the structure and IUPAC name The Cannizzaro test identifies a non-enolisable aldehyde. The benzene ring and formyl group account for seven carbon atoms, leaving an ethyl group for the formula $C_9H_{10}O$. Its oxidation to benzene-1,2-dicarboxylic acid requires the ethyl and formyl groups to be ortho to each other. The structure indicated by these observations is therefore $o\text{-}C_2H_5C_6H_4CHO$, named **2-ethylbenzaldehyde**. The hydrogens on the ethyl substituent are not α to the aldehyde carbonyl, so they do not prevent Cannizzaro reaction. Its vigorous oxidation is represented by



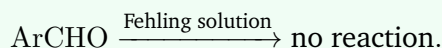
The carbon lost from the ethyl group is accounted for as carbon dioxide. This identification satisfies the formula, DNP, Cannizzaro and oxidation evidence, but not the printed Fehling observation.

Step 2: (ii)(1) Reaction with 2,4-dinitrophenylhydrazine Write $Ar = 2\text{-}C_2H_5C_6H_4$ and $D = 2, 4\text{-(NO}_2)_2C_6H_3$. Acid-catalysed condensation of the carbonyl group with the terminal amino group gives the coloured hydrazone precipitate:



The product is 2-ethylbenzaldehyde 2,4-dinitrophenylhydrazone; the aldehyde oxygen is eliminated in water.

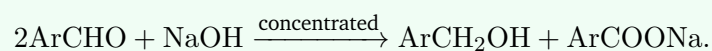
Step 3: (ii)(2) Check the Fehling reaction against the identified aldehyde Fehling solution is an alkaline copper(II)-tartrate reagent. Aliphatic aldehydes typically reduce it to a brick-red precipitate of Cu_2O , but 2-ethylbenzaldehyde is an aromatic aldehyde and gives no such reaction under the usual test conditions:



Quick Tip to Solve: Use the ortho dicarboxylic acid oxidation product to locate the ethyl group beside CHO, then check the claimed Fehling result separately: aromatic aldehydes give a negative test.

Thus no chemically valid positive Fehling equation can be written for this compound. The statement that (A) reduces Fehling solution is a contradiction in the printed question; it must not be used to assert a false reaction for an aromatic aldehyde.

Step 4: (iii) Write the Cannizzaro equation Concentrated aqueous alkali causes disproportionation: one aldehyde molecule is reduced to the benzyl alcohol derivative and another is oxidised to the carboxylate salt. With the same Ar abbreviation,



The products are (2-ethylphenyl)methanol and sodium 2-ethylbenzoate. This equation conserves the two aromatic groups and balances carbon, hydrogen, oxygen and sodium.

Step 5: Conclusion The other observations identify (A) as 2-ethylbenzaldehyde. It forms the DNP hydrazone and undergoes the Cannizzaro reaction shown above. However, it does not reduce Fehling solution, so no compound identified by the stated evidence satisfies every printed observation consistently.

Quick Tip to Solve: Use the ortho dicarboxylic oxidation product to locate the ethyl group beside CHO, then check the claimed Fehling result separately: aromatic aldehydes give a negative test.

OR

32(b)(i). Account for the following:

(1) The alpha (α)-hydrogens of aldehydes and ketones are acidic in nature.

(2) Oxidation of aldehydes is easier than ketones.

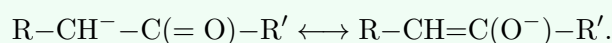
[2 marks]

Solution:

Concept:

- An alpha-hydrogen is attached to the carbon adjacent to a carbonyl group. Acidity depends on the stability of the conjugate base formed after removal of a proton.
- An aldehyde has a hydrogen directly bonded to its carbonyl carbon, whereas a ketone has two carbon groups attached to that carbon.

Step 1: (1) Explain the acidity of alpha-hydrogens The electron-withdrawing carbonyl group polarises the adjacent bonds. Removal of an alpha-hydrogen as H^+ forms an enolate ion whose negative charge is delocalised between the alpha-carbon and oxygen:

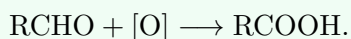


Here R' may be hydrogen for an aldehyde or a carbon group for a ketone. Resonance stabilisation of this conjugate base makes alpha-hydrogens appreciably more acidic than ordinary alkane hydrogens. Only hydrogens adjacent to the carbonyl group receive this enolate stabilisation.

Step 2: (2) Explain the easier oxidation of aldehydes An aldehyde is readily oxidised to the corre-

Quick Tip to Solve: For acidity, draw the two enolate resonance forms; for oxidation, compare the aldehyde's carbonyl hydrogen with the ketone's two carbon substituents.

sponding carboxylic acid without breaking a carbon-carbon bond:



It possesses the hydrogen on the carbonyl carbon needed for this conversion. A ketone lacks that hydrogen. Its oxidation normally requires vigorous conditions and cleavage of a carbon-carbon bond, producing smaller carboxylic acids. Consequently mild oxidising agents oxidise aldehydes easily while ketones generally resist them.

Step 3: Conclusion Alpha-hydrogens are acidic because their removal produces a resonance-stabilised enolate ion. Aldehydes oxidise more easily because they form carboxylic acids without carbon-carbon bond cleavage, whereas ketone oxidation requires such cleavage under stronger conditions.

Quick Tip to Solve: For acidity, draw the two enolate resonance forms; for oxidation, compare the aldehyde's carbonyl hydrogen with the ketone's two carbon substituents.

32(b)(ii). Arrange the following in:

(1) Decreasing reactivity towards nucleophilic addition reaction: **propanal, acetone, benzaldehyde.**

(2) Increasing order of boiling point: **Propane, Ethanol, Dimethyl ether, Propanal.** [2 marks]

Solution:

Concept:

- Nucleophilic addition begins with attack on the electron-deficient carbonyl carbon. Electron-donating groups and steric crowding reduce its reactivity.
- Boiling point increases with the strength of intermolecular attractions; hydrogen bonding is stronger than ordinary dipole-dipole attractions for these compounds.

Step 1: (1) Compare carbonyl reactivity Propanal is an aliphatic aldehyde: its carbonyl carbon has one alkyl group and one small hydrogen atom, so attack is relatively unhindered. In benzaldehyde, conjugation of the carbonyl group with the benzene ring reduces the positive character of the carbonyl carbon, making it less reactive than propanal. Acetone has two electron-donating methyl groups and greater crowding around the carbonyl carbon than either aldehyde, so it is least reactive in this comparison.

Step 2: (2) Compare intermolecular forces Propane is non-polar and has only weak dispersion forces. Dimethyl ether is polar and has dipole-dipole attractions, but cannot hydrogen-bond with itself. Propanal has stronger carbonyl dipole attractions and a larger molecular size than dimethyl ether. Ethanol forms intermolecular hydrogen bonds through its hydroxyl group, giving it the highest boiling point of these four compounds.

Step 3: Conclusion (1) Decreasing reactivity: propanal > benzaldehyde > acetone.

(2) Increasing boiling point: propane < dimethyl ether < propanal < ethanol.

Quick Tip to Solve: For carbonyl reactivity compare steric hindrance and electron donation; for boiling point first identify the compound capable of self hydrogen bonding.

32(b)(iii). Give simple chemical test to distinguish between Benzoic acid and Benzaldehyde. [1 mark]

Solution:

Concept:

- Carboxylic acids react with aqueous sodium hydrogencarbonate, liberating carbon dioxide gas.
- An aldehyde lacks the carboxylic acid group and does not liberate carbon dioxide with sodium hydrogencarbonate.

Step 1: Add the test reagent Add aqueous sodium hydrogencarbonate, NaHCO_3 , separately to small portions of the two samples. Benzoic acid produces brisk effervescence, whereas benzaldehyde does not produce this effervescence.

Step 2: Identify the evolved gas The bubbles from benzoic acid are carbon dioxide, formed by the acid-bicarbonate reaction:



The gas turns limewater milky. Benzaldehyde has no acidic carboxyl group, so this reaction does not occur.

Step 3: Conclusion The sample giving brisk CO_2 effervescence with aqueous NaHCO_3 is benzoic acid; the sample without effervescence is benzaldehyde.

Quick Tip to Solve: Use bicarbonate effervescence to detect the carboxyl group directly when comparing an acid with an aldehyde.

33. Attempt any five of the following:

- (a) Ce(III) is easily oxidised to Ce(IV) . Comment.
- (b) $E^\circ(\text{Mn}^{2+}/\text{Mn})$ is -1.18 V . Why is this value highly negative in comparison to neighbouring d block elements?
- (c) Which element of 3d series has lowest enthalpy of atomisation and why?
- (d) What happens when sodium chromate is acidified?
- (e) Zn, Cd and Hg are soft metals. Why?
- (f) Why is permanganate titration not carried out in the presence of HCl?
- (g) The lower oxides of transition metals are basic whereas the highest are amphoteric/acidic. Give reason.

[5 marks]

Solution:

Concept:

- Electronic configurations influence oxidation-state stability: empty, half-filled and completely filled subshells can confer extra stability.
- Metallic bonding depends on the availability of valence electrons for bonding; oxide acid-base character changes with the metal's oxidation state.
- Acidification shifts the chromate-dichromate equilibrium, while acidified permanganate can oxidise

Quick Tip to Solve: Write the ion's electronic configuration first for stability questions; distinguish acid-base chromate equilibrium from permanganate redox chemistry.

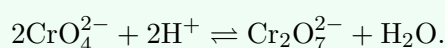
chloride ions.

Step 1: (a) Oxidation of cerium(III) Ce^{3+} has the configuration $[\text{Xe}]4f^1$. Loss of this $4f$ electron gives Ce^{4+} , with the stable noble-gas configuration $[\text{Xe}]4f^0$. Formation of this configuration accounts for the accessibility of the +4 oxidation state and the stated oxidation of Ce(III) to Ce(IV).

Step 2: (b) Highly negative manganese reduction potential Mn^{2+} has an especially stable half-filled $3d^5$ configuration. Reduction to manganese metal destroys this stable ionic configuration and is comparatively unfavourable. Consequently, the standard potential for $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$ is highly negative, -1.18 V , relative to neighbouring elements.

Step 3: (c) Lowest enthalpy of atomisation Zinc has the lowest enthalpy of atomisation in the 3d series. Its $[\text{Ar}]3d^{10}4s^2$ configuration has a completely filled d subshell with no unpaired d electrons. The d electrons contribute comparatively little to metallic bonding, so the cohesive metallic bonding is weak and relatively little energy is needed to separate the metal into gaseous atoms.

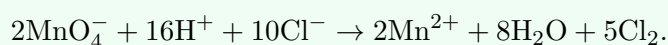
Step 4: (d) Acidification of sodium chromate Yellow chromate ions are converted into orange dichromate ions on acidification. The equilibrium shifts towards dichromate when hydrogen ions are added:



Chromium retains its +6 oxidation state; this is an acid-dependent equilibrium, not a redox reaction.

Step 5: (e) Softness of zinc, cadmium and mercury These metals have completely filled d^{10} subshells and no unpaired d electrons. Their filled d electrons participate little in metallic bonding. The resulting relatively weak metallic bonds account for their softness; mercury is liquid at room temperature.

Step 6: (f) Avoiding hydrochloric acid in permanganate titration Acidified permanganate oxidises chloride ions from HCl to chlorine. This unwanted side reaction consumes permanganate, so the titre no longer measures only the intended reducing agent:



Dilute sulphuric acid is therefore used to provide the acidic medium instead.

Step 7: (g) Acid-base character of oxides At low oxidation states, metal-oxygen bonding is more ionic and the oxides exhibit basic character, reacting with acids. At high oxidation states, the metal ion has greater polarising power and the metal-oxygen bonds become more covalent; the oxides show amphoteric or acidic behaviour. For example, CrO is basic, Cr_2O_3 is amphoteric and CrO_3 is acidic.

Step 8: Conclusion Any five of the seven responses above may be selected. The key results are stable Ce^{4+} , stable Mn^{2+} , zinc's weak metallic bonding, orange dichromate on acidification, weak bonding in Zn/Cd/Hg, chloride oxidation by permanganate, and increasing oxide acidity with oxidation state.

Quick Tip to Solve: Write the ion's electronic configuration first for stability questions; distinguish acid-base chromate equilibrium from permanganate redox chemistry.