CBSE Class 12 Chemistry Question Paper 2025 with Solution PDF-Set 56-S-3 - 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. 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 refrigerants containing carbon, chlorine and fluorine.
- Freon-12 is dichlorodifluoromethane, CCl_2F_2.

Step 1: Identify the required composition A Freon contains fluorine as well as chlorine attached to carbon. Dichlorodifluoromethane has two chlorine and two fluorine atoms bonded to its single carbon atom; its formula is CCl_2F_2.

Step 2: Check the alternatives Option (A) has precisely this formula. Option (B), CCl_2Br_2, contains bromine and no fluorine. Options (C) and (D) are chlorinated ethanes without fluorine, so neither is the Freon asked for.

Step 3: Conclusion The Freon is CCl_2F_2, Freon-12. The correct option is (A).

Quick Tip to Solve: Look for both F and Cl: the familiar refrigerant Freon-12 is dichlorodifluoromethane.

2. 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 resistance of an electrolyte between two electrodes.
- Platinum electrodes are chemically inert; platinum black increases their effective surface area.

Step 1: Select an inert electrode material The electrodes should conduct electrons without appreciably reacting with the electrolyte. Platinum meets this requirement and is the standard material used in a conductivity cell.

Step 2: Compare the given metals The platinum plates are commonly coated with platinum black

to increase surface area and reduce polarisation effects. Silver, copper and zinc are more liable to participate in electrode reactions or dissolve in suitable electrolytes, so they are not the standard answer.

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

Quick Tip to Solve: For conductivity measurements, recall platinised platinum plates and an alternating-current supply.

3. 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 gas partial pressure and x its mole fraction in solution.
- At fixed temperature and pressure, $x = p/K_H$; hence solubility varies inversely with K_H.

Step 1: Arrange the Henry constants Using the printed values in kbar,

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

These correspond respectively to $\mathrm{Ar}, \mathrm{CO_2}, \mathrm{CH_4}, \mathrm{HCHO}$.

Step 2: Reverse this order for solubility The largest constant gives the lowest dissolved mole fraction at the same gas pressure. Thus Ar is least soluble and HCHO most soluble; methane is more soluble than carbon dioxide for these supplied constants. Options (A) and (B) incorrectly place HCHO first, while (D) reverses the middle pair.

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

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

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

(A) $CH_2=CH\text{-}CH_2OH$

(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 $ZnCl_2$; alcohols form alkyl chlorides.
- Tertiary alcohols react rapidly at room temperature because the corresponding carbocation is stable; allylic and benzylic alcohols are special reactive cases.

Step 1: Apply the usual Lucas-test classification Option (D), $(CH_3)_3COH$, is tert-butyl alcohol, a tertiary alcohol. It readily gives tert-butyl chloride at room temperature, producing turbidity. Option (B), propan-1-ol, is an ordinary primary alcohol and does not show this rapid room-temperature reaction.

Step 2: Check the special primary alcohols Option (A) is allyl alcohol and option (C) is benzyl alcohol. Their resonance-stabilised allylic and benzylic intermediates also permit reaction with Lucas reagent at room temperature. Consequently, the printed wording does not uniquely distinguish (D): (A) and (C) are also chemically defensible. Option (D) is the conventional intended choice based on the tertiary-alcohol test.

Step 3: Conclusion The intended answer is (D), tert-butyl alcohol. As printed, allyl alcohol and benzyl alcohol also react at room temperature, so the question is not uniquely selective.

Quick Tip to Solve: Use the tertiary-alcohol rule for Lucas tests, but check for the allylic and benzylic exceptions.

5. Glucose on reaction with hydrogen iodide gives : [1 mark]

(A) Gluconic acid

(B) n-Hexane

(C) Saccharic acid

(D) Hexanoic acid

Correct Answer: (B) n-Hexane

Solution:

Concept:

- Prolonged heating of glucose with hydrogen iodide reduces its oxygen-containing groups.
- Formation of n-hexane establishes an unbranched chain of six carbon atoms in glucose.

Step 1: Identify the type of reaction On prolonged heating with HI, the oxygen atoms in glucose are

removed during reduction while the chain of six carbon atoms remains intact. The resulting saturated hydrocarbon is $CH_3(CH_2)_4CH_3$.

Step 2: Distinguish reduction from oxidation This hydrocarbon is n-hexane. Gluconic acid and saccharic acid are oxidation products of glucose under different conditions; they are not products of reduction by HI. Hexanoic acid retains a carboxyl group and is also not the product of this complete reduction.

Step 3: Conclusion Glucose gives n-hexane on prolonged heating with HI. The correct option is (B).

Quick Tip to Solve: HI reduction to n-hexane is the key evidence that all six glucose carbon atoms form a straight chain.

6. 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 have comparable molecular masses and can form intermolecular hydrogen bonds.
- Branching decreases molecular surface contact and weakens London dispersion attractions.

Step 1: Compare the common features All four compounds are primary amines with five carbon atoms. They possess N–H bonds and can associate through intermolecular hydrogen bonding; molecular mass therefore does not distinguish their boiling points.

Step 2: Compare branching Pentanamine has the unbranched carbon chain, whereas 2,2-dimethylpropanamine, 3-methylbutanamine and 2-methylbutanamine are branched. The unbranched molecule provides greater surface contact between neighbouring molecules and stronger dispersion attractions. More energy is consequently needed to separate its molecules into the vapour phase.

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

Quick Tip to Solve: When comparing isomeric primary amines, hold hydrogen bonding constant and select the least branched chain.

7. Which one of the following halides contains C_{sp2}-X bond ? [1 mark]

(A) Alkyl halide

(B) Allyl halide

(C) Benzyl halide

(D) Vinyl halide

Correct Answer: (D) Vinyl halide

Solution:

Concept:

- The hybridisation of the carbon directly bonded to the halogen determines whether the bond is $\mathrm{C}_{\mathrm{sp}^2} - \mathrm{X}$.
- A carbon atom in a carbon–carbon double bond is sp^2-hybridised; a saturated carbon is normally sp^3-hybridised.

Step 1: Examine a vinyl halide A vinyl halide has the group $\mathrm{CH_2 = CH - X}$. Here X is attached directly to a double-bonded carbon, so its carbon–halogen bond is $\mathrm{C}_{\mathrm{sp}^2} - \mathrm{X}$.

Step 2: Distinguish adjacent unsaturation In an alkyl halide, the bonded carbon is saturated. Allyl halides, $\mathrm{CH_2 = CH - CH_2X}$, and benzyl halides, $\mathrm{C_6H_5CH_2X}$, also have X on an sp^3 carbon: their double bond or aromatic ring is adjacent to that carbon rather than directly bearing X.

Step 3: Conclusion Vinyl halide contains the $\mathrm{C}_{\mathrm{sp}^2} - \mathrm{X}$ bond. The correct option is (D).

Quick Tip to Solve: Locate the carbon touching X before assigning hybridisation; neighbouring double bonds do not make it sp2.

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8. If the half-life period of a first order reaction is 2772 s, then the rate constant of this reaction is : [1 mark]

(A) 2.5×10^{-4} s^{-1}

(B) 2.5×10^{-3} s^{-1}

(C) 25×10^{-4} s^{-1}

(D) 25×10^{-3} s^{-1}

Correct Answer: (A) 2.5×10^{-4} s^{-1}

Solution:

Concept:

- For a first order reaction, $t_{1/2} = \ln 2/k$, where k is the rate constant.
- The half-life is independent of the initial concentration for first order kinetics.

Step 1: Use the half-life relation Rearrange the first order expression to obtain $k = 0.693/t_{1/2}$. Since the half-life is supplied in seconds, the corresponding unit of the rate constant is s^{-1}.

Step 2: Substitute and compare the options

$$k = \frac{0.693}{2772\,\mathrm{s}} = 0.000250\,\mathrm{s}^{-1} = 2.5 \times 10^{-4}\,\mathrm{s}^{-1}.$$

Option (B) is ten times this value; (C), 25×10^{-4}, is also ten times it; and (D) is one hundred times it. Only (A) reproduces the calculated value.

Step 3: Conclusion $k = 2.5 \times 10^{-4}\,\text{s}^{-1}$. Hence, the correct option is (A).

Quick Tip to Solve: Keep the half-life in seconds and use 0.693 divided by the half-life, not its reciprocal.

9. The standard electrode potentials of 'P', 'Q' and 'R' are -0.50 V, +0.68 V and -2.54 V respectively. The order of their reducing power is : [1 mark]

(A) R > P > Q

(B) Q > P > R

(C) Q > R > P

(D) P < Q < R

Correct Answer: (A) R > P > Q

Solution:

Concept:

- A reducing agent loses electrons and is itself oxidised.
- The more negative the standard reduction potential E°, the greater the tendency of the reduced species to undergo oxidation.

Step 1: Compare the given reduction potentials The supplied values are $E^\circ_R = -2.54\,\text{V}$, $E^\circ_P = -0.50\,\text{V}$, and $E^\circ_Q = +0.68\,\text{V}$. Thus, the reduction potentials increase in the order $R < P < Q$.

Step 2: Convert potential order into reducing power The species with the least tendency to accept electrons has the greatest tendency to donate them. Hence, R is the strongest reducing agent and Q the weakest. Option (B) reverses the required order, while (C) also incorrectly puts Q first. Option (D) makes P weaker than Q, contrary to their potentials.

Step 3: Conclusion The order of reducing power is $R > P > Q$. Hence, the correct option is (A).

Quick Tip to Solve: Arrange reduction potentials from most negative to most positive to rank reducing agents from strongest to weakest.

10. 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 configuration $[\text{Ar}]3d^{10}4s^1$.
- Electrons are removed from the $4s$ orbital before the $3d$ orbitals when forming these cations.

Step 1: Identify the two copper ions Loss of the $4s$ electron gives Cu^+, with configuration $[\text{Ar}]3d^{10}$. Further loss of one $3d$ electron gives Cu^{2+}, with configuration $[\text{Ar}]3d^9$. Thus copper commonly exhibits both oxidation states specified.

Step 2: Check the alternatives Scandium predominantly forms Sc^{3+}. Manganese commonly shows $+2$, $+4$ and $+7$, rather than the characteristic $+1, +2$ pair sought here. Zinc predominantly forms Zn^{2+} and is not a transition element under the incomplete-d-subshell definition. These alternatives do not give the intended pair.

Step 3: Conclusion The element is copper, Cu. Hence, the correct option is (C).

Quick Tip to Solve: Use copper's single 4s electron: removing it gives Cu(I), and removing one more electron gives Cu(II).

11. 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 vant́ Hoff factor i counts the effective solute particles formed per formula unit dissolved.
- Water of crystallisation joins the solvent and is not counted as additional solute particles.

Step 1: Write the dissociation

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

Complete dissociation produces one calcium ion and two chloride ions from each formula unit.

Step 2: Count the solute particles The number of independently dissolved ionic particles is $1 + 2 = 3$, so $i = 3$. The six water molecules become part of the bulk water solvent. Counting them would incorrectly give 9, option (A). Option (B) counts only the hydration waters, and option (C) also does not equal the ionic particle count.

Step 3: Conclusion The vant́ Hoff factor is $i = 3$. Hence, the correct option is (D).

Quick Tip to Solve: Exclude water of crystallisation from the solute-particle count when a hydrated salt dissolves in water.

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

(A) Phenol and ethyl iodide

(B) Iodobenzene and ethanol

(C) Benzene and ethanol

(D) Ethyl chloride and iodobenzene

Correct Answer: (A) Phenol and ethyl iodide

Solution:

Concept:

- HI cleaves an aryl alkyl ether at its alkyl–oxygen bond after protonation of oxygen.
- The aryl–oxygen bond has partial double-bond character through resonance and resists cleavage.

Step 1: Identify the bond that breaks Phenyl ethyl ether is $C_6H_5 - O - C_2H_5$. Protonation of oxygen activates the ether, and iodide attacks the primary ethyl carbon by an S_N2 process. The oxygen stays attached to the phenyl group.

Step 2: Write the reaction and test the choices

$$C_6H_5OC_2H_5 + HI \longrightarrow C_6H_5OH + C_2H_5I.$$

Iodobenzene is not formed because substitution at the aryl carbon is not the cleavage pathway. Benzene is not a cleavage product either. Ethyl chloride cannot form from HI, since the reagent supplies iodide and no chloride.

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

Quick Tip to Solve: For an aryl alkyl ether with HI, retain oxygen on the aryl group and put iodine on the alkyl group.

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13. 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 A and R are true and R is the correct explanation of A.

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

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

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

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

Solution:

Concept:

- A phenol is more acidic when its conjugate phenoxide ion is stabilised.
- At the para position, nitro withdraws electrons by resonance, whereas methoxy donates by resonance.

Step 1: Judge the assertion The para nitro group stabilises the negative charge of the phenoxide conjugate base by withdrawing electron density. The para methoxy group donates electron density by resonance, tending to destabilise the phenoxide ion. Therefore p-nitrophenol is the stronger acid, and the assertion is false.

Step 2: Judge the reason The reason correctly describes the dominant resonance effects of these substituents in this comparison: methoxy is electron-donating and nitro is electron-withdrawing. Thus the reason is true.

Step 3: Select the assertion–reason code The reason supports the reverse acidity order to that claimed in the assertion. Codes (A) and (B) require a true assertion, and code (C) requires a false reason. None matches the truth values found here; code (D) does.

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

Quick Tip to Solve: Compare the stability of the two phenoxide conjugate bases before ranking the parent phenols.

14. 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 A and R are true and R is the correct explanation of A.

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

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

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

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

Solution:

Concept:

- Molecularity counts reacting species in a single elementary step, not an overall multistep equation.

- A balanced equation can suggest an apparent molecularity, but the actual mechanism determines whether that inference is valid.

Step 1: Judge the assertion The equation $H_2 + Br_2 \longrightarrow 2HBr$ shows one molecule each of hydrogen and bromine on its reactant side. Merely counting these gives $1 + 1 = 2$, so its molecularity appears to be two, as the assertion carefully states. The assertion is therefore true.

Step 2: Judge the reason The hydrogen–bromine reaction actually proceeds through a multistep chain mechanism involving radicals. The displayed overall reaction is not an elementary reaction in which a hydrogen molecule and a bromine molecule directly collide to produce two HBr molecules in one event. Thus the reason incorrectly calls the given overall reaction elementary, and is false.

Step 3: Apply the answer code The apparent count in the balanced equation does not establish an elementary bimolecular mechanism. Since the assertion is true but the reason is false, codes (A) and (B), which require a true reason, are excluded. Code (D) reverses the truth values. The applicable code is (C).

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

Quick Tip to Solve: Distinguish apparent molecularity from the actual chain mechanism of hydrogen reacting with bromine.

15. 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:

- Oxidation states depend on the valence electrons available for chemical bonding.
- Radioactivity results from nuclear instability, whereas oxidation involves the electronic configuration.

Step 1: Judge the assertion Assertion (A) is true. Actinoids exhibit several oxidation states because their $5f$, $6d$ and $7s$ subshells have comparable energies. Different numbers of these electrons can participate in bonding; consequently, oxidation states in addition to the common $+3$ state occur.

Step 2: Judge the reason Reason (R) is also true. All actinoid elements are radioactive because their nuclei are unstable and undergo radioactive decay.

Step 3: Check the explanatory link Nuclear instability does not account for the availability of different numbers of electrons for bonding. The close energies of the valence subshells explain the variable oxidation states. Thus neither statement is false, ruling out (C) and (D), but the claimed explanatory link in (A) is absent.

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

Quick Tip to Solve: Separate a nuclear property (radioactivity) from an electronic property (oxidation state) before checking the explanation.

16. Assertion (A): Presence of -NO_2 group at ortho and para positions decreases 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: (D) Assertion (A) is false, but Reason (R) is true.

Solution:

Concept:

- An electron-withdrawing nitro group activates a haloarene towards nucleophilic aromatic substitution when it is ortho or para to the halogen.
- Resonance stabilisation of the anionic intermediate favours the addition-elimination pathway.

Step 1: Judge the assertion Assertion (A) is false. An ortho- or para-NO_2 group increases, rather than decreases, the reactivity of a haloarene towards nucleophilic substitution. It stabilises the negative charge developed in the intermediate formed when the nucleophile attacks.

Step 2: Judge the reason Reason (R) is true. The nitro group withdraws electrons by both its inductive and resonance effects, decreasing electron density in the benzene ring.

Step 3: Relate electron withdrawal to the reaction A nucleophile is electron-rich. Electron withdrawal makes the carbon bearing the halogen more susceptible to its attack, and an ortho or para nitro group additionally stabilises the intermediate by resonance. Therefore the true reason cannot justify the false assertion. Options (A), (B) and (C), each of which treats A as true, are excluded.

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

Quick Tip to Solve: For nucleophilic substitution, remember that ortho/para nitro substitution activates the ring by stabilising the anionic intermediate.

Section B (10 marks)

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

Solution:

Concept:

- A fuel cell is a galvanic cell: a spontaneous redox reaction directly produces electrical energy.
- The fuel and oxidant are supplied continuously from outside the cell.

Step 1: Define a fuel cell A fuel cell is an electrochemical cell that converts the chemical energy of continuously supplied fuel and oxidant directly into electrical energy. For example, a hydrogen-oxygen fuel cell consumes hydrogen and oxygen while producing water:

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

It continues to operate while the reactants are supplied and products are removed.

Step 2: State two advantages First, a fuel cell can deliver electricity continuously as long as fuel and oxidant are supplied; it does not stop simply because the small quantity of reactants initially stored inside an ordinary cell has been used up. Second, a hydrogen-oxygen fuel cell is environmentally clean at the point of use: its product is water, so it does not generate the polluting combustion products associated with many conventional energy sources or spent cell chemicals during operation.

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

Quick Tip to Solve: Include continuous external supply in the definition; for a clean-product advantage, name the hydrogen-oxygen fuel cell.

OR

17(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:

- Reduction occurs at the cathode and oxidation at the anode during electrolysis.
- Platinum is inert, so electrode material does not supply the products.

Step 1: Electrolyse dilute sulphuric acid At the cathode, hydrogen ions are reduced to hydrogen gas:

$$2H^+(aq) + 2e^- \longrightarrow H_2(g).$$

At the platinum anode, water is oxidised to oxygen gas:

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-.$$

Sulphate ions remain in solution. The net reaction is the decomposition of water, giving hydrogen and oxygen in a $2:1$ mole ratio.

Step 2: Electrolyse aqueous copper(II) chloride At the cathode, copper(II) ions are preferentially reduced and copper metal is deposited:

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s).$$

At the platinum anode, chloride ions are oxidised, releasing chlorine gas:

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^-.$$

Thus the copper ions supply the cathode deposit, while chloride supplies the gaseous anode product.

Step 3: Conclusion (i) Dilute H_2SO_4: hydrogen at the cathode and oxygen at the anode. (ii) Aqueous $CuCl_2$: copper at the cathode and chlorine at the anode.

Quick Tip to Solve: Write cathode reduction and anode oxidation separately; platinum is inert and cannot itself be the source of copper.

18. 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:

- 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.
- At fixed reactant concentrations, the rate changes with the rate constant k.

Step 1: Decrease the temperature The reaction rate decreases when temperature is lowered. Molecules have lower average kinetic energy, and a smaller fraction of collisions have energy at least equal to the activation energy. Consequently, fewer collisions are effective per unit time. For a reaction with positive activation energy, lowering T makes $-E_a/(RT)$ more negative, so the Arrhenius equation gives a smaller k, consistent with the reduced rate.

Step 2: Add a catalyst A catalyst increases the reaction rate by providing an alternative reaction pathway with a lower activation energy. At the same temperature, a larger fraction of reactant molecules can now overcome the energy barrier, so more effective reaction events occur per unit time. The catalyst is regenerated overall and does not increase the rate by raising the temperature or changing the equilibrium constant.

Step 3: Conclusion (a) Decreasing temperature decreases the reaction rate because fewer molecules

can cross the activation-energy barrier. (b) Adding a catalyst increases the rate by providing a pathway with lower activation energy.

Quick Tip to Solve: Temperature changes the fraction able to cross the existing barrier; a catalyst lowers the barrier through another pathway.

19. Give one point of difference between the following :

(a) Starch and Cellulose

(b) Primary and Secondary structure of protein [2 marks]

Solution:

Concept:

- Polysaccharides are polymers of monosaccharides; the configuration of the glucose units distinguishes starch from cellulose.
- The primary structure gives the amino-acid sequence, whereas secondary structure describes regular folding of the peptide backbone.

Step 1: (a) Starch and cellulose Starch is a polymer of α-D-glucose, whereas cellulose is a polymer of β-D-glucose. Thus, although both yield glucose on complete hydrolysis, their monomer configurations and glycosidic arrangements differ. In particular, cellulose has $\beta(1 \rightarrow 4)$ linkages, unlike the α-linkages of starch.

Step 2: (b) Primary and secondary protein structure The primary structure is the specific sequence in which amino-acid residues are joined by peptide bonds in a polypeptide chain. Secondary structure is the regular folding of that backbone into an α-helix or a β-pleated sheet, stabilised by hydrogen bonds between peptide $\mathrm{C}=\mathrm{O}$ and $\mathrm{N}-\mathrm{H}$ groups. It describes local arrangement, rather than merely listing the amino acids.

Step 3: Conclusion (a) Starch contains α-D-glucose units; cellulose contains β-D-glucose units. (b) Primary structure is amino-acid sequence; secondary structure is regular backbone folding.

Quick Tip to Solve: Use glucose configuration for the first comparison and sequence versus folding for the second.

20. Visha diluted the solutions of two electrolytes 'P' and 'Q'. She observed that Λ_m of 'P' increased 1.5 times whereas Λ_m of 'Q' increased 25 times. Which of the two is a strong electrolyte? Justify your answer by graphically explaining the behaviour of 'P' and 'Q'. [2 marks]

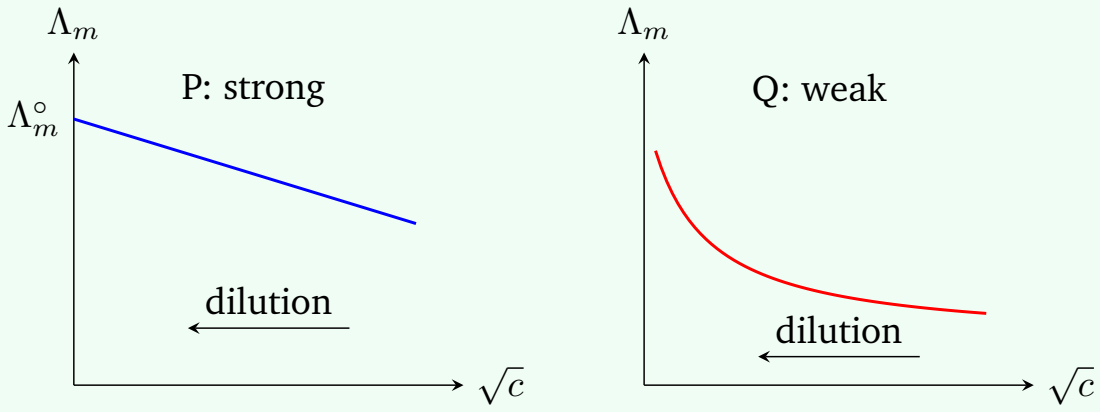
Solution:

Concept:

- Molar conductivity Λ_m is the conductivity per molar concentration; its dilution trend depends on ionisation and interionic interactions.
- For a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$, where c is concentration and $A > 0$.

Step 1: Identify the strong electrolyte Electrolyte P is strong. It is already almost completely ionised, so dilution mainly reduces interionic attractions and increases ionic mobility. Its molar conductivity therefore rises only moderately, here by a factor of 1.5. Electrolyte Q is weak: dilution considerably increases its degree of ionisation and hence the number of ions furnished by each mole, explaining the much larger 25-fold rise.

Step 2: Explain the conductivity plots Plot Λ_m against $\sqrt{c}$. The P plot is approximately a straight line with a negative slope in dilute solution and can be extrapolated to Λ_m° at $c = 0$. Q shows a curved dependence with a sharp increase as c approaches zero; a straight-line extrapolation is inappropriate. Dilution means moving leftwards along both curves. The two panels are schematic, with independent vertical scales: the factors alone do not specify absolute conductivities.



Schematic molar-conductivity trends; vertical scales are independent.

Step 3: Conclusion P is the strong electrolyte; Q is the weak electrolyte. Their small and large increases on dilution arise chiefly from increased ionic mobility and increased ionisation, respectively.

Quick Tip to Solve: On a conductivity versus square-root-concentration plot, dilution always means moving toward the vertical axis.

21. (a) Aniline cannot be prepared by Gabriel phthalimide synthesis. Give reason.
(b) Name the reaction which can be used to distinguish chemically between ethanamine and N-methylethanamine.

[2 marks]

Solution:

Concept:

- Gabriel phthalimide synthesis involves nucleophilic substitution by the phthalimide anion on a suitable alkyl halide.
- The carbylamine reaction is given by primary amines, but not by secondary or tertiary amines.

Step 1: (a) Why aniline cannot be obtained To obtain aniline by Gabriel synthesis, an aryl halide would have to undergo substitution by the phthalimide anion. Aryl halides do not undergo the required nucleophilic substitution under Gabriel conditions: the carbon bonded to halogen is sp^2-hybridised,

and resonance gives the aryl carbon-halogen bond partial double-bond character. Consequently the necessary N-arylphthalimide intermediate is not formed by this route.

Step 2: (b) Distinguish the amines Use the carbylamine reaction. Heat each amine with chloroform and alcoholic potassium hydroxide. Ethanamine, $C_2H_5NH_2$, is primary and gives foul-smelling ethyl isocyanide:

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O.$$

N-methylethanamine, $C_2H_5NHCH_3$, is secondary and gives no carbylamine reaction. Thus the positive and negative results distinguish the two compounds.

Step 3: Conclusion (a) Aryl halides do not undergo the substitution required in Gabriel synthesis. (b) The carbylamine reaction distinguishes ethanamine from N-methylethanamine.

Quick Tip to Solve: Count groups attached to nitrogen: ethanamine is primary, while N-methylethanamine is secondary.

Section C (21 marks)

22. 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:

- Steric hindrance opposes nucleophilic substitution at a tertiary carbon, while a strong base can remove a β-hydrogen and produce an alkene.
- Intermolecular hydrogen bonding increases molecular association; intramolecular hydrogen bonding reduces such association.
- Acid strength increases when the conjugate base is stabilised, as in the resonance-stabilised phenoxide ion.

Step 1: (a) Elimination from tert-butyl bromide Tert-butyl bromide is a tertiary alkyl halide. Its crowded carbon centre strongly hinders backside attack by methoxide, so the S_N2 route needed for Williamson ether formation is unfavourable. Methoxide is also a strong base and abstracts a β-hydrogen while bromide leaves, favouring elimination to 2-methylpropene:

$$(CH_3)_3CBr + NaOCH_3 \longrightarrow (CH_3)_2C{=}CH_2 + CH_3OH + NaBr.$$

Thus alkene is the main product.

Step 2: (b) Different steam volatility In o-nitrophenol the adjacent hydroxyl and nitro groups form an intramolecular hydrogen bond. This reduces hydrogen bonding between separate molecules and hence molecular association, making it steam volatile. In p-nitrophenol the groups are too far apart for such an internal bond; intermolecular hydrogen bonding produces associated molecules. Stronger

intermolecular attraction lowers its volatility, so it is not steam volatile.

Step 3: (c) Alcohol is less acidic than phenol Loss of H^+ from phenol produces phenoxide, whose negative charge is delocalised over oxygen and the aromatic ring by resonance. This stabilises the conjugate base. Loss of H^+ from an alcohol produces an alkoxide ion, with its negative charge localised mainly on oxygen and no comparable resonance stabilisation. The electron-releasing inductive effect of an alkyl group further destabilises this negative charge. Hence proton loss is more favourable for phenol than for an alcohol.

Step 4: Conclusion (a) Steric hindrance and strong-base action favour elimination. (b) o-Nitrophenol has intramolecular hydrogen bonding; p-nitrophenol has intermolecular association. (c) Phenoxide is resonance-stabilised, unlike alkoxide.

Quick Tip to Solve: Link each observation to one controlling factor: steric crowding, hydrogen-bond type, or conjugate-base stability.

23. 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:

- The Nernst equation at $298\,\text{K}$ is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the number of electrons transferred and Q is the reaction quotient.
- Pure solid electrodes have unit activity. Thus only the aqueous ionic concentrations enter the reaction quotient, using molar concentrations for this dilute solution.

Step 1: Write the spontaneous cell reaction The left electrode is the anode, where magnesium is oxidised, and the right electrode is the cathode, where copper(II) ions are reduced:

$$\text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2e^-$$
$$\text{Cu}^{2+}(aq) + 2e^- \longrightarrow \text{Cu}(s).$$

Adding the half-reactions gives $\text{Mg}(s) + \text{Cu}^{2+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cu}(s)$. Hence $n = 2$.

Step 2: Evaluate the reaction quotient The magnesium ions are products and the copper(II) ions are reactants. Therefore

$$Q = \frac{[\text{Mg}^{2+}]}{[\text{Cu}^{2+}]} = \frac{0.001}{0.0001} = 10, \qquad \log Q = 1.$$

The solids are omitted; including their concentrations would give an incorrect quotient.

Step 3: Substitute in the Nernst equation Using the supplied standard cell emf,

$$\begin{aligned} E_{\text{cell}} &= 2.71 - \frac{0.0591}{2}(1) \\ &= 2.71 - 0.02955 \\ &= 2.68045\,\text{V}. \end{aligned}$$

Since $Q > 1$, the logarithmic correction is positive and is subtracted, so the emf is slightly below its standard value.

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

Quick Tip to Solve: Write the cell reaction first: here Mg ions belong in the numerator of Q and n is 2, not 1.

24. 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 with an acid chloride forms an N-substituted amide by replacing one hydrogen on nitrogen with an acyl group.
- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into RNH_2 using bromine and aqueous alkali; the carbonyl carbon is lost.

Step 1: Identify the benzoylation product Ethanamine, $CH_3CH_2NH_2$, attacks benzoyl chloride, C_6H_5COCl, at the carbonyl carbon. Chloride is displaced and one N–H hydrogen is removed, giving

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

A base or excess amine removes the acid formed. The ethyl group remains attached to nitrogen; it does not attach to the benzene ring.

Step 2: Name X and classify its amide group The structure of X is $C_6H_5 - C(=O) - NH - CH_2CH_3$. Its IUPAC name is N-ethylbenzamide. Benzamide is the parent amide, and the prefix N-ethyl locates the ethyl substituent on the amide nitrogen. It is a secondary amide, having one hydrogen and one ethyl group on nitrogen.

Step 3: Test the requirement for Hofmann degradation The usual Hofmann bromamide reaction requires an unsubstituted $-CONH_2$ group. In X, that group has become $-CONHC_2H_5$. After initial N-bromination there is no remaining N–H hydrogen for the required base-induced rearrangement pathway. Consequently this N-substituted amide does not undergo the standard Hofmann bromamide degradation.

Step 4: Conclusion $\boxed{X = C_6H_5CONHCH_2CH_3}$, N-ethylbenzamide. It does not undergo Hofmann bromamide degradation because it lacks the primary amide group $-CONH_2$.

Quick Tip to Solve: Check the amide nitrogen: Hofmann degradation needs CONH2, whereas benzoylated ethanamine has CONHCH2CH3.

25. (a) Write IUPAC name of the complex $[CoBr_2(en)_2]^+$.

(b) Write the hybridization of the complex $[NiCl_4]^{2-}$ and predict its magnetic behaviour. [Atomic mass: Ni = 28]

(c) What type of isomerism is shown by the complex $[Co(NH_3)_5Br]SO_4$? [3 marks]

Solution:

Concept:

- For coordination nomenclature, list ligands alphabetically and state the metal oxidation state in Roman numerals; neutral ethane-1,2-diamine is abbreviated en.
- Chloride is a weak-field ligand. A tetrahedral d^8 nickel(II) complex has two unpaired electrons and is paramagnetic.
- Ionisation isomers interchange a coordinated ligand and a counter-ion, producing different ions in aqueous solution.

Step 1: (a) Name the cobalt complex In $[CoBr_2(en)_2]^+$, each bromido ligand has charge -1, while en is neutral. If cobalt has oxidation state x, then $x - 2 = +1$, giving $x = +3$. Bromido precedes ethane-1,2-diamine alphabetically. Because the latter ligand name is itself complex, two such ligands are denoted by bis. The name is dibromidobis(ethane-1,2-diamine)cobalt(III) ion.

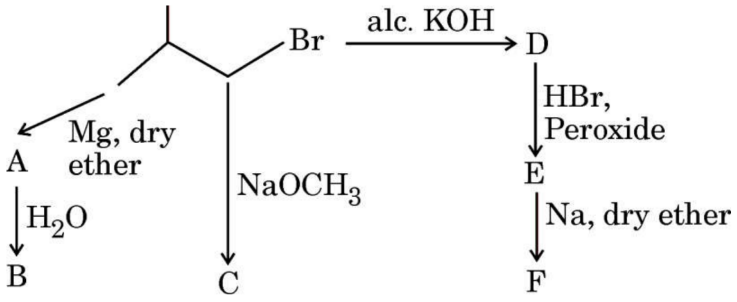
Step 2: (b) Determine hybridisation and magnetic behaviour In $[NiCl_4]^{2-}$, $x + 4(-1) = -2$, so nickel is Ni^{2+}. Nickel has electronic configuration $[Ar]3d^8 4s^2$, hence Ni^{2+} is $[Ar]3d^8$. The weak-field chloride ligands do not cause the pairing needed for an inner-orbital square-planar arrangement. One $4s$ and three $4p$ orbitals form four sp^3 hybrid orbitals. The complex is tetrahedral, with two unpaired electrons, and is therefore paramagnetic. The supplied value 28 identifies nickel by its atomic number.

Step 3: (c) Identify the isomerism In $[Co(NH_3)_5Br]SO_4$, bromide is coordinated and sulfate is the counter-ion. They can exchange roles to give $[Co(NH_3)_5SO_4]Br$. The first salt releases sulfate ions on dissolution, while the second releases bromide ions. This is ionisation isomerism.

Step 4: Conclusion (a) Dibromidobis(ethane-1,2-diamine)cobalt(III) ion. (b) sp^3 hybridisation; tetrahedral and paramagnetic with two unpaired electrons. (c) Ionisation isomerism.

Quick Tip to Solve: Find the metal oxidation state before its d count: Ni(II) is d8, and weak-field chloride gives tetrahedral sp3 coordination.

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



Solution:

Concept:

- The starting compound shown is $(CH_3)_2CHCH_2Br$, 1-bromo-2-methylpropane. The downward line is a reaction arrow.
- Magnesium forms a Grignard reagent, hydrolysis replaces its MgBr group by hydrogen, and methoxide substitutes bromide.
- Alcoholic KOH eliminates HBr; peroxide promotes anti-Markovnikov HBr addition; sodium in dry ether couples two alkyl groups.

Step 1: Identify A and B Magnesium inserts into the carbon-bromine bond in dry ether:

$$(CH_3)_2CHCH_2Br + Mg \longrightarrow (CH_3)_2CHCH_2MgBr.$$

Thus A is 2-methylpropylmagnesium bromide. Water protonates the carbon bonded to magnesium:

$$(CH_3)_2CHCH_2MgBr + H_2O \longrightarrow (CH_3)_2CHCH_3 + Mg(OH)Br.$$

B is 2-methylpropane. This protonation retains all four carbon atoms of the starting haloalkane.

Step 2: Identify C and D Methoxide, CH_3O^-, attacks the primary carbon bonded to bromine, replacing bromide to give an ether:

$$(CH_3)_2CHCH_2Br + NaOCH_3 \longrightarrow (CH_3)_2CHCH_2OCH_3 + NaBr.$$

C is 1-methoxy-2-methylpropane. Alcoholic KOH causes beta-elimination: hydrogen is removed from the neighbouring CH group and bromide leaves from the terminal carbon:

$$(CH_3)_2CHCH_2Br \xrightarrow{\text{alc. KOH}} (CH_3)_2C = CH_2 + KBr + H_2O.$$

Hence D is 2-methylpropene.

Step 3: Identify E and F Peroxide causes radical, anti-Markovnikov addition of HBr. Bromine adds to the terminal carbon of 2-methylpropene, forming

$$E = (CH_3)_2CHCH_2Br.$$

E is 1-bromo-2-methylpropane, the original haloalkane. Sodium in dry ether then produces the Wurtz

coupling product:

$$2(CH_3)_2CHCH_2Br + 2Na \longrightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2NaBr.$$

F is 2,5-dimethylhexane. The new bond joins the two carbons which originally carried bromine, giving eight carbons in total.

Step 4: Conclusion A: $(CH_3)_2CHCH_2MgBr$; B: 2-methylpropane; C: 1-methoxy-2-methylpropane; D: 2-methylpropene; E: 1-bromo-2-methylpropane; F: 2,5-dimethylhexane.

Quick Tip to Solve: Follow the carbon bearing bromine through the sequence; the Wurtz step joins two such carbon atoms and doubles the four-carbon skeleton.

OR

26(b). What happens when :

(i) ethyl chloride is treated with KCN ?

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

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

Solution:

Concept:

- Nucleophilic substitution replaces the halogen of a haloalkane by an incoming nucleophile. Carbon-bonded cyanide extends the carbon chain by one carbon.
- Finkelstein exchange uses NaI in dry acetone; Swarts fluorination replaces chlorine or bromine with fluorine using a metallic fluoride.

Step 1: (i) Reaction of ethyl chloride with KCN Cyanide ion attacks through its carbon atom in the reaction with ionic KCN. Chloride is replaced by the cyanide group:

$$CH_3CH_2Cl + KCN \longrightarrow CH_3CH_2CN + KCl.$$

The organic product is propanenitrile (ethyl cyanide). The nitrile carbon is included in the parent chain, hence the product has three carbon atoms. An isocyanide is not the expected product with KCN; silver cyanide favours that linkage.

Step 2: (ii) Reaction of ethyl bromide with NaI In dry acetone, iodide displaces bromide from the primary haloalkane:

$$CH_3CH_2Br + NaI \xrightarrow{\text{dry acetone}} CH_3CH_2I + NaBr\downarrow.$$

The product is iodoethane (ethyl iodide). This halogen-exchange reaction is the Finkelstein reaction. Sodium bromide is insoluble in acetone and precipitates, helping drive the conversion towards iodoethane.

Step 3: (iii) Reaction of ethyl bromide with silver fluoride Fluoride replaces bromide to yield fluoroethane:

$$CH_3CH_2Br + AgF \longrightarrow CH_3CH_2F + AgBr\downarrow.$$

This is a Swarts reaction. Silver bromide is formed as a precipitate. Here the carbon skeleton remains a two-carbon chain because only the halogen is exchanged, unlike cyanide substitution in part (i).

Step 4: Conclusion (i) Propanenitrile, CH_3CH_2CN; (ii) iodoethane, CH_3CH_2I; (iii) fluoroethane, CH_3CH_2F.

Quick Tip to Solve: For KCN count the carbon of CN in the product; NaI and AgF exchange only the halogen and retain two carbons.

27. Give plausible explanation for each of the following :

(a) Propanal is more reactive towards addition of HCN than propanone.

(b) Alpha (α)-hydrogens of aldehydes and ketones are acidic in nature.

(c) A base has to be added for an effective reaction of carbonyl compounds with HCN. [3 marks]

Solution:

Concept:

- Nucleophilic addition is favoured by greater positive character and lower steric hindrance at the carbonyl carbon.
- Acidity depends on stability of the conjugate base. The enolate ion is stabilised by delocalisation of negative charge between carbon and oxygen.
- HCN is a weak acid; cyanide ion, CN^-, is the nucleophile in cyanohydrin formation.

Step 1: (a) Compare propanal and propanone Propanal, CH_3CH_2CHO, has one alkyl group and one hydrogen bonded to its carbonyl carbon. Propanone, CH_3COCH_3, has two electron-donating alkyl groups. Their positive inductive effect reduces the electrophilic character of the carbonyl carbon more in propanone. In addition, two alkyl groups offer greater steric resistance to attack by CN^- than one alkyl group and a hydrogen. Both electronic and steric factors therefore make propanal more reactive towards HCN addition.

Step 2: (b) Explain alpha-hydrogen acidity An alpha-hydrogen is attached to the carbon immediately adjacent to the carbonyl group. Its removal as a proton produces a resonance-stabilised enolate ion:

$$RCOCH_2R' \xrightarrow{-H^+} RCOC^-HR' \leftrightarrow RC(O^-)=CHR'.$$

In the first contributing structure the negative charge is on the alpha-carbon; in the second it is on oxygen. Delocalisation stabilises the conjugate base, while the electron-withdrawing carbonyl group also assists proton removal. Hence these hydrogens are more acidic than hydrogens of an ordinary alkane.

Step 3: (c) Explain the role of base in HCN addition HCN alone provides only a small concentration of cyanide ions because it is weakly ionised. A small amount of base generates the effective nucleophile:

$$HCN + OH^- \rightleftharpoons CN^- + H_2O.$$

Cyanide attacks the carbonyl carbon, producing an alkoxide which takes a proton from HCN:

$$R_2C = O + CN^- \longrightarrow R_2C(O^-)CN,$$
$$R_2C(O^-)CN + HCN \longrightarrow R_2C(OH)CN + CN^-.$$

The product is a cyanohydrin and cyanide is regenerated. Thus a mild basic catalyst increases nucleophile concentration and makes addition effective.

Step 4: Conclusion (a) Propanal has less steric hindrance and a more electrophilic carbonyl carbon. (b) Alpha-hydrogens are acidic because their removal gives a resonance-stabilised enolate. (c) Base supplies CN^-, the nucleophile needed for cyanohydrin formation.

Quick Tip to Solve: For carbonyl reasoning, check three factors separately: electrophilicity, steric hindrance and stability of the conjugate base.

28. The following results have been obtained during the kinetic studies of the reaction :

2A + B → C + D

Experiment	[A]/mol L^{-1}	[B]/mol L^{-1}	Initial rate of formation of D (mol L^{-1} min^{-1})
1	0.1	0.1	6.0×10^{-3}
2	0.3	0.2	7.2×10^{-3}
3	0.3	0.4	2.88×10^{-1}
4	0.4	0.1	2.40×10^{-2}

What is the rate law ? What is the order of reaction with respect to each reactant and the overall order of reaction ? [3 marks]

Solution:

Concept:

- For the initial rate of formation of D, write $r = k[A]^m[B]^n$, where k is the rate constant and m, n are experimentally determined partial orders.
- Compare experiments with one concentration fixed; the overall order is $m + n$. A proposed rate law must reproduce every measured rate, not just selected rows.

Step 1: Determine the order in A Experiments 1 and 4 have the same $[B] = 0.1\,\text{mol L}^{-1}$. Therefore

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \left(\frac{0.4}{0.1}\right)^m, \qquad 4 = 4^m.$$

Thus these two experiments give $m = 1$. The coefficient 2 of A in the balanced equation does not determine this experimental order.

Step 2: Use experiments 1 and 3 With $m = 1$, the rate ratio gives

$$\frac{2.88 \times 10^{-1}}{6.0 \times 10^{-3}} = \frac{0.3}{0.1}\left(\frac{0.4}{0.1}\right)^n, \qquad 48 = 3 \times 4^n.$$

Hence $4^n = 16$, so $n = 2$. Experiments 1, 3 and 4 therefore imply $r = k[A][B]^2$, an overall order of 3. Experiment 1 gives $k = 6.0\,\text{L}^2\text{mol}^{-2}\text{min}^{-1}$.

Step 3: Check the remaining printed result For experiment 2 the same law predicts

$$r_2 = 6.0(0.3)(0.2)^2 = 7.2 \times 10^{-2}\,\text{mol L}^{-1}\text{min}^{-1}.$$

However, the printed rate is 7.2×10^{-3} mol $\text{L}^{-1}\text{min}^{-1}$, which is ten times smaller. Thus experiment 2 contradicts the law fixed by the other three rows; the four printed results cannot all satisfy a single power-law rate equation with constant orders.

Step 4: Conclusion The printed data are inconsistent, so no single rate law and overall order fit all four experiments. Experiments 1, 3 and 4 imply $r = k[A][B]^2$: order in A $= 1$, order in B $= 2$, overall order $= 3$; experiment 2 fails this law.

Quick Tip to Solve: After finding orders from convenient pairs, substitute all remaining rows: experiment 2 here exposes a factor-of-ten inconsistency.

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.

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

Answer the following questions :

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

Solution:

Concept:

- The crystal field splitting energy measures the separation of the two sets of metal d orbitals in a ligand field. Its size depends on the ligand and the coordination geometry.
- For the same metal ion and the same ligands, the tetrahedral splitting Δ_t is approximately four-

ninths of the octahedral splitting Δ_o.

Step 1: Define the spectrochemical series The spectrochemical series is an experimentally determined arrangement of ligands in increasing order of their ability to cause crystal field splitting of the metal d orbitals. Ligands near the beginning are weak field ligands, giving smaller splitting, while those near the end are strong field ligands, giving larger splitting. For example, the relative order $Cl^- < H_2O < NH_3 < CN^-$ places chloride below cyanide in field strength.

Step 2: Relate the two geometries For a given metal ion with the same ligands,

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

Thus tetrahedral splitting is smaller than octahedral splitting. This comparison concerns the magnitude of the energy gap; the lower and upper d-orbital sets have different identities in tetrahedral and octahedral fields.

Step 3: Conclusion The spectrochemical series orders ligands by increasing crystal field splitting strength, and $\boxed{\Delta_t \simeq \frac{4}{9}\Delta_o}$ for the same metal ion and ligands.

Quick Tip to Solve: Write the comparison for the same metal and ligands; the tetrahedral energy gap is the smaller one.

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:

- Use the absorbed wavelength in the supplied table, rather than the observed colour of the complex.
- Increasing wavelength means ordering the numerical wavelength values from smallest to largest; photon energy instead follows $E = hc/\lambda$.

Step 1: Read the tabulated wavelengths The table gives 310 nm for $[Co(CN)_6]^{3-}$, 475 nm for $[Co(NH_3)_6]^{3+}$, and 600 nm for $[Cu(H_2O)_4]^{2+}$.

Step 2: Compare the values Since $310 < 475 < 600$, the cyanide complex absorbs the shortest wavelength and the copper aqua complex absorbs the longest. The complementary colour seen by an observer is not the wavelength being ordered.

Step 3: Conclusion

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

Quick Tip to Solve: Copy 310, 475 and 600 nm beside the corresponding complexes before arranging them in increasing order.

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 lower set is t_{2g} and the upper set is e_g; the gap between them is Δ_o.
- When $\Delta_o < P$, promotion to the upper set costs less energy than pairing, so a high spin configuration is formed.

Step 1: Choose the spin arrangement The given d5 ion contains five electrons in its d subshell. Because the splitting is smaller than the pairing energy P, electrons remain unpaired where possible rather than pairing in the lower t_{2g} orbitals.

Step 2: Fill the orbitals The first three electrons singly occupy the three t_{2g} orbitals. The next two singly occupy the two e_g orbitals. Hence all five d orbitals contain one electron, giving five unpaired electrons.

Step 3: Conclusion The high spin electronic configuration is $\boxed{t_{2g}^3 e_g^2}$, with five unpaired electrons.

Quick Tip to Solve: For octahedral d5 with splitting smaller than pairing energy, place one electron in each of the five orbitals.

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

Solution:

Concept:

- In a free metal ion, the five d orbitals are degenerate, meaning they have equal energy.
- The electric field of surrounding ligands removes this degeneracy and separates the d orbitals into sets with different energies.

Step 1: Identify the split levels For an octahedral complex the d orbitals separate into the lower t_{2g} set and the higher e_g set because their interactions with the approaching ligands differ.

Step 2: Specify the energy gap The difference between the energies of these sets is the crystal field splitting energy. In an octahedral field it is written $\Delta_o = E(e_g) - E(t_{2g})$; the corresponding tetrahedral gap is denoted Δ_t.

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

Quick Tip to Solve: Define splitting as the energy gap between d-orbital sets, rather than the total energy of the metal ion.

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 are biomolecules that serve as sources of energy and as reserves of metabolic fuel.
- Glucose is oxidised during cellular respiration; excess carbohydrate can be stored as polysaccharides such as starch or glycogen.

Step 1: Supply energy Carbohydrates are a major source of energy for living organisms. Glucose obtained from dietary carbohydrates undergoes oxidation during cellular respiration, releasing energy needed for cellular activities. Thus carbohydrate consumption supplies fuel for processes such as movement, transport and maintenance of the body.

Step 2: Store energy Carbohydrates also act as food reserves. Plants store carbohydrate chiefly as starch, whereas animals store it as glycogen, especially in the liver and muscles. These polysaccharides can be broken down to provide glucose when an organism needs energy between meals or during increased activity.

Step 3: Conclusion Two functions are: (1) supplying energy through oxidation of glucose, and (2) storing energy as starch in plants and glycogen in animals.

Quick Tip to Solve: Give each function with a named carbohydrate example: glucose for energy, starch or glycogen for storage.

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

Solution:

Concept:

- Monosaccharides are the simplest carbohydrate units and cannot be hydrolysed into simpler carbohydrate molecules.
- Glucose, fructose and ribose are examples of monosaccharides.

Step 1: Apply the hydrolysis criterion A carbohydrate is classified as a monosaccharide when hydrolysis cannot split it into smaller carbohydrate units. The definition concerns breakdown into simpler carbohydrates, rather than whether the molecule can undergo other chemical reactions.

Step 2: Distinguish from larger carbohydrates Glucose and fructose each constitute a single carbohy-

drate unit. In contrast, sucrose is a disaccharide because hydrolysis produces glucose and fructose. This distinction identifies the essential feature of a monosaccharide.

Step 3: Conclusion Monosaccharides are carbohydrates that cannot be hydrolysed further into simpler carbohydrates; examples include glucose and fructose.

Quick Tip to Solve: Use the phrase "cannot be hydrolysed into simpler carbohydrates" in the definition.

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

Solution:

Concept:

- Vitamin D supports normal calcium and phosphate utilisation and the mineralisation of bones.
- Deficiency of a vitamin is identified by its characteristic deficiency disease.

Step 1: Identify the vitamin deficiency The question names vitamin D. Insufficient vitamin D impairs normal bone mineralisation, producing weak or soft bones; it is therefore associated with a bone disorder.

Step 2: Name the deficiency disease The standard deficiency disease associated with lack of vitamin D is rickets, particularly in children. In adults, inadequate mineralisation due to vitamin D deficiency is called osteomalacia. Scurvy and night blindness are associated with different vitamins.

Step 3: Conclusion Lack of vitamin D causes rickets in children (and osteomalacia in adults).

Quick Tip to Solve: Recall the pair vitamin D–rickets; scurvy belongs to vitamin C and night blindness to vitamin A.

OR

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

Solution:

Concept:

- Hormones are chemical messengers that regulate physiological processes such as blood glucose concentration.
- Insulin is a peptide hormone secreted by the beta cells of the pancreatic islets.

Step 1: Identify the hormone The hormone expected here is insulin. It is released by the pancreas, particularly when blood glucose rises after food is absorbed, and participates in maintaining normal blood glucose concentration.

Step 2: Relate its action to glucose control Insulin promotes uptake and utilisation of glucose and its storage as glycogen, thereby lowering an elevated blood glucose level. Its deficiency can produce type 1 diabetes, as stated in the passage. This links the named hormone directly to the regulation asked

about.

Step 3: Conclusion The hormone is insulin.

Quick Tip to Solve: Use the passage clue: deficiency of insulin causes type 1 diabetes, linking insulin to blood glucose control.

Section E (15 marks)

31(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 flow of solvent through a semipermeable membrane from pure solvent into a solution. The membrane allows solvent molecules through but prevents the passage of solute particles.
- For a dilute solution, $\pi = nRT/V = CRT$, where π is osmotic pressure, n is the amount of solute, V is solution volume, C is molar concentration, R is the gas constant and T is absolute temperature.
- Raoult's law for an ideal binary liquid mixture gives $P = x_A p_A^\circ + x_B p_B^\circ$, where $x_A + x_B = 1$ and the superscript denotes the vapour pressure of the pure liquid at the same temperature.

Step 1: (i) Define osmotic pressure Osmotic pressure is the minimum excess pressure that must be applied to the solution to prevent the passage of solvent into it through a semipermeable membrane separating the solution from the pure solvent. At this pressure, net osmosis stops. The definition refers to the pressure needed to oppose solvent flow, rather than the rate or amount of solvent transfer.

Step 2: (i) Explain why it is a colligative property The relation $\pi = nRT/V$ shows that at fixed temperature and volume, osmotic pressure depends on the number of dissolved solute particles and is independent of their chemical identity. Hence, dilute solutions with equal solute particle concentrations have the same osmotic pressure at the same temperature. This dependence on particle concentration makes osmotic pressure a colligative property. If the solute dissociates or associates, its effective particle concentration is included using the van't Hoff factor, giving $\pi = iCRT$.

Step 3: (ii) Apply Raoult's law to the liquid mixture At $400\,\text{K}$, the pure-liquid vapour pressures are $p_A^\circ = 450\,\text{mmHg}$ and $p_B^\circ = 700\,\text{mmHg}$. Use $x_B = 1 - x_A$ in the expression for the total pressure:

$$\begin{aligned} P &= x_A p_A^\circ + (1 - x_A) p_B^\circ, \\ 600 &= 450 x_A + 700(1 - x_A), \\ 600 &= 700 - 250 x_A, \\ 250 x_A &= 100. \end{aligned}$$

Here all pressure terms are in mmHg, so their common unit cancels when calculating a mole fraction.

Step 4: (ii) Calculate and verify the composition Therefore $x_A = 100/250 = 0.40$ and $x_B = 1 - 0.40 = 0.60$. These are the mole fractions of the components in the liquid phase. To verify, the partial pressures are $p_A = 0.40(450) = 180$ mmHg and $p_B = 0.60(700) = 420$ mmHg. Their sum is 600 mmHg, equal to the given total vapour pressure. Both mole fractions lie between zero and one and their sum is unity. The composition can also be expressed as a mole ratio $n_A : n_B = 0.40 : 0.60 = 2 : 3$.

Step 5: Conclusion (i) Osmotic pressure is the minimum excess pressure applied to a solution to stop osmosis; it is colligative because it depends on solute particle concentration at fixed temperature. (ii) The liquid mixture has $\boxed{x_A = 0.40, \quad x_B = 0.60}$, or 40% A and 60% B by mole.

Quick Tip to Solve: For an ideal binary mixture, directly use $x_A = (p_B^\circ - P)/(p_B^\circ - p_A^\circ)$, then find $x_B = 1 - x_A$; these are liquid mole fractions.

OR

31(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 attractions between unlike molecules exceed those between like molecules in the pure liquids. Escaping tendency and vapour pressure decrease.
- For a dilute solution of a non-volatile solute, boiling-point elevation is $\Delta T_b = iK_b m$, where m is the number of moles of solute per kilogram of solvent. Sucrose is a non-electrolyte, so $i = 1$.

Step 1: (i) Identify the deviation On mixing phenol and aniline, strong hydrogen bonds form between the phenolic $-$OH group and the nitrogen atom of aniline. These unlike-molecule attractions exceed the average interactions in the separate pure liquids. Molecules therefore escape less readily into the vapour phase, and the vapour pressure lies below the value predicted by Raoult's law. The mixture exhibits negative deviation.

Step 2: (i) State the volume and enthalpy changes The stronger attractions bring the molecules closer together. The mixture contracts, so its volume is less than the sum of the initial volumes: $\Delta V_{\text{mix}} < 0$. Forming the stronger interactions releases heat, making mixing exothermic: $\Delta H_{\text{mix}} < 0$. These signs describe the change on mixing the two liquids, rather than a change caused by external heating.

Step 3: (ii) Find the elevation and molality Compare both boiling points at the stated external pressure of 750 mmHg. Pure water boils at 99.48°C at this pressure, so

$$\Delta T_b = 100.00 - 99.48 = 0.52\,\text{K}.$$

Using the given $K_b = 0.52\,\text{K kg mol}^{-1}$,

$$m = \frac{\Delta T_b}{K_b} = \frac{0.52}{0.52} = 1.00\,\text{mol kg}^{-1}.$$

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

Step 4: (ii) Convert molality to mass of sucrose The mass of solvent is $500\,\text{g} = 0.500\,\text{kg}$, hence the amount of sucrose needed is

$$n = m \times m_{\text{water}} = 1.00 \times 0.500 = 0.500\,\text{mol}.$$

With the given molar mass $M = 342\,\text{g mol}^{-1}$,

$$w = nM = 0.500 \times 342 = 171\,\text{g}.$$

Molality uses the mass of water alone, not the total mass after adding sucrose. Substitution gives $0.52 \times (171/342)/0.500 = 0.52\,\text{K}$, which restores the required final boiling point.

Step 5: Conclusion (i) Phenol-aniline shows negative deviation from Raoult's law, with $\Delta V_{\text{mix}} < 0$ and $\Delta H_{\text{mix}} < 0$. (ii) Add $\boxed{171\,\text{g}}$ of sucrose to $500\,\text{g}$ of water.

Quick Tip to Solve: Use the pure-water boiling point at 750 mmHg: the required elevation is 0.52 K. Convert the solvent mass to 0.500 kg before applying molality.

32(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 the acetyl group, $-COCH_3$, into benzene when acetyl chloride reacts in the presence of anhydrous $AlCl_3$.
- A secondary alcohol oxidises to a ketone without changing the carbon skeleton. A methyl ketone, $RCOCH_3$, gives $RCOONa$ and yellow iodoform, CHI_3, with iodine and aqueous sodium hydroxide.

Step 1: Identify Q from the independent preparation The benzene reaction fixes the structure of Q unambiguously. Acetyl chloride supplies the acetyl group in the following reaction:

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

Thus Q is acetophenone (1-phenylethan-1-one). Its carbonyl carbon is bonded to a phenyl group and a methyl group.

Step 2: Identify the alcohol P To obtain this ketone by oxidation, replace its carbonyl group by the

corresponding secondary alcohol group:

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

Therefore P is 1-phenylethan-1-ol. Counting atoms in $C_6H_5CH(OH)CH_3$ gives $C_8H_{10}O$, in agreement with the supplied molecular formula. The hydroxyl-bearing carbon has one hydrogen, so its oxidation gives a ketone.

Step 3: Identify the products of the iodoform reaction Acetophenone contains the required $-COCH_3$ group. Iodine in aqueous alkali replaces the three methyl hydrogens, followed by cleavage to a carboxylate and iodoform:

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

The phenyl-containing fragment is sodium benzoate, R, while the yellow precipitate is iodoform, S. Since the medium is alkaline and no acidification is specified, R is the sodium salt, not free benzoic acid.

Step 4: Conclusion P is 1-phenylethan-1-ol, $C_6H_5CH(OH)CH_3$; Q is acetophenone, $C_6H_5COCH_3$. The other products are R, sodium benzoate, C_6H_5COONa; and S, iodoform, CHI_3.

Quick Tip to Solve: Identify the ketone from Friedel–Crafts acylation first; then work backwards to the secondary alcohol and forwards through the iodoform test.

32(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 the Cannizzaro reaction with concentrated alkali: one molecule is reduced to an alcohol and another is oxidised to a carboxylate salt.
- Benzaldehyde, C_6H_5CHO, has no alpha hydrogen and therefore undergoes disproportionation.

Step 1: Apply the Cannizzaro reaction On heating benzaldehyde with concentrated KOH, two molecules react as follows:

$$2C_6H_5CHO + KOH \xrightarrow{\Delta} C_6H_5CH_2OH + C_6H_5COOK.$$

The aldehyde group of one molecule becomes $-CH_2OH$, while that of the other becomes $-COO^-K^+$.

Step 2: State the structures in the reaction medium The reduced product is benzyl alcohol, $C_6H_5 - CH_2 - OH$. The oxidised product is potassium benzoate, $C_6H_5 - C(=O)O^-K^+$. Concentrated KOH keeps the acid-derived product in its salt form; benzoic acid would be obtained only after a separate acidification.

Step 3: Conclusion The products are benzyl alcohol, $\boxed{C_6H_5CH_2OH}$, and potassium benzoate, $\boxed{C_6H_5COOK}$.

Quick Tip to Solve: With concentrated KOH, write potassium benzoate directly; do not replace it by benzoic acid unless acidification is given.

OR

32(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, using $\mathrm{Zn(Hg)/conc.\ HCl}$, converts a ketone carbonyl group $> \mathrm{C=O}$ into $> \mathrm{CH_2}$.
- A methyl ketone undergoes the iodoform reaction to give a carboxylate, which gives the carboxylic acid on acidification.
- An alkyl halide reacts with alcoholic KCN to give a nitrile. Hydrolysis of the nitrile gives a carboxylic acid with one additional carbon.

Step 1: (I) Convert propanone to propane Reduce the carbonyl group of propanone completely by Clemmensen reduction:

$$\mathrm{CH_3COCH_3} \xrightarrow{\mathrm{Zn(Hg),\ conc.\ HCl}} \mathrm{CH_3CH_2CH_3}.$$

The carbon skeleton remains unchanged; the oxygen is removed and the carbonyl carbon becomes a methylene group. A reagent that reduces only to an alcohol would stop at propan-2-ol and would not complete this conversion.

Step 2: (II) Convert acetophenone to benzoic acid Treat acetophenone with iodine and aqueous sodium hydroxide, then acidify the sodium benzoate formed:

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

The first reaction also produces yellow $\mathrm{CHI_3}$. Acidification is essential to obtain benzoic acid from its sodium salt.

Step 3: (III) Convert benzyl chloride to phenylethanoic acid First carry out nucleophilic substitution with alcoholic KCN to introduce an extra carbon as a nitrile group. Then hydrolyse the nitrile with dilute acid on heating:

$$\mathrm{C_6H_5CH_2Cl} \xrightarrow{\mathrm{alc.\ KCN}} \mathrm{C_6H_5CH_2CN}$$
$$\mathrm{C_6H_5CH_2CN} \xrightarrow{\mathrm{dil.\ HCl,\ H_2O,\ \Delta}} \mathrm{C_6H_5CH_2COOH}.$$

The intermediate is benzyl cyanide (phenylacetonitrile). Its nitrile carbon becomes the carboxyl carbon, giving phenylethanoic acid (phenylacetic acid).

Step 4: Conclusion (I) Use $\mathrm{Zn(Hg)/conc.\ HCl}$. (II) Use $\mathrm{I_2/aq.\ NaOH}$, then acidify. (III) Use alcoholic KCN, then hydrolyse with dilute acid and heat.

Quick Tip to Solve: Count the carbons first: benzyl chloride needs one extra carbon, supplied by KCN before nitrile hydrolysis.

32(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:

- Phenols form a coloured complex with neutral ferric chloride; an ordinary aldehyde does not give this phenolic test.
- Tollens' reagent, ammoniacal silver nitrate, oxidises aldehydes to carboxylate ions while silver ions are reduced to metallic silver. Simple ketones do not respond.

Step 1: (I) Distinguish benzaldehyde and phenol Add a few drops of freshly prepared neutral $FeCl_3$ solution to separate samples. Phenol produces a violet colour due to formation of a ferric phenoxide complex. Benzaldehyde does not produce this violet colour because it has no phenolic hydroxyl group. Thus the sample showing violet colour is phenol.

Step 2: (II) Distinguish butanal and butan-2-one Warm separate samples gently with freshly prepared Tollens' reagent in a water bath. Butanal forms a silver mirror (or a deposit of silver); butan-2-one gives no silver mirror. The aldehyde reaction is

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

Step 3: Conclusion Neutral ferric chloride gives a violet colour with phenol only. Tollens' reagent gives a silver mirror with butanal only, distinguishing it from butan-2-one.

Quick Tip to Solve: Choose a test for the functional group: neutral ferric chloride for phenol and Tollens' reagent for an aldehyde.

33(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:

- Preparation of permanganate involves oxidation of manganese from $+4$ in MnO_2 to $+6$ in manganate, followed by oxidation to $+7$ in permanganate.
- The colour of most transition-metal ions is due to electronic transitions between split d orbitals. A d^0 ion has no d electron for such a transition.
- The standard reduction potential depends on the combined effects of atomisation, ionisation and

hydration. Strong metallic bonding requires considerable energy to separate metal atoms into gaseous atoms.

Step 1: (i) Convert pyrolusite into potassium manganate Fuse finely powdered pyrolusite with potassium hydroxide in the presence of air or another oxidising agent. Green potassium manganate is formed:

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

Manganese is oxidised from $+4$ to $+6$ in this step.

Step 2: Oxidise manganate to permanganate Electrolytic oxidation of an alkaline manganate solution gives permanganate. The anode reaction is

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

With hydrogen evolution at the cathode, the overall equation is

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

The purple solution is concentrated to obtain potassium permanganate crystals.

Step 3: (ii)(I) Explain the white colour of scandium salts Scandium has atomic number 21 and configuration $[\mathrm{Ar}]3\mathrm{d}^1 4\mathrm{s}^2$. Its usual ion, Sc^{3+}, has configuration $[\mathrm{Ar}]3\mathrm{d}^0$. With no d electrons, d–d transitions cannot occur, so the ion does not absorb visible light by this mechanism. Hence its ordinary salts are white and their solutions are colourless.

Step 4: (ii)(II) Compare copper and manganese electrode potentials For formation of $\mathrm{Cu}^{2+}(\mathrm{aq})$ from copper metal, the high atomisation and ionisation energy requirements are not compensated by hydration. Thus copper resists oxidation to its aqueous ion, and the reverse reduction $\mathrm{Cu}^{2+} + 2\mathrm{e}^- \rightarrow \mathrm{Cu}$ has a positive standard potential. For manganese, formation of $\mathrm{Mn}^{2+}(\mathrm{aq})$ is favoured by hydration and the especially stable half-filled $3d^5$ configuration of Mn^{2+}. Oxidation of manganese is therefore favourable relative to the standard hydrogen electrode, and $E^\circ_{\mathrm{Mn}^{2+}/\mathrm{Mn}}$ is negative.

Step 5: (ii)(III) Explain high enthalpies of atomisation Transition metals have several valence electrons, including unpaired d electrons as well as s electrons, available for metallic bonding. Their extensive participation in bonding gives strong interatomic attraction in the metal lattice. A large energy input is therefore needed to separate the solid into individual gaseous atoms, producing high enthalpies of atomisation.

Step 6: Conclusion Pyrolusite is oxidised through green manganate to purple permanganate. The d^0 configuration explains white scandium salts; the energy balance and stable d^5 manganese(II) ion explain the electrode-potential signs; strong metallic bonds explain high atomisation enthalpies.

Quick Tip to Solve: Track manganese as $+4 \rightarrow +6 \rightarrow +7$, and use the configuration of the ion, not the neutral atom, when explaining salt colour.

OR

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

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

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

(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 redox equations by equalising the electrons exchanged.
- Copper(II) oxidises iodide to iodine; the copper(I) formed precipitates as insoluble copper(I) iodide, CuI.
- Similar ionic radii and the common $+3$ oxidation state make lanthanoid chemistry similar. Metallic bonding depends on electron participation; removing an electron from a filled $3d^{10}$ subshell requires substantial energy.

Step 1: (i)(I) Balance dichromate with hydrogen sulphide The reduction and oxidation half-reactions in acidic medium are

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O,$$
$$H_2S \longrightarrow S + 2H^+ + 2e^-.$$

Multiply the second equation by three, add, and cancel electrons and six hydrogen ions. The balanced equation is

$$\boxed{Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O}.$$

Dichromate and chromium(III) are aqueous, hydrogen sulphide is a gas, sulphur is solid, and water is liquid. Both sides contain two chromium atoms, seven oxygen atoms, fourteen hydrogen atoms and three sulphur atoms; each side has net charge $+6$.

Step 2: (i)(II) Balance copper(II) with iodide Two copper(II) ions each accept one electron, while two iodide ions lose two electrons to form iodine. Two further iodide ions combine with the resulting copper(I) ions to give the precipitate. Thus,

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

There are four iodine atoms on either side and the net charge on each side is zero. Writing only copper(I) ions would omit the precipitation that drives this reaction.

Step 3: (ii)(I) Explain the difficult separation of lanthanoids Lanthanoids predominantly form Ln^{3+} ions. Successive elements have very similar ionic radii because lanthanoid contraction produces only a gradual decrease in size across the series. Their ions therefore have closely similar chemical properties, including similar compound formation and solubility behaviour. Ordinary chemical separation methods distinguish them only poorly, making separation of a mixture difficult.

Step 4: (ii)(II) Compare the melting points of chromium and manganese Chromium has configuration $[\mathrm{Ar}]3d^5 4s^1$, whereas manganese has $[\mathrm{Ar}]3d^5 4s^2$. Chromium has more unpaired valence electrons available for participation in metallic bonding. In manganese, the particularly stable half-filled $3d^5$ arrangement contributes to anomalously weaker metallic bonding. Consequently the metallic bonds in chromium are stronger, and more thermal energy is needed to melt it; chromium therefore has the higher melting point.

Step 5: (ii)(III) Explain the oxidation-state limit of zinc Zinc has configuration $[\mathrm{Ar}]3d^{10}4s^2$. Loss of its two $4s$ electrons gives Zn^{2+} with the stable completely filled $3d^{10}$ subshell. Formation of an oxidation state greater than $+2$ would require removal of an electron from this filled inner subshell. The third ionisation enthalpy is consequently very high, so such oxidation states 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. Lanthanoids are hard to separate because of similar trivalent-ion chemistry; stronger metallic bonding gives Cr its higher melting point; stable $3d^{10}$ makes oxidation of Zn beyond $+2$ difficult.

Quick Tip to Solve: For Cu(II) with iodide, reserve two iodide ions for the CuI precipitate as well as two for oxidation to iodine; this gives the coefficient four for iodide.