CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-S-1 - Compartment

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. A conductivity cell contains electrodes made up of : [1 mark]

(A) Silver

(B) Copper

(C) Platinum

(D) Zinc

Correct Answer: (C) Platinum

Solution:

Concept:

- A conductivity cell measures the conductance of an electrolyte between two electrodes of known geometry.
- The electrodes should conduct electricity well and resist chemical attack by the solution.

Step 1: Identify the electrode material Conductivity cells use platinum electrodes, usually coated with finely divided platinum (platinum black). Platinum is chemically inert under the measurement conditions; the coating increases the effective surface area and helps reduce electrode polarisation.

Step 2: Compare the alternatives Silver, copper and zinc are more liable to participate in electrode reactions or undergo chemical change with suitable electrolytes. They are therefore not the standard electrode material used for a general conductivity cell.

Step 3: Conclusion The electrodes are made of platinum. Hence, the correct option is (C).

Quick Tip to Solve: For a conductivity cell, recall platinised platinum electrodes: inert metal with a large effective surface area.

2. The value of K_H at 298 K for Ar(g), CO_2(g), HCHO(g) and CH_4(g) are 40.32, 1.68, 1.84x10^{-5} and 0.416 kbar respectively. When these gases are arranged in increasing order of solubility, the correct order is : [1 mark]

(A) HCHO $<$ CH_4 $<$ CO_2 $<$ Ar

(B) HCHO $<$ CO_2 $<$ CH_4 $<$ Ar

(C) Ar $<$ CO_2 $<$ CH_4 $<$ HCHO

(D) Ar $<$ CH_4 $<$ CO_2 $<$ HCHO

Correct Answer: (C) Ar $<$ CO_2 $<$ CH_4 $<$ HCHO

Solution:

Concept:

- Henry's law is $p = K_H x$, where p is the gas partial pressure and x its mole fraction in solution.
- At a fixed temperature and equal gas partial pressure, $x = p/K_H$; hence solubility decreases as K_H increases.

Step 1: Arrange the Henry constants The given constants, in decreasing order, are

$$40.32 > 1.68 > 0.416 > 1.84 \times 10^{-5}.$$

These correspond respectively to $\mathrm{Ar}, \mathrm{CO_2}, \mathrm{CH_4}, \mathrm{HCHO}$. All constants have the same unit, so they can be compared directly.

Step 2: Reverse the order for solubility Since solubility varies inversely with K_H, the gas with the largest constant is least soluble. Thus Ar is least soluble and HCHO is most soluble. Options (A) and (B) reverse the end members; option (D) incorrectly interchanges methane and carbon dioxide.

Step 3: Conclusion The increasing order is $\mathrm{Ar} < \mathrm{CO_2} < \mathrm{CH_4} < \mathrm{HCHO}$. Hence, the correct option is (C).

Quick Tip to Solve: Write the Henry constants from largest to smallest to obtain increasing solubility at equal pressure.

3. Out of the following organic compounds, the one which will react with Lucas reagent at room temperature is : [1 mark]

(A) CH_2=CH-CH_2OH

(B) $CH_3CH_2CH_2OH$

(C) $C_6H_5CH_2OH$

(D) $(CH_3)_3COH$

Correct Answer: (D) $(CH_3)_3COH$

Solution:

Concept:

- Lucas reagent is concentrated HCl with anhydrous $\mathrm{ZnCl_2}$; alcohols form alkyl chlorides, producing turbidity.
- Formation of a stable carbocation favours rapid substitution; tertiary, benzylic and allylic alcohols can react at room temperature.

Step 1: Apply the usual alcohol classification Option (D), $(\mathrm{CH_3})_3\mathrm{COH}$, is tert-butyl alcohol. Its tertiary carbocation is stabilised by alkyl groups, so it reacts rapidly with Lucas reagent at room temperature:

$$(\mathrm{CH_3})_3\mathrm{COH} + \mathrm{HCl} \longrightarrow (\mathrm{CH_3})_3\mathrm{CCl} + \mathrm{H_2O}.$$

Option (B), propan-1-ol, is an ordinary primary alcohol and does not give rapid turbidity at room temperature.

Step 2: Check the special primary alcohols Option (A) is allyl alcohol and option (C) is benzyl alcohol. Although formally primary, both can react at room temperature because the corresponding allylic and benzylic carbocations are resonance stabilised. Therefore, the printed question does not have a chemically unique choice: the usual intended tertiary-alcohol answer is (D), while (A) and (C) are also defensible for the wording given.

Step 3: Conclusion Option (D), tert-butyl alcohol, is the standard intended answer. The allylic and benzylic alcohols also react at room temperature, so the printed choice is not unique.

Quick Tip to Solve: In a Lucas test, check for allylic or benzylic resonance before applying the ordinary primary-alcohol rule.

4. Identify the Freon from the following compounds : [1 mark]

(A) CCl_2F_2

(B) CCl_2Br_2

(C) $CH_2Cl\text{-}CHCl_2$

(D) $CHCl_2\text{-}CHCl_2$

Correct Answer: (A) CCl_2F_2

Solution:

Concept:

- Freons are chlorofluorocarbon compounds containing carbon, chlorine and fluorine.
- Freon-12 is dichlorodifluoromethane, CCl_2F_2, formerly widely used as a refrigerant.

Step 1: Identify the chlorofluorocarbon Option (A), CCl_2F_2, contains two chlorine and two fluorine atoms attached to a single carbon atom. This is the formula of Freon-12.

Step 2: Eliminate the other compounds Option (B), CCl_2Br_2, contains bromine but no fluorine. Options (C) and (D) are chlorinated ethanes and also contain no fluorine. Thus none of these three compounds is the Freon represented in this question.

Step 3: Conclusion Freon is CCl_2F_2. Hence, the correct option is (A).

Quick Tip to Solve: Look for both chlorine and fluorine: Freon-12 has formula CCl2F2, with no hydrogen atoms.

5. If the half-life period of a first order reaction is 1386 s, then the rate constant of this reaction is : [1 mark]

(A) $0.5x10^{-2}\ s^{-1}$

(B) $0.5x10^{-3}\ s^{-1}$

(C) $5x10^{-2}\ s^{-1}$

(D) $5x10^{-3}\ s^{-1}$

Correct Answer: (B) $0.5x10^{-3}\ s^{-1}$

Solution:

Concept:

- For a first order reaction, $t_{1/2} = \ln 2/k = 0.693/k$, where k is the rate constant.
- When half-life is measured in seconds, the first order rate constant has unit s^{-1}.

Step 1: Substitute the half-life Rearranging the first order half-life formula gives

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{1386\,\text{s}}.$$

The half-life is independent of initial concentration, so no concentration data are required.

Step 2: Evaluate and compare the options Since $1386 = 2 \times 693$,

$$k = 0.0005\,\text{s}^{-1} = 0.5 \times 10^{-3}\,\text{s}^{-1}.$$

Options (A) and (D) both equal $0.005\,\text{s}^{-1}$, ten times the required value; option (C) is one hundred times the required value.

Step 3: Conclusion The rate constant is $0.5 \times 10^{-3}\,\text{s}^{-1}$. Hence, the correct option is (B).

Quick Tip to Solve: Use k = 0.693/half-life, then check the decimal value before matching powers of ten.

6. The standard electrode potential of 'A', 'B' and 'C' are +0.68 V, -2.54 V and -0.50 V respectively. The order of their reducing power is : [1 mark]

(A) A > B > C

(B) A > C > B

(C) B > C > A

(D) C > B > A

Correct Answer: (C) B > C > A

Solution:

Concept:

- A reducing agent donates electrons and itself undergoes oxidation.
- For standard reduction potentials, a more negative E° means a greater tendency of the reduced species to undergo oxidation and hence stronger reducing power.

Step 1: Compare the potentials The standard reduction potentials are

$$E^\circ_B = -2.54\,\text{V} < E^\circ_C = -0.50\,\text{V} < E^\circ_A = +0.68\,\text{V}.$$

Thus reduction is least favourable for B and most favourable for A.

Step 2: Infer electron-donating tendency Reverse the reduction tendency to rank the reducing agents. B most readily loses electrons, followed by C, whereas A is the weakest reducing agent of the three. Therefore, options placing A first or placing C ahead of B are inconsistent with the given reduction potentials.

Step 3: Conclusion The reducing power decreases as $B > C > A$. Hence, the correct option is (C).

Quick Tip to Solve: For reducing power, put the most negative standard reduction potential first.

7. Glucose on reaction with Br_2 water gives : [1 mark]

(A) Gluconic acid

(B) Hexanoic acid

(C) Saccharic acid

(D) Glycolic acid

Correct Answer: (A) Gluconic acid

Solution:

Concept:

- Bromine water is a mild oxidising agent that oxidises an aldehyde group to a carboxylic acid group.
- In the open-chain form of glucose, the aldehyde group is oxidised while the terminal primary alcohol group remains unchanged.

Step 1: Identify the group oxidised The open-chain structure of glucose is $CHO(CHOH)_4CH_2OH$. Bromine water converts only its $-CHO$ group into $-COOH$:

$$CHO(CHOH)_4CH_2OH + Br_2 + H_2O$$

$$\longrightarrow COOH(CHOH)_4CH_2OH + 2HBr.$$

Step 2: Name the product and reject alternatives The product is gluconic acid. Saccharic acid requires oxidation of both terminal groups, as with strong nitric acid oxidation. Hexanoic acid would lack the hydroxyl groups retained here, and glycolic acid has only two carbon atoms, so neither can be the product of this mild oxidation.

Step 3: Conclusion Glucose gives gluconic acid with bromine water. Hence, the correct option is (A).

Quick Tip to Solve: Bromine water oxidises only glucose's aldehyde end; nitric acid oxidises both ends to saccharic acid.

8. A compound $CaCl_2.6H_2O$ undergoes complete dissociation in water. The Van't Hoff factor (i) is : [1 mark]

(A) 9

(B) 6

(C) 4

(D) 3

Correct Answer: (D) 3

Solution:

Concept:

- The van't Hoff factor i is the ratio of solute particles after dissolution to formula units initially dissolved.
- Complete dissociation of one formula unit of calcium chloride produces one calcium ion and two chloride ions.

Step 1: Write the dissociation In aqueous solution,

$$\mathrm{CaCl_2 \cdot 6H_2O(s)} \longrightarrow \mathrm{Ca^{2+}(aq) + 2Cl^{-}(aq) + 6H_2O(l)}.$$

The six waters of crystallisation join the water solvent; they are not counted as additional solute particles.

Step 2: Count solute particles Each formula unit gives $1 + 2 = 3$ dissolved ions, so $i = 3$. Counting the six water molecules as solute would incorrectly give 9; 6 and 4 likewise do not equal the ionic particle count.

Step 3: Conclusion The van't Hoff factor is $\boxed{3}$. Hence, the correct option is (D).

Quick Tip to Solve: Count only the dissociated solute ions; waters of crystallisation become part of the solvent.

9. The transition element which shows both +1 and +2 oxidation states is : [1 mark]

(A) Sc

(B) Mn

(C) Cu

(D) Zn

Correct Answer: (C) Cu

Solution:

Concept:

- Copper has ground-state electronic configuration $[\mathrm{Ar}]3d^{10}4s^1$.
- On ionisation, the outer $4s$ electron is lost before a $3d$ electron.

Step 1: Form the two copper ions Loss of one electron gives $\mathrm{Cu^+}$: $[Ar]3d^{10}$, whereas loss of a further electron gives $\mathrm{Cu^{2+}}$: $[Ar]3d^9$. Thus copper commonly exhibits both $+1$ and $+2$ oxidation states.

Step 2: Compare the alternatives Scandium characteristically shows $+3$; manganese commonly shows states beginning with $+2$, with $+1$ not its characteristic simple-ion state in this comparison. Zinc characteristically forms $\mathrm{Zn^{2+}}$ and is not a transition element because its atom and usual ion have complete d subshells.

Step 3: Conclusion $\boxed{\mathrm{Cu}}$ shows both oxidation states. Hence, the correct option is (C).

Quick Tip to Solve: For copper, remove the single 4s electron first, then one 3d electron to obtain Cu(I) and Cu(II).

10. Which one of the following halides contains $C_{sp^2} - X$ bond ? [1 mark]

(A) Alkyl halide

(B) Allyl halide

(C) Benzyl halide

(D) Vinyl halide

Correct Answer: (D) Vinyl halide

Solution:

Concept:

- The carbon directly bonded to the halogen determines whether the bond is $C_{sp^2} - X$ or $C_{sp^3} - X$.
- A carbon in a carbon-carbon double bond is sp^2 hybridised.

Step 1: Locate the halogen-bearing carbon A vinyl halide has the form $CH_2 = CH - X$. The halogen is bonded directly to a double-bonded carbon, so the required bond is $C_{sp^2} - X$.

Step 2: Eliminate neighbouring unsaturation An alkyl halide has its halogen on an sp^3 carbon. In an allyl halide, $CH_2 = CH - CH_2 - X$, the halogen-bearing carbon is adjacent to the double bond but remains sp^3. In a benzyl halide, $C_6H_5 - CH_2 - X$, it is the side-chain CH_2 carbon, also sp^3.

Step 3: Conclusion $\boxed{\text{Vinyl halide}}$ contains the stated bond. Hence, the correct option is (D).

Quick Tip to Solve: Inspect the carbon bonded directly to X; a nearby double bond or benzene ring is not sufficient.

11. Which of the following amines has the highest boiling point ? [1 mark]

(A) 2,2-Dimethyl propanamine

(B) 3-Methylbutanamine

(C) 2-Methylbutanamine

(D) Pentanamine

Correct Answer: (D) Pentanamine

Solution:

Concept:

- Isomeric primary amines can form intermolecular hydrogen bonds through their $N - H$ groups.
- For comparable hydrogen bonding and equal molar mass, a less branched chain has greater surface contact and stronger dispersion attractions.

Step 1: Compare the common features All four choices are primary amines with five carbon atoms and the same molecular formula. Their similar functional groups permit intermolecular hydrogen bonding, so the principal comparison here is the extent of carbon-chain branching.

Step 2: Identify the least branched molecule Pentanamine has a straight carbon chain. The methylbutanamines are branched, and 2,2-dimethylpropanamine is more compact. Branching decreases effective molecular surface contact and dispersion attraction; the unbranched pentanamine therefore

requires the greatest thermal energy for vaporisation.

Step 3: Conclusion Pentanamine has the highest boiling point. Hence, the correct option is (D).

Quick Tip to Solve: Among isomeric primary amines, compare branching after confirming that their hydrogen-bonding groups match.

12. When phenyl methyl ether is heated with HI, it produces : [1 mark]

(A) Methyl chloride and Iodobenzene

(B) Benzene and Methanol

(C) Iodobenzene and Methanol

(D) Phenol and Methyl iodide

Correct Answer: (D) Phenol and Methyl iodide

Solution:

Concept:

- Protonation of an ether oxygen by HI makes ether cleavage possible.
- In an aryl methyl ether, iodide attacks the methyl carbon by S_N2; the aryl carbon-oxygen bond is resistant to this attack.

Step 1: Activate and cleave the ether Phenyl methyl ether is anisole, $C_6H_5 - O - CH_3$. After oxygen protonation, I^- attacks the unhindered methyl carbon, breaking the methyl-oxygen bond. The products are

$$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I.$$

Step 2: Check the proposed product pairs Iodobenzene is not produced because iodide does not displace the phenoxy group at the aryl sp^2 carbon by the usual S_N2 route. Thus options (A) and (C) fail; HI also supplies no chlorine for (A). Option (B) is inconsistent with acid cleavage, which yields methyl iodide rather than benzene and methanol.

Step 3: Conclusion The products are phenol and methyl iodide. Hence, the correct option is (D).

Quick Tip to Solve: For anisole with HI, break the O-methyl bond and retain the aryl-O bond to obtain phenol.

13. Assertion (A): Actinoids show a wide range of oxidation states.

Reason (R): Actinoids are radioactive in nature. [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:

- Actinoid oxidation states depend on the availability of $5f$, $6d$ and $7s$ electrons for bonding.
- Radioactivity is a property of an unstable atomic nucleus.

Step 1: Judge the assertion The assertion is true. Actinoids show many oxidation states because their $5f$, $6d$ and $7s$ subshells have comparable energies, allowing different numbers of electrons to participate in bonding.

Step 2: Judge the reason The reason is also true: actinoids are radioactive. Their nuclei can undergo spontaneous decay with emission of radiation.

Step 3: Test the explanatory connection Radioactive decay concerns nuclear instability, whereas variable oxidation states arise from electronic structure and the similar subshell energies. Radioactivity therefore does not explain the assertion. The codes claiming a false assertion or false reason are also excluded.

Step 4: Conclusion Both statements are true, but R does not explain A. Hence, the correct option is (B).

Quick Tip to Solve: Separate nuclear properties from electronic properties when testing an explanation about oxidation states.

14. Assertion (A): Presence of -NO_2 group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reactions.

Reason (R): Nitro group decreases the electron density over the benzene ring. [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:

- The nitro group withdraws electron density by inductive and resonance effects.
- Ortho or para nitro substitution stabilises the anionic intermediate in nucleophilic aromatic substitution.

Step 1: Judge the assertion The assertion is true. A nitro group ortho or para to the halogen increases a haloarene's reactivity towards nucleophilic substitution, relative to the corresponding unsubstituted haloarene.

Step 2: Judge the reason The reason is true. The electron-withdrawing nitro group reduces electron density in the aromatic ring, making attack by a nucleophile more favourable.

Step 3: Connect the statements At an ortho or para position, the nitro group also accepts electron density by resonance from the negatively charged substitution intermediate. This stabilisation promotes substitution and explains the stated activation. Both truth and the explanatory connection hold, excluding the other three codes.

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

Quick Tip to Solve: For nucleophilic aromatic substitution, an ortho or para nitro group stabilises the anionic intermediate.

15. Assertion (A): The molecularity of the reaction $H_2 + Br_2 \rightarrow 2HBr$ appears to be 2.

Reason (R): Two molecules of the reactants are involved in the given elementary reaction. [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:

- Molecularity counts the reacting species in a single elementary step; it is not generally inferred from an overall balanced equation.
- An overall reaction may involve several elementary steps even when its equation contains only two reactant molecules.

Step 1: Judge Assertion (A) The equation $H_2 + Br_2 \rightarrow 2HBr$ shows one molecule each of hydrogen and bromine. Counting these gives an apparent molecularity of $1 + 1 = 2$. Since the assertion carefully says "appears to be", it is true.

Step 2: Judge Reason (R) The formation of hydrogen bromide is a complex chain reaction, rather than the single elementary collision claimed in the reason. Consequently, the overall equation cannot establish its molecularity. Reason (R) is false.

Step 3: Select the code The true assertion and false reason select code (C). Codes (A) and (B) incorrectly make the reason true, while (D) incorrectly makes the assertion false.

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

Quick Tip to Solve: Notice "appears": counting overall reactants does not prove that a reaction is elementary.

16. Assertion (A): p-methoxyphenol is a stronger acid than p-nitrophenol.

Reason (R): Methoxy group is electron-donating group whereas nitro group is electron-withdrawing.

[1 mark]

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

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

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

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

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

Solution:

Concept:

- An acid is stronger when its conjugate base is more stable.
- An electron-withdrawing substituent stabilises phenoxide charge, whereas an electron-donating substituent tends to destabilise it.

Step 1: Judge Assertion (A) On losing H^+, each phenol forms a phenoxide ion. The para nitro group withdraws electron density and stabilises the negative charge through resonance. The para methoxy group donates electron density by resonance and makes the phenoxide ion less stable. Thus p-nitrophenol is the stronger acid, so Assertion (A) is false.

Step 2: Judge Reason (R) The methoxy group is electron donating through its resonance effect on the aromatic ring, whereas the nitro group is electron withdrawing. The stated reason is therefore true.

Step 3: Select the code False A and true R correspond to (D). Options (A), (B) and (C) all require a true assertion and therefore cannot apply.

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

Quick Tip to Solve: Compare phenoxide stability: a para nitro group favours acidity; a para methoxy group opposes it.

Section B (10 marks)

17. Give one point of difference between the following :

(a) Starch and Cellulose

(b) Primary and Secondary structure of protein

[2 marks]

Solution:

Concept:

- Polysaccharides differ in the configuration of their glucose units and the glycosidic linkages joining them.
- Protein structure is described at successive levels: amino acid sequence, then local folding of the

polypeptide chain.

Step 1: (a) Starch and cellulose Starch is a polymer of α-D-glucose, whereas cellulose is a polymer of β-D-glucose. Starch contains $\alpha(1 \rightarrow 4)$ linkages along its chains (and $\alpha(1 \rightarrow 6)$ branch linkages in amylopectin); cellulose contains $\beta(1 \rightarrow 4)$ linkages.

Step 2: (b) Primary and secondary protein structure Primary structure is the specific sequence of amino acids linked by peptide bonds in a polypeptide. Secondary structure is the regular local folding of that chain, such as an α-helix or β-pleated sheet, stabilised mainly by hydrogen bonding between backbone $\mathrm{C}=\mathrm{O}$ and $\mathrm{N}-\mathrm{H}$ groups. Thus sequence and local spatial arrangement describe different levels of the same protein.

Step 3: Conclusion Starch has α-glucose units; cellulose has β-glucose units. Primary structure specifies amino acid sequence, whereas secondary structure specifies regular local folding.

Quick Tip to Solve: For the protein comparison, pair "sequence" with primary and "helix or sheet" with secondary.

18. Visha diluted the solutions of two electrolytes A and B. She observed that Λ_m of A increased 28 times whereas Λ_m of B increased 1.8 times. Which of the two is a strong electrolyte ? Justify your answer by graphically explaining the behaviour of A and B. [2 marks]

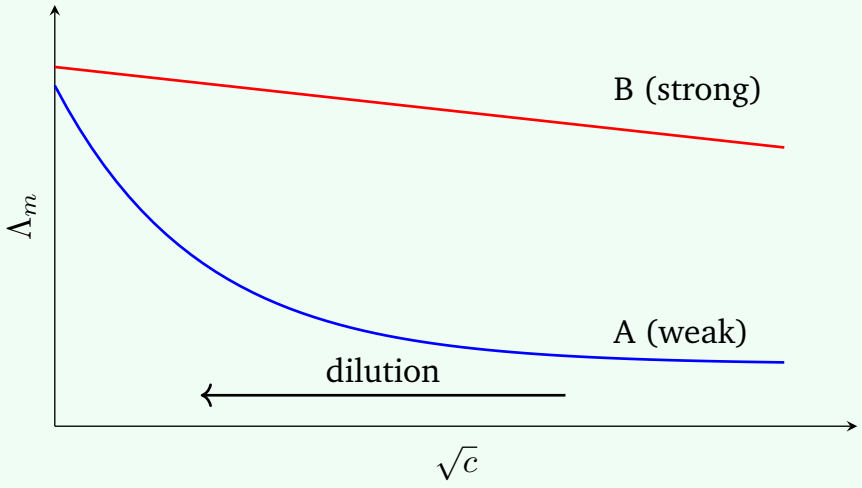
Solution:

Concept:

- Molar conductivity Λ_m is conductivity per unit molar concentration; it rises on dilution as ionic mobility and, for weak electrolytes, ionisation increase.
- For a strong electrolyte, $\Lambda_m = \Lambda_m^\circ - K\sqrt{c}$ at low concentration, where c is concentration and K is a positive constant.

Step 1: Identify the electrolyte Electrolyte B shows only a 1.8-fold increase in Λ_m, consistent with a strong electrolyte that is already almost completely dissociated. Dilution mainly reduces interionic attractions and increases ionic mobility. Electrolyte A shows a much larger, 28-fold increase: it is a weak electrolyte whose degree of ionisation rises markedly on dilution.

Step 2: Explain the graph Plot Λ_m vertically against $\sqrt{c}$ horizontally. Dilution moves left towards $c = 0$. B gives an approximately straight descending line as concentration increases, so dilution raises its molar conductivity gradually. A gives a curved plot that rises steeply on approaching zero concentration because many more ions are formed. The curves below are schematic; their relative heights do not represent measured values.



Schematic molar conductivity plots; dilution is towards the left.

Step 3: Conclusion B is the strong electrolyte and A is the weak electrolyte. Their gradual linear and sharp nonlinear increases on dilution explain the observed factors.

Quick Tip to Solve: On a conductivity-versus-square-root-concentration graph, dilution means moving to the left.

19(a). Define Fuel cell. Write two advantages of fuel cell over ordinary cell. [2 marks]

Solution:

Concept:

- A galvanic cell converts the chemical energy of a spontaneous redox reaction into electrical energy.
- A fuel cell receives a continuous supply of fuel and oxidant at its electrodes, allowing continued generation of electricity while reactants are supplied.

Step 1: Define a fuel cell A fuel cell is a galvanic cell in which a continuously supplied fuel is oxidised and an oxidant is reduced, directly converting their chemical energy into electrical energy. For example, a hydrogen-oxygen fuel cell operates with the overall reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l).$$

The reactants are fed from outside the cell rather than being present only as a fixed internal charge.

Step 2: State two advantages First, a fuel cell can operate continuously as long as the fuel and oxidant are supplied and products are removed; it does not require replacement or recharging after exhausting a fixed amount of stored electrode reactant. Second, the hydrogen-oxygen fuel cell is environmentally clean in operation because its reaction product is water, avoiding the harmful chemical waste associated with many ordinary cells.

Step 3: Conclusion A fuel cell directly produces electricity from continuously supplied fuel and oxidant. Two advantages are continuous operation with reactant supply and clean operation of the hydrogen-oxygen cell, producing water.

Quick Tip to Solve: Use the hydrogen-oxygen example to connect the two advantages to continuous feed and water formation.

OR

19(b). Predict the products of electrolysis in each of the following :

(i) A dilute solution of H_2SO_4 with platinum electrodes

(ii) An aqueous solution of $CuCl_2$ with platinum electrodes [2 marks]

Solution:

Concept:

- Electrolysis involves reduction at the cathode and oxidation at the anode. Platinum electrodes are inert and do not themselves supply ions.
- The products depend on preferential discharge of the species present; sulfate ions remain in solution during electrolysis of dilute sulfuric acid.

Step 1: (i) Dilute sulfuric acid At the cathode, hydrogen ions gain electrons and hydrogen gas is evolved. At the anode, water is oxidised to oxygen gas:

$$\text{Cathode: } 2\text{H}^+ + 2e^- \longrightarrow \text{H}_2(g)$$
$$\text{Anode: } 2\text{H}_2\text{O} \longrightarrow \text{O}_2(g) + 4\text{H}^+ + 4e^-.$$

Thus, water is decomposed overall, giving hydrogen and oxygen in the volume ratio $2 : 1$.

Step 2: (ii) Aqueous copper(II) chloride Copper(II) ions are preferentially reduced, depositing copper metal at the cathode. Chloride ions are oxidised at the inert anode, liberating chlorine:

$$\text{Cathode: } \text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}(s)$$
$$\text{Anode: } 2\text{Cl}^- \longrightarrow \text{Cl}_2(g) + 2e^-.$$

The overall reaction is $\text{CuCl}_2(aq) \longrightarrow \text{Cu}(s) + \text{Cl}_2(g)$.

Step 3: Conclusion (i) Cathode: hydrogen; anode: oxygen. (ii) Cathode: copper; anode: chlorine.

Quick Tip to Solve: For inert Pt electrodes, list cathodic reduction and anodic oxidation separately before naming the products.

20. (a) Name the reaction which can be used to distinguish chemically between aniline and N,N-dimethylaniline.

(b) Why can aniline not be prepared by the ammonolysis of chlorobenzene under normal conditions ?

[2 marks]

Solution:

Concept:

- The carbylamine reaction is a characteristic test for primary amines; secondary and tertiary amines do not give this test.
- In an aryl halide, resonance gives the carbon-halogen bond partial double-bond character, making ordinary nucleophilic substitution difficult.

Step 1: (a) Apply the carbylamine test Heat the amine with chloroform and alcoholic potassium hydroxide. Aniline, a primary aromatic amine, forms foul-smelling phenyl isocyanide:

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \xrightarrow{heat} C_6H_5NC + 3\,KCl + 3\,H_2O.$$

N,N-dimethylaniline is a tertiary amine and has no N–H bond, so it does not form an isocyanide. This difference distinguishes the two compounds.

Step 2: (b) Explain the resistance of chlorobenzene In chlorobenzene, a lone pair on chlorine is delocalised into the benzene ring. Consequently, the $C-Cl$ bond acquires partial double-bond character and becomes shorter and stronger than the corresponding bond in an alkyl chloride. Also, chlorine is bonded to an sp^2-hybridised carbon. Ammonia therefore cannot readily displace chloride under normal conditions, so normal ammonolysis does not produce aniline.

Step 3: Conclusion (a) Carbylamine reaction. (b) Resonance strengthens the aryl $C-Cl$ bond, preventing its easy cleavage by ammonia under normal conditions.

Quick Tip to Solve: Identify the amine class first: aniline is primary, whereas N,N-dimethylaniline is tertiary and fails the carbylamine test.

21. By giving reasons, explain how the rate of the reaction for a given reaction will be affected when :
(a) the temperature at which the reaction was taking place is decreased.
(b) a catalyst is added. [2 marks]

Solution:

Concept:

- For fixed reactant concentrations, the reaction rate depends on its rate constant k. The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where E_a is activation energy, T absolute temperature, R the gas constant and A the frequency factor.
- Only collisions with sufficient energy and suitable orientation lead to products. A catalyst provides an alternative reaction pathway with a lower activation barrier.

Step 1: (a) Decrease the temperature On lowering the temperature, the average kinetic energy of reactant molecules decreases. The fraction of molecules possessing energy equal to or greater than the activation energy becomes smaller, so fewer effective collisions occur per unit time. For a reaction with positive activation energy, the Arrhenius factor $e^{-E_a/(RT)}$ and hence k decrease. Thus, at the same concentrations, the reaction rate decreases.

Step 2: (b) Add a catalyst A suitable catalyst supplies an alternative mechanism with lower activation energy. At the same temperature, a larger fraction of reacting molecules can cross this smaller barrier; the number of effective reaction events increases and the rate increases. The catalyst is regenerated during the reaction. It does not change the reaction enthalpy or the equilibrium constant; it speeds attainment of equilibrium by increasing both forward and reverse reaction rates.

Step 3: Conclusion (a) Decreasing temperature decreases the rate. (b) Adding a suitable catalyst increases the rate by lowering the activation barrier.

Quick Tip to Solve: Use the activation-energy picture: cooling reduces the energetic fraction, while a catalyst lowers the energy threshold.

Section C (21 marks)

22. (a) Write IUPAC name of the complex $[Co(NH_3)_5(ONO)]^{2+}$.

(b) Write the hybridization of $[Ni(CN)_4]^{2-}$ and predict its magnetic behaviour. [Atomic number: Ni = 28]

(c) What type of isomerism is shown by the given complex: $[Co(NH_3)_6][Cr(CN)_6]$? [3 marks]

Solution:

Concept:

- Name neutral NH_3 ligands as ammine. For the ambidentate nitrite ligand, ONO denotes attachment through oxygen, named nitrito-O.
- A strong-field ligand such as CN^- can pair the $3d$ electrons of Ni^{2+}, allowing square-planar dsp^2 hybridisation.
- Coordination isomerism is possible when both the cation and anion are complex ions and ligands can be interchanged between their metal centres.

Step 1: (a) Name the cobalt complex Let the oxidation state of cobalt in $[Co(NH_3)_5(ONO)]^{2+}$ be x. The five ammine ligands are neutral and nitrite has charge -1, so $x - 1 = +2$, giving $x = +3$. Since the complex is cationic, the metal is named cobalt. The oxygen-bound nitrite ligand is nitrito-O. The IUPAC name is therefore pentaammine(nitrito-O)cobalt(III) ion.

Step 2: (b) Determine hybridisation and magnetism Nickel has atomic number 28 and configuration $[Ar]3d^8 4s^2$. In $[Ni(CN)_4]^{2-}$, $x + 4(-1) = -2$, so nickel is Ni^{2+}, with configuration $3d^8$. Strong-field cyanide ligands cause pairing in the $3d$ subshell, leaving one $3d$ orbital available. One $3d$, one $4s$ and two $4p$ orbitals form four dsp^2 hybrid orbitals. The complex is square planar and has no unpaired electrons; hence it is diamagnetic.

Step 3: (c) Identify the isomerism The compound $[Co(NH_3)_6][Cr(CN)_6]$ contains a complex cobalt cation and a complex chromium anion. Interchanging the ligands between the two metal centres gives $[Cr(NH_3)_6][Co(CN)_6]$, with the same overall composition but different distribution of ligands. This is coordination isomerism.

Step 4: Conclusion (a) Pentaammine(nitrito-O)cobalt(III) ion. (b) dsp^2, square planar and diamagnetic. (c) Coordination isomerism.

Quick Tip to Solve: Read ONO as oxygen-bound nitrite; for nickel, calculate the oxidation state before assigning the d-electron count.

23. Give reasons for the following :

(a) t-butyl bromide on reaction with sodium methoxide gives alkene as main product and not ether.

(b) o-nitrophenol is steam volatile while p-nitrophenol is not.

(c) Alcohol is less acidic than phenol. [3 marks]

Solution:

Concept:

- A strong base can remove a beta hydrogen from a haloalkane to form an alkene by elimination; steric hindrance suppresses the competing S_N2 substitution.
- Hydrogen bonding affects molecular association and volatility. Acid strength increases when the conjugate base is better stabilised.

Step 1: Explain alkene formation from tert-butyl bromide The carbon bonded to bromine in $(CH_3)_3CBr$ is tertiary and is crowded by three methyl groups. Backside attack by methoxide, needed for ether formation through S_N2 substitution, is therefore hindered. Methoxide is also a strong base: it abstracts a beta hydrogen while bromide leaves, favouring elimination. Thus 2-methylpropene is the major product:

$$(CH_3)_3CBr + NaOCH_3 \longrightarrow CH_2 = C(CH_3)_2 + CH_3OH + NaBr.$$

Step 2: Compare the hydrogen bonding in nitrophenols In o-nitrophenol, the adjacent nitro and hydroxyl groups form intramolecular hydrogen bonding within one molecule. This reduces association between different molecules and makes the compound steam volatile. In p-nitrophenol, the groups are too far apart for this intramolecular bond; instead, intermolecular hydrogen bonding associates molecules. More energy is required to separate them, so p-nitrophenol is not steam volatile.

Step 3: Compare the conjugate bases of alcohol and phenol Phenol loses H^+ to give phenoxide, whose negative charge is delocalised over oxygen and the aromatic ring through resonance. Alcohol gives an alkoxide ion, in which the negative charge is localised mainly on oxygen. Moreover, an alkyl group has an electron-releasing $+I$ effect that destabilises this negative charge. The better stabilised phenoxide ion forms more readily, making phenol more acidic than an alcohol.

Step 4: Conclusion (a) Steric hindrance and the strong basicity of methoxide favour elimination. (b) Intramolecular hydrogen bonding makes o-nitrophenol steam volatile, whereas intermolecular association reduces the volatility of p-nitrophenol. (c) Resonance stabilisation of phenoxide makes phenol more acidic.

Quick Tip to Solve: For acidity compare conjugate-base stability; for volatility distinguish hydrogen bonds within and between molecules.

24. Calculate emf of the following cell at 298 K :

Mg(s) | Mg^{2+} (0.001 M) || Cu^{2+} (0.0001 M) | Cu(s)

Given: E°_{cell} = 2.71 V, log 10 = 1 [3 marks]

Solution:

Concept:

- At 298 K, the Nernst equation is $E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of transferred electrons and Q is the reaction quotient.
- Pure solid electrodes have unit activity and do not appear in Q; dilute-ion activities are represented by their molar concentrations.

Step 1: Write the electrode reactions Magnesium is oxidised at the left electrode and copper ions are reduced at the right electrode:

$$\text{Anode: } \mathrm{Mg(s)} \longrightarrow \mathrm{Mg^{2+}(aq)} + 2\mathrm{e^-},$$
$$\text{Cathode: } \mathrm{Cu^{2+}(aq)} + 2\mathrm{e^-} \longrightarrow \mathrm{Cu(s)}.$$

Adding them gives $\mathrm{Mg(s)} + \mathrm{Cu^{2+}(aq)} \longrightarrow \mathrm{Mg^{2+}(aq)} + \mathrm{Cu(s)}$. Hence $n = 2$, even though both ionic concentrations differ from their standard values.

Step 2: Calculate the reaction quotient The product ion is $\mathrm{Mg^{2+}}$ and the reactant ion is $\mathrm{Cu^{2+}}$. Therefore

$$Q = \frac{[\mathrm{Mg^{2+}}]}{[\mathrm{Cu^{2+}}]} = \frac{0.001}{0.0001} = 10.$$

The ratio is dimensionless when each concentration is divided by its standard concentration. The metal electrodes are omitted because they are pure solids. The given value $\log 10 = 1$ can now be used directly.

Step 3: Substitute in the Nernst equation Using $E^{\circ}_{\text{cell}} = 2.71\,\text{V}$,

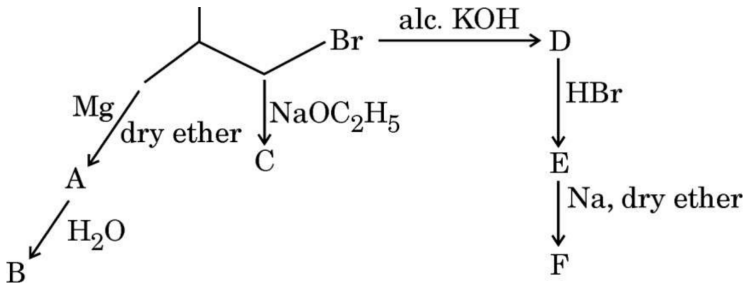
$$\begin{aligned} E_{\text{cell}} &= 2.71 - \frac{0.0591}{2}\log 10 \\ &= 2.71 - 0.02955 \\ &= 2.68045\,\text{V}. \end{aligned}$$

Since $Q > 1$, the correction subtracts from the standard emf, consistent with the higher concentration of product ions relative to reactant ions.

Step 4: Conclusion The cell emf at 298 K is $\boxed{E_{\text{cell}} \approx 2.68\,\text{V}}$.

Quick Tip to Solve: Write the net cell reaction first: it fixes both the electron count and the order of the concentration ratio.

25(a). **Identify 'A' to 'F' in the following reaction sequence :** [3 marks]



Solution:

Concept:

- Magnesium in dry ether converts RBr into the Grignard reagent RMgBr; water then gives RH.
- A primary haloalkane gives an ether with sodium ethoxide by Williamson synthesis. Alcoholic KOH promotes beta elimination; HBr adds to an unsymmetrical alkene by Markovnikov addition.
- In Wurtz coupling, two alkyl halide molecules react with sodium in dry ether to form a carbon-carbon bond between the carbon atoms bearing halogen.

Step 1: Identify A and B from the magnesium branch The starting compound is $(\mathrm{CH_3})_2\mathrm{CHCH_2Br}$, a primary bromide. Magnesium inserts into its carbon-bromine bond:

$$(\mathrm{CH_3})_2\mathrm{CHCH_2Br} \xrightarrow{\mathrm{Mg/dry\ ether}} (\mathrm{CH_3})_2\mathrm{CHCH_2MgBr}\ (A).$$

Hydrolysis protonates the carbon bonded to magnesium:

$$(\mathrm{CH_3})_2\mathrm{CHCH_2MgBr} + \mathrm{H_2O} \longrightarrow (\mathrm{CH_3})_3\mathrm{CH}\ (B) + \mathrm{Mg(OH)Br}.$$

Thus A is 2-methylpropylmagnesium bromide and B is 2-methylpropane.

Step 2: Identify C from sodium ethoxide substitution The brominated carbon is primary, so ethoxide displaces bromide to give the Williamson ether:

$$(\mathrm{CH_3})_2\mathrm{CHCH_2Br} + \mathrm{NaOC_2H_5} \longrightarrow (\mathrm{CH_3})_2\mathrm{CHCH_2OC_2H_5}\ (C) + \mathrm{NaBr}.$$

C is 1-ethoxy-2-methylpropane. The oxygen links the original 2-methylpropyl group to an ethyl group; this branch is substitution, unlike the alcoholic-KOH branch.

Step 3: Identify D and E by elimination and addition Alcoholic KOH removes a beta hydrogen from the adjacent methine carbon and bromide from the terminal carbon, forming $D = \mathrm{CH_2} = \mathrm{C(CH_3)_2}$, 2-methylpropene. Addition of HBr without peroxide follows Markovnikov orientation: hydrogen attaches to the terminal carbon and bromine to the more substituted carbon. Thus

$$\mathrm{CH_2} = \mathrm{C(CH_3)_2} + \mathrm{HBr} \longrightarrow (\mathrm{CH_3})_3\mathrm{CBr}\ (E),$$

where E is 2-bromo-2-methylpropane.

Step 4: Identify F by the indicated Wurtz reaction Coupling the two tert-butyl groups in the printed

sodium/dry-ether step gives

$$2(CH_3)_3CBr + 2Na \longrightarrow (CH_3)_3C - C(CH_3)_3\ (F) + 2NaBr.$$

Thus the identified coupling product F is 2,2,3,3-tetramethylbutane. It contains eight carbon atoms, since two four-carbon alkyl groups have been joined.

Step 5: Conclusion $A = (CH_3)_2CHCH_2MgBr$; $B = (CH_3)_3CH$; $C = (CH_3)_2CHCH_2OC_2H_5$; $D = CH_2 = C(CH_3)_2$; $E = (CH_3)_3CBr$; $F = (CH_3)_3C - C(CH_3)_3$.

Quick Tip to Solve: Keep the four-carbon skeleton through A-E; only the final Wurtz step doubles it to eight carbons.

OR

25(b). What happens when :

(i) methyl chloride is treated with KCN ?

(ii) methyl bromide is treated with NaI in dry acetone ?

(iii) methyl bromide is treated with silver fluoride ? [3 marks]

Solution:

Concept:

- Nucleophilic substitution replaces the halogen of a methyl halide by the attacking nucleophile. The methyl carbon is readily attacked because it is least sterically hindered.
- Cyanide is an ambident nucleophile, but ionic KCN supplies cyanide ions that predominantly bond through carbon to form nitriles. Halogen exchange gives iodides or fluorides with suitable metal halides.

Step 1: Treat methyl chloride with KCN The carbon end of CN^- attacks the methyl carbon and displaces chloride:

$$CH_3Cl + KCN \longrightarrow CH_3CN + KCl.$$

The organic product is ethanenitrile (acetonitrile), containing one more carbon atom than methyl chloride. KCN gives the nitrile, whereas covalent silver cyanide would predominantly give an isocyanide.

Step 2: Treat methyl bromide with sodium iodide In dry acetone, iodide replaces bromide in the Finkelstein reaction:

$$CH_3Br + NaI \xrightarrow{\text{dry acetone}} CH_3I + NaBr \downarrow.$$

The organic product is iodomethane. Sodium bromide is insoluble in acetone and precipitates; its removal helps drive the halogen-exchange reaction towards the product.

Step 3: Treat methyl bromide with silver fluoride Silver fluoride replaces bromine by fluorine in the Swarts reaction:

$$CH_3Br + AgF \longrightarrow CH_3F + AgBr \downarrow.$$

The organic product is fluoromethane, and silver bromide is formed as the inorganic product. This is halogen substitution, so the carbon skeleton remains unchanged.

Step 4: Conclusion The organic products are (i) ethanenitrile, CH_3CN; (ii) iodomethane, CH_3I; and (iii) fluoromethane, CH_3F.

Quick Tip to Solve: For methyl halides, pair KCN with nitrile formation, NaI/dry acetone with Finkelstein exchange, and AgF with Swarts fluorination.

26. Ethanamine reacts with benzoyl chloride to form a product 'X'. Give the structure and IUPAC name of 'X'. Can 'X' undergo Hoffmann bromamide degradation reaction ? If yes, then give the structure of the product. If no, then give reason. [3 marks]

Solution:

Concept:

- Acylation of a primary amine by an acid chloride replaces one hydrogen attached to nitrogen by an acyl group, producing a secondary amide.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into RNH_2 with one fewer carbon atom, using bromine and aqueous alkali. The primary-amide group is essential.

Step 1: Form the benzoylation product Ethanamine, $CH_3CH_2NH_2$, attacks the carbonyl carbon of benzoyl chloride. Chloride is replaced by the amino group and HCl is eliminated:

$$C_6H_5COCl + H_2NCH_2CH_3 \longrightarrow C_6H_5CONHCH_2CH_3 + HCl.$$

Thus the structural formula of X is $C_6H_5 - C(=O) - NH - CH_2CH_3$. A base or excess amine can neutralise the HCl liberated during acylation.

Step 2: Give the IUPAC name The parent amide is benzamide, $C_6H_5CONH_2$. In the product, one hydrogen on its nitrogen has been replaced by an ethyl group. Therefore, the IUPAC name is N-ethylbenzamide. The prefix N- locates the ethyl substituent on nitrogen, rather than on the benzene ring.

Step 3: Test eligibility for Hofmann degradation The product is a secondary amide, $C_6H_5CONHC_2H_5$, rather than a primary amide of the form $RCONH_2$. Hofmann degradation requires the unsubstituted amide group $-CONH_2$. Although X retains one nitrogen-bound hydrogen, its ethyl substituent means that it does not possess this required group. Hence it does not undergo the Hofmann bromamide degradation reaction, and no degradation-product structure applies.

Step 4: Conclusion $X = C_6H_5CONHCH_2CH_3$, named N-ethylbenzamide. It does not undergo Hofmann bromamide degradation because it is a secondary amide and lacks $-CONH_2$.

Quick Tip to Solve: Before applying Hofmann degradation, inspect the amide nitrogen: the required group is -CONH2, not an N-substituted amide.

27. The following data were obtained during the kinetic studies of the reaction :

A + 2B $\rightarrow$ C + 2D

Experiment	Initial [A] (mol/L)	Initial [B] (mol/L)	Initial rate of formation of C (M min^{-1})
1	0.10	0.10	3.0×10^{-4}
2	0.30	0.30	9.0×10^{-4}
3	0.10	0.30	3.0×10^{-4}
4	0.20	0.40	6.0×10^{-4}

Determine the order of reaction with respect to each reactant and the overall order of the reaction. Write the rate law expression for the reaction. [3 marks]

Solution:

Concept:

- For the initial-rate method, assume $r = k[A]^m[B]^n$, where $r = d[C]/dt$, k is the rate constant, and m, n are the experimentally determined orders in A and B.
- Compare experiments in which one reactant concentration stays constant to isolate the order of the other. The overall order is $m + n$; stoichiometric coefficients alone do not determine reaction orders.

Step 1: Determine the order with respect to B Compare experiments 1 and 3. The concentration of A remains $0.10\,\text{mol}\,\text{L}^{-1}$, while B increases from 0.10 to $0.30\,\text{mol}\,\text{L}^{-1}$. The rate remains $3.0 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{min}^{-1}$. Thus

$$\frac{r_3}{r_1} = \left(\frac{[B]_3}{[B]_1}\right)^n \quad \Rightarrow \quad 1 = 3^n \quad \Rightarrow \quad n = 0.$$

The reaction is zero order in B over the studied range.

Step 2: Determine the order with respect to A Compare experiments 3 and 2, for which B remains $0.30\,\text{mol}\,\text{L}^{-1}$. A triples from 0.10 to $0.30\,\text{mol}\,\text{L}^{-1}$, and the rate also triples:

$$\frac{r_2}{r_3} = \frac{9.0 \times 10^{-4}}{3.0 \times 10^{-4}} = 3^m, \qquad 3 = 3^m \quad \Rightarrow \quad m = 1.$$

Therefore, the reaction is first order in A.

Step 3: Write and check the rate law Substituting the orders gives

$$r = \frac{d[C]}{dt} = k[A]^1[B]^0 = k[A].$$

The overall order is $1 + 0 = 1$. As a consistency check, experiment 1 gives $k = (3.0 \times 10^{-4})/0.10 = 3.0 \times 10^{-3}\,\text{min}^{-1}$. With experiment 4, this predicts $r = k(0.20) = 6.0 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}\,\text{min}^{-1}$, agreeing with the table even though B changes.

Step 4: Conclusion Order with respect to A: 1; order with respect to B: 0; overall order: 1. The rate law is $r = k[A]$.

Quick Tip to Solve: Use experiments 1 and 3 to isolate B, then experiments 3 and 2 to isolate A; never infer orders from the coefficients A + 2B.

28. Give plausible explanation for each of the following :

(a) Sodium hydrogen sulphite is used for separation and purification of aldehydes.

(b) 2,2,6-trimethylcyclohexanone does not form cyanohydrin.

(c) Only one -NH_2 group of semicarbazide is involved in the formation of semicarbazone. [3 marks]

Solution:

Concept:

- Carbonyl compounds undergo nucleophilic addition: the electrophilic carbonyl carbon is attacked by a nucleophile such as HSO_3^- or CN^-.
- Steric crowding reduces access to a carbonyl group, while resonance delocalisation reduces the availability of a nitrogen lone pair.

Step 1: (a) Formation and decomposition of a crystalline derivative Aldehydes react with saturated sodium hydrogen sulphite solution to form crystalline, water-soluble addition compounds:

$$RCHO + NaHSO_3 \rightleftharpoons RCH(OH)SO_3Na.$$

The crystals can be separated from impurities that do not form this derivative. Treatment of the isolated addition compound with dilute acid or alkali decomposes it and regenerates the aldehyde. Thus reversible derivative formation allows both separation and purification.

Step 2: (b) Steric hindrance to cyanide attack In 2,2,6-trimethylcyclohexanone, the two methyl groups at carbon 2 and the methyl group at carbon 6 crowd the carbonyl group at carbon 1. They hinder the approach of CN^- to the carbonyl carbon and make formation of the tetrahedral addition product unfavourable. Consequently, cyanohydrin formation does not occur readily.

Step 3: (c) Different lone-pair availability in semicarbazide Semicarbazide has the structure $H_2N - NH - C(=O) - NH_2$. The lone pair of the $-NH_2$ group directly attached to $C = O$ is delocalised into that carbonyl group by resonance, so this nitrogen is a poor nucleophile. The terminal hydrazino H_2N- group has an available lone pair and attacks the aldehyde or ketone. Condensation then gives $R_2C = N - NH - C(=O) - NH_2$ with loss of water.

Step 4: Conclusion (a) Reversible crystalline bisulphite addition permits purification. (b) Methyl-group crowding prevents cyanohydrin formation. (c) Only the terminal hydrazino amino group is sufficiently nucleophilic to form the semicarbazone.

Quick Tip to Solve: In semicarbazide, first identify which amino nitrogen is directly bonded to the carbonyl carbon.

Section D (8 marks)

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

29(a). One of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over. If green light is absorbed by the complex, it appears red. Table given below, gives the relationship between different wavelengths of the light absorbed and the colour observed.

Answer the following questions :

What is spectrochemical series ? Write the relationship between Δ_t and Δ_o. [2 marks]

Coordination Entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue-green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow-orange
$[Co(CN)_6]^{3-}$	310	Ultra-Violet (U.V.)	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue-green	Violet

Solution:

Concept:

- Ligands differ in their ability to split the energies of metal d orbitals; their splitting strength defines their position in the spectrochemical series.
- Δ_o and Δ_t denote octahedral and tetrahedral crystal field splitting energies, respectively.

Step 1: Define the spectrochemical series The spectrochemical series is the arrangement of ligands in increasing order of their crystal field splitting power, that is, increasing magnitude of the splitting energy produced for a given metal ion. Weak-field ligands occur towards the beginning and strong-field ligands towards the end. A representative order is

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < CN^- < CO.$$

This comparison concerns the ability of the ligand to split the metal d-orbital energies, rather than the observed colour alone.

Step 2: Relate tetrahedral and octahedral splitting For the same metal ion, oxidation state and ligands, tetrahedral splitting is smaller than octahedral splitting:

$$\Delta_t = \frac{4}{9}\Delta_o.$$

Tetrahedral coordination has fewer ligands and none approaches directly along the axes of the d orbitals, giving a weaker splitting. The subscripts t and o refer to tetrahedral and octahedral environments.

Step 3: Conclusion The spectrochemical series orders ligands by increasing splitting strength; for

corresponding complexes, $\boxed{\Delta_t = \frac{4}{9}\Delta_o}$.

Quick Tip to Solve: Attach the factor 4/9 to tetrahedral splitting: it is the smaller of the two energies.

29(b). Arrange $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$ and $[Cu(H_2O)_4]^{2+}$ in increasing order of wavelength of light absorbed. [1 mark]

Solution:

Concept:

- For this question, use the absorbed wavelengths listed in the supplied table, rather than ranking the observed colours.
- The photon energy obeys $E = hc/\lambda$; increasing wavelength corresponds to decreasing absorbed photon energy.

Step 1: Read the three wavelengths The table gives 310 nm for $[Co(CN)_6]^{3-}$, 475 nm for $[Co(NH_3)_6]^{3+}$, and 600 nm for $[Cu(H_2O)_4]^{2+}$. These are the wavelengths absorbed, not the wavelengths of the complementary colours seen.

Step 2: Compare the numerical values Since $310 < 475 < 600$, the cyanide complex comes first, followed by the ammine complex and then the aqua complex. No comparison of ligand strengths across different metals is needed because the required measurements are explicitly supplied.

Step 3: Conclusion Increasing absorbed wavelength:

$$\boxed{[Co(CN)_6]^{3-} < [Co(NH_3)_6]^{3+} < [Cu(H_2O)_4]^{2+}}.$$

Quick Tip to Solve: Write the table values beneath the three complexes before arranging them by wavelength.

OR

29(b). On the basis of crystal field theory, write the electronic configuration of d^5 ion if $\Delta_o < P$. [1 mark]

Solution:

Concept:

- In an octahedral field, the three t_{2g} orbitals have lower energy than the two e_g orbitals.
- P is the electron-pairing energy. If $\Delta_o < P$, occupying a higher orbital costs less energy than pairing electrons.

Step 1: Choose high-spin occupation The inequality $\Delta_o < P$ describes a weak-field, high-spin case. Electrons therefore occupy all five available d orbitals singly before pairing, following Hundś rule. The fourth electron enters an e_g orbital instead of pairing in a t_{2g} orbital.

Step 2: Distribute the five electrons The first three electrons occupy the three t_{2g} orbitals separately. The remaining two occupy the two e_g orbitals separately. Thus the lower set contains three electrons and the upper set contains two; all five electrons remain unpaired. The low-spin alternative $t_{2g}^5 e_g^0$ would require the opposite energy preference.

Step 3: Conclusion For d^5 with $\Delta_o < P$, the electronic configuration is $\boxed{t_{2g}^3 e_g^2}$, with five unpaired electrons.

Quick Tip to Solve: When splitting costs less than pairing, put one electron in each d orbital before making a pair.

29(c). Define crystal field splitting energy. [1 mark]

Solution:

Concept:

- Ligand approach removes the equal-energy degeneracy of the five metal d orbitals.
- Crystal field splitting energy measures the energy separation of the resulting sets of orbitals.

Step 1: Identify the splitting caused by ligands In a free metal ion the five d orbitals are degenerate. In a complex, their different orientations cause different repulsions from the surrounding ligands. They consequently separate into groups with different energies.

Step 2: Specify the energy gap The energy difference between these split sets is called the crystal field splitting energy, denoted by Δ. For an octahedral complex, it is $\Delta_o = E(e_g) - E(t_{2g})$, with t_{2g} the lower-energy set and e_g the higher-energy set. It is an energy gap, rather than the energy required to pair electrons.

Step 3: Conclusion Crystal field splitting energy is the energy difference between the sets of metal d orbitals produced by the ligand field.

Quick Tip to Solve: Define splitting as an energy difference between orbital sets; distinguish it from pairing energy.

30(a). Reduce carbohydrates, increase protein to check diabetes, older people may need greater carbohydrates reduction. An average Indian derives 61-64% of energy from consumption of food rich in carbohydrates. A study published in the Journal of Diabetes Care has recommended reducing this to 49-56% for remission or prevention of Type 2 diabetes, one of the leading cause of death worldwide. Along with reducing carbohydrate intake, the study suggests that one should also increase protein intake up to 14-20% of the total energy consumption. Fat should contribute not more than 21-27% of the total energy consumption. In simple words, 50% of the plate should consist of fruits and green vegetables, 25% carbohydrates, 25% food rich in protein. Type 1 diabetes is due to deficiency of insulin.

Answer the following questions :

Write any two functions of carbohydrates. [2 marks]

Solution:

Concept:

- Carbohydrates act as a principal source of energy in living organisms. Glucose is oxidised during cellular respiration to release energy.
- Polysaccharides also provide structural support; cellulose forms the major structural component of plant cell walls.

Step 1: Energy supply Carbohydrates in food are digested to simple sugars such as glucose. Cells oxidise glucose, releasing energy that supports growth, movement and other life processes. The overall oxidation can be represented as

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy}.$$

Thus, carbohydrates serve as an important fuel for the body.

Step 2: Structural support Cellulose is a carbohydrate present in plant cell walls. Its long chains form strong fibres that give the wall rigidity and mechanical support, helping plant cells retain their shape. This is a structural function distinct from their role as an energy source.

Step 3: Conclusion Two functions of carbohydrates are supplying energy and providing structural support as cellulose in plant cell walls.

Quick Tip to Solve: Give two distinct roles: glucose supplies energy, while cellulose supports plant cell walls.

30(b). What are monosaccharides ? [1 mark]

Solution:

Concept:

- Monosaccharides are the simplest carbohydrate units and cannot be hydrolysed into simpler carbohydrates.
- Hydrolysis is cleavage by water; this distinguishes monosaccharides from di- and polysaccharides.

Step 1: Apply the hydrolysis criterion A monosaccharide is a carbohydrate that cannot be hydrolysed

further to give simpler carbohydrate units. It is already a single sugar unit, so the definition concerns the products of hydrolysis, rather than merely whether the substance tastes sweet.

Step 2: Identify examples Glucose, fructose and ribose are examples. In contrast, sucrose can be hydrolysed into glucose and fructose, and is therefore a disaccharide rather than a monosaccharide.

Step 3: Conclusion Monosaccharides are carbohydrates that cannot be hydrolysed into simpler carbohydrates, for example glucose and fructose.

Quick Tip to Solve: Use the phrase cannot be hydrolysed into simpler carbohydrates to define a monosaccharide precisely.

30(c). Write the name of the deficiency diseases caused due to the lack of Vitamin D. [1 mark]

Solution:

Concept:

- Vitamin D helps the body absorb calcium and phosphorus, which are needed for normal mineralisation of bones.
- Its deficiency produces characteristic bone disorders, with different names in growing children and adults.

Step 1: Identify the childhood deficiency disease In children, insufficient vitamin D impairs mineralisation of developing bones, producing rickets. The bones become soft and may show deformities such as bowed legs.

Step 2: Identify the adult deficiency disease In adults, vitamin D deficiency causes osteomalacia, in which bones become soft because of inadequate mineralisation. These disorders should be distinguished from scurvy, which results from vitamin C deficiency.

Step 3: Conclusion Vitamin D deficiency causes rickets in children and osteomalacia in adults.

Quick Tip to Solve: Link vitamin D with bone mineralisation: rickets in children and osteomalacia in adults.

OR

30(c). (ii) Name the hormone which maintains the glucose level within narrow limit in the blood. [1 mark]

Solution:

Concept:

- Insulin is a peptide hormone secreted by the beta cells of the pancreas.
- It regulates blood glucose by promoting glucose utilisation and its storage as glycogen.

Step 1: Identify the hormone The hormone asked for is insulin. It is secreted by pancreatic beta cells and plays a central role in maintaining the blood glucose concentration within a narrow range.

Step 2: Connect its action with glucose regulation Insulin promotes the uptake and utilisation of

glucose by tissues and the conversion of excess glucose into glycogen, thereby lowering an elevated blood glucose concentration. Its deficiency is associated with type 1 diabetes, as stated in the passage. Glucagon has an opposing glucose-raising action.

Step 3: Conclusion The hormone is insulin.

Quick Tip to Solve: Use the passage clue: the deficiency associated with type 1 diabetes identifies insulin.

Section E (15 marks)

31(a). (i) Write the chemical equations involved in the preparation of potassium permanganate from pyrolusite ore (MnO_2).

(ii) Give reasons for the following :

(I) Sc (Atomic No. 21) salts are white.

(II) $E^\circ_{Cu2+/Cu}$ is positive whereas $E^\circ_{Mn2+/Mn}$ is negative.

(III) Transition metals have high enthalpies of atomisation. [5 marks]

Solution:

Concept:

- Pyrolusite contains MnO_2. Oxidation in hot alkaline medium gives green manganate(VI), which is then oxidised to purple permanganate(VII).
- The colour of transition-metal ions commonly involves electronic transitions between split d orbitals. Standard reduction potentials reflect the combined effects of atomisation, ionisation and hydration energies.
- Metallic bonding is strengthened when more valence electrons, including d electrons, participate in bonding.

Step 1: (i) Prepare potassium manganate Fuse powdered pyrolusite with potassium hydroxide in the presence of atmospheric oxygen. Manganese is oxidised from $+4$ to $+6$:

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\Delta} 2K_2MnO_4 + 2H_2O.$$

The green fusion product is potassium manganate.

Step 2: (i) Convert manganate into permanganate Extract the manganate with water and oxidise it electrolytically. At the anode,

$$MnO_4^{2-} \longrightarrow MnO_4^- + e^-.$$

The corresponding overall equation, including hydrogen evolution at the cathode, is

$$2K_2MnO_4 + 2H_2O \xrightarrow{\text{electrolysis}} 2KMnO_4 + 2KOH + H_2.$$

Manganese changes from $+6$ to $+7$; concentration of the solution gives potassium permanganate crystals.

Step 3: (ii)(I) White scandium salts Scandium has configuration $[Ar]3d^14s^2$, while its usual ion Sc^{3+}

has configuration $[\mathrm{Ar}]3d^0$. There is no d electron available for a d-d transition that absorbs visible light. Consequently scandium salts with colourless counterions are white, and their aqueous solutions are colourless.

Step 4: (ii)(II) Opposite signs of the reduction potentials For copper, the energy required for atomisation and ionisation to form Cu^{2+} is not sufficiently compensated by hydration. Thus oxidation of Cu to aqueous Cu^{2+} is unfavourable relative to the standard hydrogen electrode, and the reverse reduction has a positive standard potential (about $+0.34\,\mathrm{V}$). For manganese, formation of strongly hydrated Mn^{2+} also produces the especially stable half-filled $3d^5$ configuration. Oxidation of Mn is therefore favoured and its reverse reduction has a negative standard potential (about $-1.18\,\mathrm{V}$).

Step 5: (ii)(III) High enthalpies of atomisation Transition metals generally have several unpaired d electrons in addition to their outer s electrons. Participation of these electrons produces strong metallic bonding between atoms. Considerable energy is therefore needed to separate the solid metal completely into isolated gaseous atoms, giving high enthalpies of atomisation.

Step 6: Conclusion Pyrolusite is converted first into $\mathrm{K_2MnO_4}$, then into $\mathrm{KMnO_4}$. The reasons are the d^0 configuration of Sc^{3+}, the energy balance and stability of Mn^{2+}, and strong metallic bonding in transition metals.

Quick Tip to Solve: Track Mn oxidation states as +4 to +6 to +7; for electrode potentials compare the complete energy balance, not configuration alone.

OR

31(b). (i) Complete and balance the following chemical equations :

(I) $\mathbf{Cr_2O_7^{2-}(aq) + H_2S(g) + H^+ \rightarrow}$

(II) $\mathbf{Cu^{2+}(aq) + I^-(aq) \rightarrow}$

(ii) Give reasons :

(I) Separation of mixture of lanthanoids is difficult.

(II) Chromium has higher melting point than manganese.

(III) It is difficult to obtain oxidation state greater than two for Zn. [5 marks]

Solution:

Concept:

- In acidic solution dichromate is reduced from chromium(VI) to chromium(III), while hydrogen sulphide is oxidised to sulphur. Balance both atoms and net charge.
- Precipitation of sparingly soluble CuI favours reduction of Cu^{2+} by iodide. Electronic configurations and ionic sizes explain the remaining trends.

Step 1: (i)(I) Dichromate and hydrogen sulphide The reduction half-equation is

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6}e^- \longrightarrow 2\mathrm{Cr^{3+}} + 7\mathrm{H_2O}.$$

The oxidation half-equation is $\mathrm{H_2S} \longrightarrow \mathrm{S} + 2\mathrm{H}^+ + 2e^-$. Multiply the latter by three and cancel

electrons and common hydrogen ions:

$$\boxed{\mathrm{Cr_2O_7^{2-}}(aq) + 3\mathrm{H_2S}(g) + 8\mathrm{H^+}(aq) \longrightarrow 2\mathrm{Cr^{3+}}(aq) + 3\mathrm{S}(s) + 7\mathrm{H_2O}(l).}$$

Both sides have net charge $+6$, two chromium atoms, three sulphur atoms and seven oxygen atoms.

Step 2: (i)(II) Copper(II) and iodide Iodide reduces copper(II) to copper(I), while itself being oxidised to iodine. Copper(I) precipitates as white copper(I) iodide:

$$\boxed{2\mathrm{Cu^{2+}}(aq) + 4\mathrm{I^-}(aq) \longrightarrow 2\mathrm{CuI}(s) + \mathrm{I_2}.}$$

Of the four iodide ions, two supply the electrons by forming iodine and two combine with copper(I) in the precipitate. The net charge on each side is zero.

Step 3: (ii)(I) Difficulty of lanthanoid separation Lanthanoids predominantly form $+3$ ions. Their ionic radii differ only slightly because the gradual lanthanoid contraction makes neighbouring ions similar in size. As a result, their chemical properties, complex formation tendencies and solubilities are very similar, making separation of a mixture difficult.

Step 4: (ii)(II) Melting points of chromium and manganese Chromium has configuration $[\mathrm{Ar}]3d^5 4s^1$, whereas manganese is $[\mathrm{Ar}]3d^5 4s^2$. Chromium has more unpaired valence electrons available for participation in metallic bonding. Manganese has a particularly stable half-filled $3d^5$ subshell and shows comparatively weaker metallic bonding. The stronger metallic bonding in chromium requires more thermal energy to overcome, so chromium has the higher melting point.

Step 5: (ii)(III) Oxidation states of zinc Zinc has configuration $[\mathrm{Ar}]3d^{10}4s^2$. Loss of the two outer $4s$ electrons gives $\mathrm{Zn^{2+}}$, with the stable completely filled $3d^{10}$ subshell. Any further oxidation would remove an electron from this filled inner subshell and requires a very large third ionisation enthalpy. Hence oxidation states greater than $+2$ are difficult to obtain.

Step 6: Conclusion The balanced reactions give $\mathrm{Cr^{3+}}, \mathrm{S}, \mathrm{H_2O}$ and $\mathrm{CuI}, \mathrm{I_2}$, respectively. Similar trivalent ionic sizes hinder lanthanoid separation; stronger metallic bonding raises chromiumś melting point; stable $3d^{10}$ makes further oxidation of $\mathrm{Zn^{2+}}$ difficult.

Quick Tip to Solve: In the copper reaction count iodide twice: it both reduces copper(II) and supplies the iodide needed to precipitate copper(I).

32(a). (i) Define osmotic pressure. Why is it considered as a colligative property ?

(ii) The vapour pressure of two pure liquids A and B at 400 K are 450 and 700 mmHg respectively. Find out the composition of liquid mixture if the total vapour pressure of mixture is 600 mmHg. [5 marks]

Solution:

Concept:

- Osmosis is the passage of solvent through a semipermeable membrane from pure solvent (or a dilute solution) to a more concentrated solution. Osmotic pressure is the excess pressure needed on the solution side to stop this flow.

- For a dilute solution, $\pi V = nRT$, so $\pi = CRT$, where n is the amount of solute particles, V is solution volume, $C = n/V$, R is the gas constant and T is absolute temperature.
- For an ideal binary liquid mixture, Raoult's law gives $p_A = x_A p_A^0$, $p_B = x_B p_B^0$, and $P = p_A + p_B$, with $x_A + x_B = 1$.

Step 1: (i) Define osmotic pressure Place the solution and pure solvent on opposite sides of a membrane permeable only to solvent. Solvent tends to enter the solution. The minimum additional pressure applied to the solution that just prevents this net inward flow is its osmotic pressure, π. At this pressure the solvent levels show no further change due to osmosis.

Step 2: (i) Explain its colligative nature At fixed temperature and solution volume, $\pi = nRT/V$ depends only on the number of dissolved solute particles, and not on their chemical identity. Hence osmotic pressure is a colligative property. Equal particle concentrations of different dilute solutes have equal osmotic pressures at the same temperature.

Step 3: (ii) Form the total vapour-pressure equation At $400\,\text{K}$, the pure-liquid vapour pressures are $p_A^0 = 450\,\text{mmHg}$ and $p_B^0 = 700\,\text{mmHg}$. Applying Raoult's law to the mixture,

$$600 = 450x_A + 700x_B.$$

Use $x_B = 1 - x_A$ to express this in terms of one mole fraction.

Step 4: (ii) Calculate and check the liquid composition

$$\begin{aligned} 600 &= 450x_A + 700(1 - x_A), \\ 250x_A &= 100, \\ x_A &= 0.40, \qquad x_B = 0.60. \end{aligned}$$

As a check, the partial pressures are $p_A = 0.40(450) = 180\,\text{mmHg}$ and $p_B = 0.60(700) = 420\,\text{mmHg}$. Their sum is $600\,\text{mmHg}$, as required. The requested composition is the liquid composition, so these mole fractions, rather than vapour mole fractions, are used.

Step 5: Conclusion Osmotic pressure is the excess pressure that stops osmosis; it is colligative because it depends on solute particle concentration. The liquid contains $x_A = 0.40$ and $x_B = 0.60$, i.e. 40% A and 60% B by mole.

Quick Tip to Solve: For a binary ideal mixture, first use $x_A + x_B = 1$; check the resulting composition by adding the two partial pressures.

OR

32(b). (i) What type of deviation from Raoult's law is expected when phenol and aniline are mixed with each other ? What change in the net volume of the mixture and enthalpy is expected ?
(ii) Boiling point of water at 750 mmHg is 99.48°C. How much sucrose (M = 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 K kg mol^{-1}] [5 marks]

Solution:

Concept:

- Negative deviation from Raoult's law occurs when unlike-molecule attractions are stronger than the relevant attractions in the pure liquids, reducing the escaping tendency and vapour pressure.
- For a dilute solution of a nonvolatile nonelectrolyte, boiling-point elevation is $\Delta T_b = K_b m$, where m is moles of solute per kilogram of solvent and K_b is the molal elevation constant.
- Boiling-point elevation must be measured relative to the pure solvent at the same external pressure. Sucrose remains molecular, so its van't Hoff factor is $i = 1$.

Step 1: (i) Identify the deviation and its cause Phenol and aniline form strong intermolecular hydrogen bonds between phenol's hydroxyl group and aniline's nitrogen atom. These phenol-aniline attractions are stronger than the interactions replaced on mixing. The molecules escape into the vapour phase less readily; therefore the mixture shows negative deviation from Raoult's law, with vapour pressure below the ideal value.

Step 2: (i) State the volume and enthalpy changes The stronger attractions bring molecules closer together, so mixing causes contraction: $\Delta V_{\text{mix}} < 0$. Formation of these favourable interactions releases heat, so mixing is exothermic: $\Delta H_{\text{mix}} < 0$. Thus the final volume is less than the sum of the initial liquid volumes.

Step 3: (ii) Find the required elevation at 750 mmHg The pure-water boiling point at the stated pressure is $99.48°$C. The target solution boiling point is $100°$C at that same pressure. Hence

$$\Delta T_b = 100 - 99.48 = 0.52\,\text{K}.$$

A temperature difference has the same numerical value in kelvin and degrees Celsius.

Step 4: (ii) Calculate molality and sucrose mass Using $K_b = 0.52\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_b}{K_b} = \frac{0.52}{0.52} = 1.0\,\text{mol kg}^{-1}.$$

The solvent mass is $500\,\text{g} = 0.500\,\text{kg}$, so

$$n_{\text{sucrose}} = m \times 0.500 = 0.500\,\text{mol},$$
$$w_{\text{sucrose}} = nM = 0.500 \times 342 = 171\,\text{g}.$$

The solvent mass, not the final solution mass, belongs in the molality calculation. Substitution back gives $\Delta T_b = 0.52(1.0) = 0.52\,\text{K}$, which raises the boiling point to the required value.

Step 5: Conclusion Phenol-aniline shows negative deviation, volume contraction $\Delta V_{\text{mix}} < 0$, and exothermic mixing $\Delta H_{\text{mix}} < 0$. Add 171 g of sucrose to 500 g of water.

Quick Tip to Solve: Always subtract the pure-solvent boiling point at the given pressure before applying $\Delta T_b = K_b m$; use solvent mass in kilograms.

33(a)(i). An organic compound 'P' ($C_8H_{10}O$) on oxidation gave compound 'Q'. The compound 'Q' can also be obtained from a reaction of benzene with acetyl chloride in the presence of anhydrous $AlCl_3$. 'Q' on treatment with I_2 in aq. NaOH gave 'R' and a yellow compound 'S'. Identify 'P', 'Q', 'R' and 'S'. [4 marks]

Solution:

Concept:

- Friedel–Crafts acylation introduces an acyl group into benzene. Acetyl chloride introduces $-COCH_3$ in the presence of anhydrous $AlCl_3$.
- Oxidation of a secondary alcohol gives a ketone without changing the carbon skeleton. A methyl ketone gives a carboxylate salt and yellow iodoform with alkaline iodine.

Step 1: Identify Q from its preparation Benzene reacts with acetyl chloride by electrophilic substitution, attaching the acetyl group directly to the ring:

$$C_6H_6 + CH_3COCl \xrightarrow{\text{anhyd. } AlCl_3} C_6H_5COCH_3 + HCl.$$

Hence Q is acetophenone (1-phenylethanone), $C_6H_5COCH_3$. This independent preparation fixes the carbonyl position; the product is not an aldehyde at the end of a two-carbon side chain.

Step 2: Identify P from oxidation The secondary alcohol which yields acetophenone on oxidation is 1-phenylethanol:

$$C_6H_5CH(OH)CH_3 + [O] \longrightarrow C_6H_5COCH_3 + H_2O.$$

Thus $P = C_6H_5CH(OH)CH_3$. Its formula is $C_8H_{10}O$, agreeing with the given molecular formula. The hydroxyl-bearing carbon is attached to phenyl and methyl groups, so oxidation changes CH(OH) into a carbonyl without changing the skeleton.

Step 3: Apply the iodoform reaction Acetophenone contains the methyl ketone unit $-COCH_3$. With iodine in aqueous sodium hydroxide, the methyl group produces yellow iodoform and the remaining acyl group gives sodium benzoate:

$$C_6H_5COCH_3 + 3I_2 + 4NaOH \longrightarrow C_6H_5COONa + CHI_3 \downarrow + 3NaI + 3H_2O.$$

Therefore R is sodium benzoate and S is iodoform. Since the reaction medium is alkaline and acidification is not specified, the benzoate remains a sodium salt rather than free benzoic acid.

Step 4: Conclusion $P = C_6H_5CH(OH)CH_3$ (1-phenylethanol); $Q = C_6H_5COCH_3$ (acetophenone); $R = C_6H_5COONa$ (sodium benzoate); $S = CHI_3$ (yellow iodoform).

Quick Tip to Solve: Identify the Friedel–Crafts product first, then replace its carbonyl by CH(OH) to recover the alcohol.

33(a)(ii). Give the structure(s) of the product(s) when benzaldehyde is heated in the presence of conc. KOH. [1 mark]

Solution:

Concept:

- An aldehyde without an alpha-hydrogen undergoes Cannizzaro disproportionation in concentrated alkali: one molecule is reduced while another is oxidised.
- In alkaline solution, the oxidation product exists as a carboxylate salt.

Step 1: Check the reaction condition Benzaldehyde, C_6H_5CHO, has no alpha-hydrogen and is heated with concentrated KOH. It therefore undergoes the Cannizzaro reaction rather than aldol condensation.

Step 2: Write the product structures Two molecules disproportionate to give benzyl alcohol and potassium benzoate:

$$2C_6H_5CHO + KOH \longrightarrow C_6H_5CH_2OH + C_6H_5COOK.$$

The aldehyde carbon is reduced to $-CH_2OH$ in one molecule and oxidised to $-COO^-K^+$ in the other. No acid work-up is given, so the salt is retained.

Step 3: Conclusion The products are benzyl alcohol, $C_6H_5 - CH_2 - OH$, and potassium benzoate, $C_6H_5 - C(=O) - O^-K^+$.

Quick Tip to Solve: With concentrated KOH, check for absence of alpha-hydrogen and write both Cannizzaro products.

OR

33(b)(i). Carry out the following conversions :

(I) Propanone to Propane

(II) Acetophenone to Benzoic acid

(III) Benzyl chloride to Phenylethanoic acid [3 marks]

Solution:

Concept:

- Clemmensen reduction converts a ketone carbonyl group into a methylene group using zinc amalgam and concentrated hydrochloric acid.
- The haloform reaction converts a methyl ketone to a carboxylate; acidification then gives the acid.
- Cyanide substitution introduces one extra carbon, which becomes the carboxyl carbon on nitrile hydrolysis.

Step 1: (I) Propanone to propane Reduce the carbonyl group using zinc amalgam and concentrated hydrochloric acid (Clemmensen reduction):

$$CH_3COCH_3 \xrightarrow{Zn(Hg)/\text{conc. } HCl} CH_3CH_2CH_3.$$

The carbonyl oxygen is removed and the central carbon becomes a methylene group. The three-carbon skeleton remains unchanged.

Step 2: (II) Acetophenone to benzoic acid First treat acetophenone with iodine and aqueous NaOH, then acidify the sodium benzoate formed:

$$C_6H_5COCH_3 \xrightarrow{I_2/\text{aq. NaOH}} C_6H_5COONa$$
$$C_6H_5COONa + HCl \longrightarrow C_6H_5COOH + NaCl.$$

The methyl ketone unit gives iodoform as the other organic product in the first step. Acidification is essential to convert benzoate into benzoic acid.

Step 3: (III) Benzyl chloride to phenylethanoic acid Use alcoholic KCN for nucleophilic substitution, then hydrolyse the nitrile by heating with dilute aqueous acid:

$$C_6H_5CH_2Cl \xrightarrow{\text{alc. KCN}} C_6H_5CH_2CN$$
$$C_6H_5CH_2CN \xrightarrow[\text{heat}]{\text{dil. HCl, } H_2O} C_6H_5CH_2COOH.$$

The intermediate is benzyl cyanide (phenylacetonitrile). Its nitrile carbon supplies the additional carbon needed in phenylethanoic acid. KCN is used because carbon attack yields the nitrile required for hydrolysis.

Step 4: Conclusion The required sequences are: (I) Zn(Hg)/concentrated HCl; (II) iodine/aqueous NaOH followed by acidification; (III) alcoholic KCN followed by acidic hydrolysis on heating, giving $C_6H_5CH_2COOH$.

Quick Tip to Solve: For benzyl chloride to phenylethanoic acid, count carbons: KCN supplies the extra carbon before hydrolysis.

33(b)(ii). Give a simple chemical test to distinguish between the following pairs of compounds :

(I) Benzaldehyde and Phenol

(II) Butanal and Butan-2-one [2 marks]

Solution:

Concept:

- A distinguishing test must give different visible observations with the two compounds under the same conditions.
- Phenol gives a violet colour with neutral ferric chloride solution, whereas benzaldehyde does not. Aldehydes reduce Tollens' reagent to metallic silver; ordinary ketones do not.

Step 1: (I) Benzaldehyde and phenol: neutral ferric chloride test Add a few drops of freshly prepared neutral $FeCl_3$ solution to separate samples. Phenol gives a violet colour because it forms a coloured complex with ferric ions. Benzaldehyde gives no violet colour, since it lacks the phenolic $-OH$ group. Thus the sample showing the violet colour is phenol; the other is benzaldehyde.

Step 2: (II) Butanal and butan-2-one: Tollens' test Warm separate samples gently with freshly

prepared Tollens' reagent in a water bath. Butanal gives a silver mirror on the inner wall of the test tube, while butan-2-one gives no silver mirror. Butanal is oxidised to butanoate as silver(I) ions are reduced to silver:

$$\mathrm{CH_3CH_2CH_2CHO} + 2[\mathrm{Ag(NH_3)_2}]^{+} + 3\mathrm{OH}^{-} \longrightarrow \mathrm{CH_3CH_2CH_2COO}^{-} + 2\mathrm{Ag} + 4\mathrm{NH_3} + 2\mathrm{H_2O}.$$

Butan-2-one is a ketone and is not oxidised by this mild reagent, so metallic silver is not deposited.

Step 3: Conclusion (I) Neutral ferric chloride: phenol gives a violet colour; benzaldehyde does not. (II) Tollens' reagent: butanal gives a silver mirror; butan-2-one does not.

Quick Tip to Solve: For each pair, name the reagent and state observations for both samples: violet colour identifies phenol, and a silver mirror identifies the aldehyde.