CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-4-1

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 3 hours **Maximum Marks: 70**

General Instructions

(i) This question paper contains **33** questions. **All** questions are **compulsory**.

(ii) Question paper is divided into **FIVE** sections – Section **A, B, C, D** and **E**.

(iii) **Section A** – question number **1** to **16** are multiple choice type questions. Each question carries **1** mark.

(iv) **Section B** – question number **17** to **21** are very short answer type questions. Each question carries **2** marks.

(v) **Section C** – question number **22** to **28** are short answer type questions. Each question carries **3** marks.

(vi) **Section D** – question number **29** and **30** are case-based questions. Each question carries **4** marks.

(vii) **Section E** – question number **31** to **33** are long answer type questions. Each question carries **5** marks.

(viii) There is no overall choice given in the question paper. However, an internal choice has been provided in few questions in all the Sections except Section –A.

(ix) Kindly note that there is a separate question paper for Visually Impaired candidates.

(x) Use of calculator is NOT allowed.

Section A (16 marks)

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

1. The molar ionic conductivities of Ca^{2+} and Cl^- are 119.0 and 76.3 S cm^2 mol^{-1} respectively. The value of limiting molar conductivity of $CaCl_2$ will be : [1 mark]

(A) 195.3 S cm^2 mol^{-1}

(B) 43.3 S cm^2 mol^{-1}

(C) 314.3 S cm^2 mol^{-1}

(D) 271.6 S cm^2 mol^{-1}

Correct Answer: (D) 271.6 S cm^2 mol^{-1}

Solution:

Concept:

- Kohlrausch's law: $\Lambda_m^\circ = \sum_i \nu_i \lambda_i^\circ$, where ν_i is the number of ions of type i per formula unit.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle One mole of $CaCl_2$ dissociates into one mole of Ca^{2+} and two moles of Cl^-. Thus the chloride contribution must be counted twice; the calcium contribution is counted once.

Step 2: Evaluate the choices

$$\Lambda_m^\circ(CaCl_2) = 119.0 + 2(76.3) = 271.6\,\text{S cm}^2\,\text{mol}^{-1}.$$

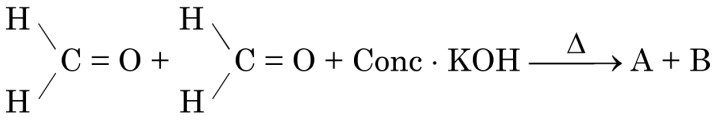
Option A counts chloride only once. Subtraction in B is invalid because both ions carry current; C does not give the stoichiometric sum.

Step 3: Conclusion The limiting molar conductivity is $271.6\,\text{S cm}^2\,\text{mol}^{-1}$. Hence, the correct option is (D).

Quick Tip to Solve: Write the ionic dissociation first: the subscript 2 means two chloride contributions, not twice the entire sum.

2. Consider the following reaction :

Identify A and B from the given options : [1 mark]



(A) A – Methanol, B – Potassium formate

(B) A – Ethanol, B – Potassium formate

(C) A – Methanal, B – Ethanol

(D) A – Methanol, B – Potassium acetate

Correct Answer: (A) A – Methanol, B – Potassium formate

Solution:

Concept:

- Aldehydes without an α-hydrogen undergo Cannizzaro disproportionation with concentrated alkali.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle Methanal, HCHO, has no α-carbon and therefore no α-hydrogen. In concentrated KOH, one molecule is reduced to an alcohol and the other is oxidised to a carboxylate salt.

Step 2: Evaluate the choices

$$2HCHO + KOH \longrightarrow CH_3OH + HCOOK.$$

The alcohol is methanol and the salt is potassium formate. Ethanol and potassium acetate each contain two carbon atoms, so options B, C and D cannot represent these products; methanal in C is also the starting aldehyde.

Step 3: Conclusion A is methanol and B is potassium formate. Hence, the correct option is (A).

Quick Tip to Solve: For methanal with concentrated KOH, pair the one-carbon alcohol methanol with the one-carbon salt potassium formate.

3. Which of the following acids represents Vitamin C ? [1 mark]

(A) Saccharic acid

(B) Gluconic acid

(C) Ascorbic acid

(D) Benzoic acid

Correct Answer: (C) Ascorbic acid

Solution:

Concept:

- Vitamin C is ascorbic acid, a water-soluble vitamin with antioxidant activity.

Quick Tip to Solve: Link vitamin C directly with ascorbic acid and scurvy; glucose-derived acids in the options are distractors.

- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle Recall the chemical name of vitamin C: it is ascorbic acid. Its deficiency causes scurvy, and it supports normal collagen formation. These familiar biological roles help distinguish its name from unrelated organic acids.

Step 2: Evaluate the choices Saccharic acid and gluconic acid are oxidation products associated with glucose chemistry, rather than the name of vitamin C. Benzoic acid is an aromatic carboxylic acid used as a preservative; it is also not vitamin C. Therefore only the ascorbic-acid option matches the requested vitamin.

Step 3: Conclusion Vitamin C is ascorbic acid. Hence, the correct option is (C).

Quick Tip to Solve: Link vitamin C directly with ascorbic acid and scurvy; glucose-derived acids in the options are distractors.

4. Rosenmund reduction is used for the preparation of Aldehydes. The catalyst used in this reaction is : [1 mark]

(A) Pd-$BaSO_4$

(B) Anhydrous $AlCl_3$

(C) Iron (III) oxide

(D) $HgSO_4$

Correct Answer: (A) Pd-$BaSO_4$

Solution:

Concept:

- Rosenmund reduction converts an acyl chloride into an aldehyde by catalytic hydrogenation using palladium on barium sulphate.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle The reaction is $RCOCl + H_2 \longrightarrow RCHO + HCl$. Palladium supported on $BaSO_4$ provides the controlled catalyst required for this reduction; its reduced activity helps prevent further reduction of the aldehyde to an alcohol.

Step 2: Evaluate the choices Anhydrous $AlCl_3$ is a Lewis acid used in Friedel–Crafts reactions. Iron(III) oxide is associated with the iron catalyst used in ammonia manufacture, while $HgSO_4$ catalyses alkyne hydration. None substitutes for the Rosenmund catalyst.

Step 3: Conclusion The catalyst is $Pd/BaSO_4$. Hence, the correct option is (A).

Quick Tip to Solve: Associate Rosenmund reduction with an acyl chloride and controlled hydrogenation over Pd supported on barium sulphate.

5. Which alkyl halide from the given options will undergo S_N1 reaction faster ? [1 mark]

(A) $(CH_3)_3C$–Br

(B) $(CH_3)_2CH$–Br

(C) CH_3–CH_2–Br

(D) $(CH_3)_3C$–CH_2–Br

Correct Answer: (A) $(CH_3)_3C$–Br

Solution:

Concept:

- The rate-determining step of an S_N1 reaction is ionisation of the alkyl halide to a carbocation; greater carbocation stability favours faster ionisation.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle All four options are bromides, so compare the carbon bearing Br. Option A, $(CH_3)_3CBr$, forms a tertiary carbocation, stabilised by three alkyl groups through their electron-donating effect and hyperconjugation.

Step 2: Evaluate the choices Option B forms a secondary carbocation, while C forms a primary carbocation. In D, Br is attached to the terminal CH_2, so the initially formed neopentyl carbocation is primary despite the adjacent highly substituted carbon. Thus the tertiary bromide ionises fastest.

Step 3: Conclusion $(CH_3)_3CBr$ undergoes the fastest S_N1 reaction. Hence, the correct option is (A).

Quick Tip to Solve: Classify the carbon actually bonded to Br; the nearby tertiary carbon in neopentyl bromide does not make its leaving-group carbon tertiary.

6. From the elements of 3d series given below, which element shows the maximum number of oxidation states ? [1 mark]

(A) Scandium

(B) Manganese

(C) Chromium

(D) Titanium

Correct Answer: (B) Manganese

Solution:

Concept:

- Variable oxidation states arise because both $4s$ and $3d$ electrons can participate in bonding in transition elements.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle Manganese has the configuration $[Ar]\,3d^5 4s^2$. It displays oxidation states from $+2$ to $+7$, giving the widest range among these choices. Its five d electrons and two s electrons allow several different numbers of electrons to participate.

Quick Tip to Solve: Use Mn: $3d^5 4s^2$ and the familiar range $+2$ through $+7$ to identify the broadest oxidation-state range.

Step 2: Evaluate the choices Scandium predominantly exhibits $+3$. Titanium commonly shows $+2, +3, +4$, and chromium commonly shows $+2, +3, +6$, with other less common states possible. These elements do not show as many oxidation states as manganese in the standard comparison of the 3d series.

Step 3: Conclusion Manganese shows the maximum number of oxidation states. Hence, the correct option is (B).

Quick Tip to Solve: Use Mn: $3d^5 4s^2$ and the familiar range $+2$ through $+7$ to identify the broadest oxidation-state range.

7. The correct Mathematical expression of Arrhenius equation is : [1 mark]

(A) $k = -A\, e^{E_a/RT}$

(B) $k = e^{E_a/RT}$

(C) $k = A\, e^{-E_a/RT}$

(D) $k = -A\, e^{-E_a/RT}$

Correct Answer: (C) $k = A\, e^{-E_a/RT}$

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A the frequency factor, E_a the activation energy, R the gas constant and T the absolute temperature.
- The correct option must agree with the governing principle and the stated chemical species.

Step 1: Apply the governing principle For positive activation energy, $e^{-E_a/(RT)}$ represents the fraction associated with crossing the activation barrier. The exponent is dimensionless because E_a and RT both have energy-per-mole units. Multiplying by positive A gives a positive rate constant.

Step 2: Evaluate the choices Option A and option D place a minus sign before A, giving an unphysical negative rate constant. Option B omits the frequency factor and has a positive exponent. Only C has both the factor A and the negative activation-energy exponent required by the Arrhenius equation.

Step 3: Conclusion $k = Ae^{-E_a/(RT)}$. Hence, the correct option is (C).

Quick Tip to Solve: Check two signs separately: the rate constant stays positive, while the activation-energy exponent carries the minus sign.

8. Identify the tertiary amine from the following : [1 mark]

(A) $CH_3-\underset{\displaystyle CH_3-}{\overset{\displaystyle CH_3}{\overset{|}{N}}}-CH_3$

(B) $\underset{\displaystyle NH_2}{\overset{\displaystyle CH_3}{\overset{|}{CH}}}-CH_3$

(C) $CH_3 - NH - CH_2 - CH_3$

(D) $(C_2H_5)_2CHNH_2$

Correct Answer: (A) $CH_3-\underset{\displaystyle CH_3-}{\overset{\displaystyle CH_3}{\overset{|}{N}}}-CH_3$

Solution:

Concept:

- Amines are classified by the number of carbon groups directly bonded to nitrogen, not by the type of carbon bearing nitrogen.
- Primary, secondary and tertiary amines have the forms RNH_2, R_2NH and R_3N, respectively.

Step 1: Count groups bonded to nitrogen In option (A), the nitrogen atom is directly bonded to three methyl groups. Its formula is $(CH_3)_3N$, so there is no N–H bond and the nitrogen has three organic substituents.

Step 2: Check the other structures In (B), nitrogen occurs as $-NH_2$, so the amine is primary despite the substituted carbon. In (C), nitrogen has one methyl group, one ethyl group and one hydrogen: it is secondary. In (D), the $-NH_2$ group again makes the amine primary; the two ethyl groups attach to carbon, not directly to nitrogen.

Step 3: Conclusion Trimethylamine, $(CH_3)_3N$, is the tertiary amine. Hence, the correct option is (A).

Quick Tip to Solve: Circle nitrogen and count only the carbon groups directly attached to it; three groups identify a tertiary amine.

9. Nucleophilic addition of Grignard reagent to ketones followed by hydrolysis with dilute acids forms : [1 mark]

(A) Alkene

(B) Primary alcohol

(C) Tertiary alcohol

(D) Secondary alcohol

Correct Answer: (C) Tertiary alcohol

Solution:

Concept:

- A Grignard reagent RMgX supplies a nucleophilic carbon group that attacks the electrophilic carbonyl carbon.
- Acidic hydrolysis protonates the alkoxide to give an alcohol; alcohol class depends on carbon groups bonded to the carbon bearing OH.

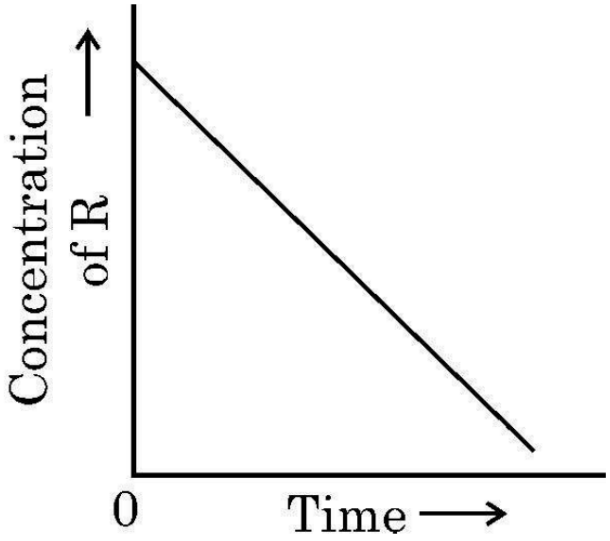
Step 1: Add the Grignard carbon group A ketone already has two carbon groups on its carbonyl carbon. Attack by RMgX adds a third carbon group and forms the magnesium alkoxide $\mathrm{R^1R^2C(OMgX)R}$.

Step 2: Hydrolyse and classify Dilute acid converts the O–MgX group into OH. The product $\mathrm{R^1R^2C(OH)R}$ has three carbon groups attached to the OH-bearing carbon, hence it is tertiary. A primary alcohol is obtained from methanal, and other aldehydes give secondary alcohols with Grignard reagents. Alkene formation would require a subsequent dehydration, which is not the stated hydrolysis.

Step 3: Conclusion The product is a tertiary alcohol. Hence, the correct option is (C).

Quick Tip to Solve: Count the carbon groups on the carbonyl carbon: a ketone has two, and Grignard addition supplies the third.

10. In a given graph of zero order reaction, the slope and intercept are : [1 mark]



(A) Slope = k, Intercept = $[R]_0$

(B) Slope = –k, Intercept = $[R]_0$

(C) Slope = k/2.303, Intercept = $\ln[R]_0$

(D) Slope = –k/2.303, Intercept = ln A

Correct Answer: (B) Slope = –k, Intercept = $[R]_0$

Solution:

Concept:

- For a zero order reaction, $-d[R]/dt = k$, where $[R]$ is reactant concentration and k is the rate constant.
- The integrated rate equation is $[R] = [R]_0 - kt$, with initial concentration $[R]_0$ at $t = 0$.

Step 1: Compare with a straight-line equation The graph plots $[R]$ vertically against time t horizontally. Comparing $[R] = (-k)t + [R]_0$ with $y = mx + c$, the coefficient of time gives the slope and the constant term gives the vertical intercept.

Step 2: Check signs and alternatives The plotted concentration decreases with time, so its slope is negative, namely $-k$. At $t = 0$, the concentration is $[R]_0$. Option (A) has the wrong slope sign. Options (C) and (D) introduce logarithms and the factor 2.303, which do not occur in the concentration-time equation for a zero order reaction; their intercepts also do not match the plotted variable.

Step 3: Conclusion Slope $= -k$ and intercept $= [R]_0$. Hence, the correct option is (B).

Quick Tip to Solve: Write the rate equation as concentration = constant minus rate constant times time, then read slope and intercept directly.

11. Match the reagents required for the given reactions :

I. Oxidation of primary alcohols to aldehydes (p) $NaBH_4$

II. Butan-2-one to Butan-2-ol (q) 85% phosphoric acid at 440 K

III. Bromination of Phenol to 2, 4, 6-Tribromophenol (r) PCC

IV. Dehydration of propan-2-ol to propene (s) Bromine water [1 mark]

(A) I-(r), II-(p), III-(s), IV-(q)

(B) I-(q), II-(r), III-(p), IV-(s)

(C) I-(s), II-(q), III-(p), IV-(r)

(D) I-(p), II-(s), III-(r), IV-(q)

Correct Answer: (A) I-(r), II-(p), III-(s), IV-(q)

Solution:

Concept:

- Choose a reagent by identifying the required change: oxidation, reduction, electrophilic substitution or elimination.
- PCC oxidises primary alcohols to aldehydes, while $\mathrm{NaBH_4}$ reduces ketones to secondary alcohols.

Step 1: Match oxidation and reduction I requires controlled oxidation of a primary alcohol to an aldehyde, so PCC is reagent (r). II converts the ketone butan-2-one into the secondary alcohol butan-2-ol, so sodium borohydride is reagent (p). These are opposite changes and their reagents cannot be interchanged.

Step 2: Match substitution and dehydration III requires bromination of activated phenol at both ortho positions and the para position, giving 2,4,6-tribromophenol with bromine water, reagent (s). IV removes water from propan-2-ol to form propene; 85% phosphoric acid at $440\,\mathrm{K}$, reagent (q), promotes this dehydration. Only option (A) contains all four correct pairings; (B), (C) and (D) misassign oxidation, reduction or bromination reagents.

Step 3: Conclusion The matching is I-(r), II-(p), III-(s), IV-(q). Hence, the correct option is (A).

Quick Tip to Solve: First fix PCC for alcohol-to-aldehyde and NaBH4 for ketone-to-alcohol; then match bromine water and hot phosphoric acid.

12. The general electronic configuration of d-block elements is : [1 mark]

(A) $(n-1)d^{1-10}ns^{1-2}$

(B) $(n-1)d^{10}ns^{1-2}$

(C) $(n-1)d^{10}ns^{2-3}$

(D) $(n-1)d^{0}ns^{1-2}$

Correct Answer: (A) $(n-1)d^{1-10}ns^{1-2}$

Solution:

Concept:

- In d-block elements, the differentiating electron enters the $(n-1)d$ subshell.

Quick Tip to Solve: For the general d-block pattern, choose a variable d occupancy up to ten and remember that an s subshell holds at most two electrons.

- The d subshell contains five orbitals and can accommodate up to ten electrons; the outer s subshell accommodates up to two.

Step 1: Identify the general range Across a d-block series, the occupancy of the penultimate d subshell varies from 1 to 10. The conventional general configuration is therefore $(n-1)d^{1-10}ns^{1-2}$, represented by option (A). This describes the broad series pattern rather than a single element.

Step 2: Eliminate restricted or impossible alternatives Options (B) and (C) fix the d occupancy at 10, so they cannot represent elements throughout the series. Option (C) additionally permits three electrons in an s subshell, although its maximum capacity is two. Option (D) specifies an empty d subshell and therefore does not express the d-block general pattern. Individual configurations, such as palladium with ns^0, have exceptions to the usual outer-s range; these do not make the other printed options general configurations.

Step 3: Conclusion The general electronic configuration is $(n-1)d^{1-10}ns^{1-2}$. Hence, the correct option is (A).

Quick Tip to Solve: For the general d-block pattern, choose a variable d occupancy up to ten and remember that an s subshell holds at most two electrons.

13. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).

Assertion (A) : p-nitrophenol is less acidic than phenol.

Reason (R) : Nitro group is electron withdrawing and helps in the stabilisation of p-nitrophenoxide ion. [1 mark]

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

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

- Acid strength increases when the conjugate base formed after loss of H^+ is stabilised.
- The para nitro group withdraws electrons through inductive and resonance effects and stabilises the nitrophenoxide anion.

Step 1: Evaluate the assertion Phenol loses H^+ to give phenoxide. The para nitro substituent provides additional stabilisation to the corresponding conjugate base, so p-nitrophenol is more acidic than phenol. The assertion says less acidic and is therefore false.

Step 2: Evaluate the reason The nitro group is electron withdrawing. At the para position, resonance withdrawal permits delocalisation of negative charge from the phenoxide system towards the nitro group, in addition to its inductive effect. Thus the statement that it stabilises p-nitrophenoxide is true.

Step 3: Assess the connection The reason supports increased acidity, which is opposite to the assertion as printed. Therefore the codes requiring both statements true, or assertion true and reason false,

Quick Tip to Solve: Compare the conjugate bases: a para electron-withdrawing nitro group stabilises the anion and makes the phenol more acidic.

cannot apply. The appropriate code is the one specifying a false assertion and a true reason.

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

Quick Tip to Solve: Compare the conjugate bases: a para electron-withdrawing nitro group stabilises the anion and makes the phenol more acidic.

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14. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).

Assertion (A) : Benzoic acid does not undergo Friedel - Crafts reaction.

Reason (R) : Carboxyl group is deactivating and the catalyst aluminium chloride gets bonded to the carboxyl group. [1 mark]

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

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

Solution:

Concept:

- Friedel–Crafts alkylation and acylation are electrophilic aromatic substitution reactions requiring a sufficiently reactive aromatic ring.
- The $-COOH$ group withdraws electron density and can interact with the Lewis acid catalyst $AlCl_3$.

Step 1: Evaluate the assertion Benzoic acid contains the strongly electron-withdrawing carboxyl group attached to its benzene ring. Its ring is too deactivated for the usual Friedel–Crafts alkylation or acylation conditions, so the statement that benzoic acid does not undergo this reaction is true.

Step 2: Evaluate the reason The carboxyl group deactivates the ring by withdrawing electron density through inductive and resonance effects. Its oxygen atoms also coordinate to the Lewis acid aluminium chloride. Thus the reason correctly describes both ring deactivation and binding of the catalyst to the carboxyl group.

Step 3: Connect reason to assertion Electrophilic attack required for Friedel–Crafts substitution is hindered by the reduced electron density of the ring, while coordination of the carboxyl group with $AlCl_3$ interferes with normal catalyst action. These are the stated causes of the failure of the reaction. Consequently the reason explains the true assertion; code (B) misses this causal connection and (C) and (D) assign an incorrect truth value.

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

Quick Tip to Solve: Before predicting Friedel–Crafts substitution, check for a strongly deactivating group and whether it binds the Lewis acid catalyst.

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15. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).

Assertion (A) : Fructose is a reducing sugar.

Reason (R) : Fructose does not reduce Fehling solution and Tollen's reagent. [1 mark]

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

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

- A reducing sugar reduces Fehling's solution or Tollens' reagent under the conditions of the test.
- In alkaline solution fructose can undergo enediol rearrangement to the aldoses glucose and mannose.

Step 1: Judge the assertion Assertion (A) is true. Although fructose is a ketose, it is a reducing sugar because the alkaline medium of the reducing-sugar tests permits its conversion into aldoses.

Step 2: Judge the reason Reason (R) is false. Fructose does reduce Fehling's solution, producing a red precipitate of Cu_2O, and Tollens' reagent, depositing silver.

Step 3: Select the logical relation Since the assertion is true and the reason is false, the reason cannot explain the assertion. Options (A) and (B) wrongly treat the reason as true, while (D) wrongly treats the assertion as false.

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

Quick Tip to Solve: For fructose, remember that alkaline test conditions allow ketose-to-aldose rearrangement.

16. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).

Assertion (A) : For a Daniell cell, $Zn/Zn^{2+}(1M)\ ||\ Cu^{2+}(1M)/Cu$ with $E^\circ_{cell} = 1.1$ V, if the external opposing potential is more than 1.1 V, the electrons flow from Cu to Zn.

Reason (R) : Cell acts like a galvanic cell. [1 mark]

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

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

- A galvanic Daniell cell spontaneously transfers electrons from zinc to copper.
- An opposing external potential greater than the cell emf reverses the reaction and makes the cell

Quick Tip to Solve: Compare the opposing voltage with the cell emf before assigning the direction of electron flow.

electrolytic.

Step 1: Judge the assertion Assertion (A) is true. For the stated standard Daniell cell, $E^\circ_{\text{cell}} = 1.1\,\text{V}$. When the opposing external potential exceeds $1.1\,\text{V}$, it drives electrons from Cu to Zn through the external circuit.

Step 2: Judge the reason Reason (R) is false under these imposed conditions. The reaction is forced in its non-spontaneous direction: copper is oxidised, $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$, and zinc ions are reduced, $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$. Thus the cell acts as an electrolytic cell.

Step 3: Choose the relation Both (A) and (B) incorrectly call the reason true. Option (D) incorrectly calls the assertion false. The imposed voltage reverses the usual galvanic electron flow, so only option (C) gives the correct truth values.

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

Quick Tip to Solve: Compare the opposing voltage with the cell emf before assigning the direction of electron flow.

Section B (10 marks)

17. Define the following terms :

(a) Order of a reaction

(b) Activation energy [2 marks]

Solution:

Concept:

- The rate law relates the measured reaction rate to reactant concentrations.
- Activation energy describes the energy barrier between reactants and the activated complex.

Step 1: (a) Define the order of a reaction The order of a reaction is the sum of the powers of the concentrations of reactants in the experimentally determined rate law. For

$$r = k[A]^m[B]^n,$$

the overall order is $m+n$, where m and n are the partial orders with respect to A and B. These powers must be obtained experimentally; they need not equal the coefficients in the balanced chemical equation. Order may be zero, integral or fractional.

Step 2: (b) Define activation energy Activation energy, E_a, is the minimum additional energy that reactant molecules must acquire to form the activated complex and undergo reaction. Equivalently, it is the energy difference between the activated complex and the reactants. In the Arrhenius equation,

$$k = Ae^{-E_a/(RT)},$$

A is the frequency factor, R the gas constant and T the absolute temperature. Only suitably oriented collisions with sufficient energy can lead to products.

Quick Tip to Solve: Read order from the rate law, and measure activation energy from the reactant energy level.

Step 3: Conclusion Order is the sum of concentration exponents in the experimental rate law; activation energy is the energy barrier required to reach the activated complex.

Quick Tip to Solve: Read order from the rate law, and measure activation energy from the reactant energy level.

18. 18 g of a non-volatile solute is dissolved in 200 g of H_2O freezes at 272.07 K. Calculate the molecular mass of solute. (K_f for water = 1.86 K kg mol^{-1}) [2 marks]

Solution:

Concept:

- For a dilute solution of a non-electrolyte, freezing-point depression is $\Delta T_f = K_f m$, where m is molality.
- Molality is moles of solute per kilogram of solvent; pure water freezes at $273.15\,\text{K}$.

Step 1: Calculate the freezing-point depression The depression is the freezing point of pure solvent minus that of the solution:

$$\Delta T_f = 273.15 - 272.07 = 1.08\,\text{K}.$$

The solvent mass is $200\,\text{g} = 0.200\,\text{kg}$. Use the solvent mass, not the combined mass of solute and solvent, in the molality calculation.

Step 2: Calculate the molecular mass Let the molar mass of the solute be M g mol^{-1}. Its amount is $18/M$ mol, so

$$1.08 = 1.86\frac{18/M}{0.200},$$
$$M = \frac{1.86 \times 18}{1.08 \times 0.200}$$
$$= 155\,\text{g mol}^{-1}.$$

Here the usual dilute non-electrolyte relation is applied with van't Hoff factor $i = 1$, since no dissociation or association is specified. Substitution gives $m = 0.58065$ mol kg^{-1}, and $1.86m = 1.08\,\text{K}$, confirming the result.

Step 3: Conclusion The molecular mass of the solute is $155\,\text{u}$, corresponding to a molar mass of $155\,\text{g mol}^{-1}$.

Quick Tip to Solve: Convert the 200 g of water to kilograms and subtract the solution temperature from 273.15 K.

19. (a) Which compound in the given pair would undergo S_N2 reaction at a faster rate and why ?
CH_3–CH_2–I and CH_3–CH_2–Br
(b) Arrange the following compounds in the increasing order of their boiling points :
Butane, 1-Bromobutane, 1-Iodobutane, 1-Chlorobutane [2 marks]

Solution:

Concept:

- For comparable substrates, an S_N2 reaction is faster with a better leaving group.
- For the same alkyl group, boiling point generally increases with halogen size and polarisability because dispersion forces strengthen.

Step 1: (a) Compare the substitution rates CH_3CH_2I undergoes the S_N2 reaction faster than CH_3CH_2Br. Both molecules have the same primary ethyl group, so steric hindrance at the carbon undergoing backside attack is comparable. The decisive difference is the leaving group: the C–I bond is weaker than the C–Br bond, and I^- is a better leaving group than Br^-. Consequently, displacement of iodide by the nucleophile occurs more readily under otherwise identical conditions.

Step 2: (b) Arrange the boiling points Butane has the lowest boiling point. For the three 1-halobutanes, the alkyl chain is unchanged, while molecular mass and electron-cloud polarisability increase from chlorine to bromine to iodine. The resulting stronger intermolecular dispersion attractions require more energy to separate the molecules on boiling. Thus the increasing order is

$$\text{Butane} < \text{1-Chlorobutane} < \text{1-Bromobutane} < \text{1-Iodobutane}.$$

This comparison concerns intermolecular attractions; it is distinct from the C–halogen bond strength used to compare substitution rates.

Step 3: Conclusion (a) Iodoethane reacts faster because iodide is the better leaving group. (b) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane.

Quick Tip to Solve: Keep the ethyl steric environment fixed in (a); compare halogen polarisability for boiling in (b).

20(a). Write the stepwise mechanism of nucleophilic addition reactions in the carbonyl compounds. [2 marks]

Solution:

Concept:

- The carbonyl bond is polar: oxygen is partially negative and carbon is partially positive, so a nucleophile attacks the carbonyl carbon.
- Addition converts the planar carbonyl group into a tetrahedral product; the alkoxide intermediate is subsequently protonated.

Step 1: Step 1: Nucleophilic attack Let Nu^- denote a nucleophile and R′ be hydrogen or an alkyl group. The nucleophile donates its electron pair to the electron-deficient carbonyl carbon.

Quick Tip to Solve: Place Nu on the carbonyl carbon and the negative charge on oxygen before showing protonation.

Simultaneously, the π-bond electron pair moves to oxygen, giving a tetrahedral alkoxide intermediate:

$$\mathrm{R-C(=O)-R' + Nu^- \longrightarrow R-C(O^-)(Nu)-R'.}$$

A new carbon-nucleophile bond forms and carbon changes from sp^2 to sp^3 hybridisation.

Step 2: Step 2: Protonation The negatively charged oxygen accepts a proton from a suitable proton donor in the reaction medium. This gives the neutral addition product containing an alcohol group:

$$\mathrm{R-C(O^-)(Nu)-R' + H^+ \longrightarrow R-C(OH)(Nu)-R'.}$$

Protonation follows nucleophilic attack in this general mechanism for an anionic nucleophile.

Step 3: Conclusion Nucleophilic addition proceeds by attack on carbonyl carbon to form a tetrahedral alkoxide, followed by protonation to give $\mathrm{R-C(OH)(Nu)-R'}$.

Quick Tip to Solve: Place Nu on the carbonyl carbon and the negative charge on oxygen before showing protonation.

OR

20(b). How will you convert the following :

(i) Toluene to benzoic acid.

(ii) Ethanol to 3-Hydroxybutanal [2 marks]

Solution:

Concept:

- Hot alkaline potassium permanganate oxidises a benzylic side chain to a carboxylate; acidification gives the carboxylic acid.
- Ethanal has alpha hydrogen atoms and undergoes aldol addition with cold dilute alkali to form a beta-hydroxy aldehyde.

Step 1: (i) Convert toluene to benzoic acid Heat toluene with alkaline $\mathrm{KMnO_4}$, then acidify the resulting potassium benzoate using dilute acid:

$$\mathrm{C_6H_5CH_3 \xrightarrow[\Delta]{\text{alkaline } KMnO_4} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH.}$$

Oxidation changes the methyl side chain into the carboxyl group while retaining the benzene ring. Acidification is necessary because the oxidation medium initially gives the salt.

Step 2: (ii) Convert ethanol to 3-hydroxybutanal First pass ethanol vapour over heated copper at $573\,\mathrm{K}$ to obtain ethanal by dehydrogenation. Then treat ethanal with cold dilute sodium hydroxide for aldol addition:

$$\mathrm{CH_3CH_2OH \xrightarrow{Cu,\,573\,K} CH_3CHO + H_2,}$$

$$\mathrm{2CH_3CHO \xrightarrow{\text{cold dilute NaOH}} CH_3CH(OH)CH_2CHO.}$$

Quick Tip to Solve: Make ethanal first, then use cold dilute NaOH to retain the hydroxyl group in the aldol product.

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Avoid heating the aldol product, since dehydration would form an unsaturated aldehyde.

Step 3: Conclusion Toluene gives benzoic acid by alkaline permanganate oxidation followed by acidification. Ethanol gives ethanal, whose aldol addition produces 3-hydroxybutanal.

Quick Tip to Solve: Make ethanal first, then use cold dilute NaOH to retain the hydroxyl group in the aldol product.

21. (a) What happens when glucose reacts with bromine water ? Write chemical equation.

(b) Two bases are mentioned below, identify which is present in DNA and which one is present in RNA :

(i) Thymine (ii) Uracil [2 marks]

Solution:

Concept:

- Bromine water is a mild oxidising agent that converts the aldehyde group of glucose into a carboxyl group, forming gluconic acid.
- DNA contains thymine among its pyrimidine bases; RNA contains uracil in the corresponding place.

Step 1: (a) Reaction of glucose with bromine water Glucose is oxidised to gluconic acid and the colour of bromine water is discharged. Using the open-chain formula of glucose, the balanced equation is

$$\begin{aligned} &\mathrm{CHO-(CHOH)_4-CH_2OH + Br_2 + H_2O} \\ &\longrightarrow \mathrm{COOH-(CHOH)_4-CH_2OH + 2HBr.} \end{aligned}$$

The aldehyde end is oxidised while the terminal primary alcohol group remains unchanged under these mild conditions. This reaction therefore provides evidence for an aldehyde group in glucose.

Step 2: (b) Identify the nitrogenous bases (i) Thymine is present in DNA. Its usual complementary partner is adenine.

(ii) Uracil is present in RNA, where it takes the place occupied by thymine in DNA and pairs with adenine. Both thymine and uracil are pyrimidine bases; the common bases adenine, guanine and cytosine occur in both nucleic acids.

Step 3: Conclusion Bromine water oxidises glucose to gluconic acid. Thymine is present in DNA, whereas uracil is present in RNA.

Quick Tip to Solve: Remember DNA uses T and RNA uses U; bromine water changes glucose's CHO end to COOH only.

Section C (21 marks)

22. (a) Draw the geometrical isomers of the given complex :

$[Pt(en)_2Cl_2]^{2+}$

(b) Write the electronic configuration for d^{14} ion if $\Delta_0 < P$ on the basis of crystal field theory.

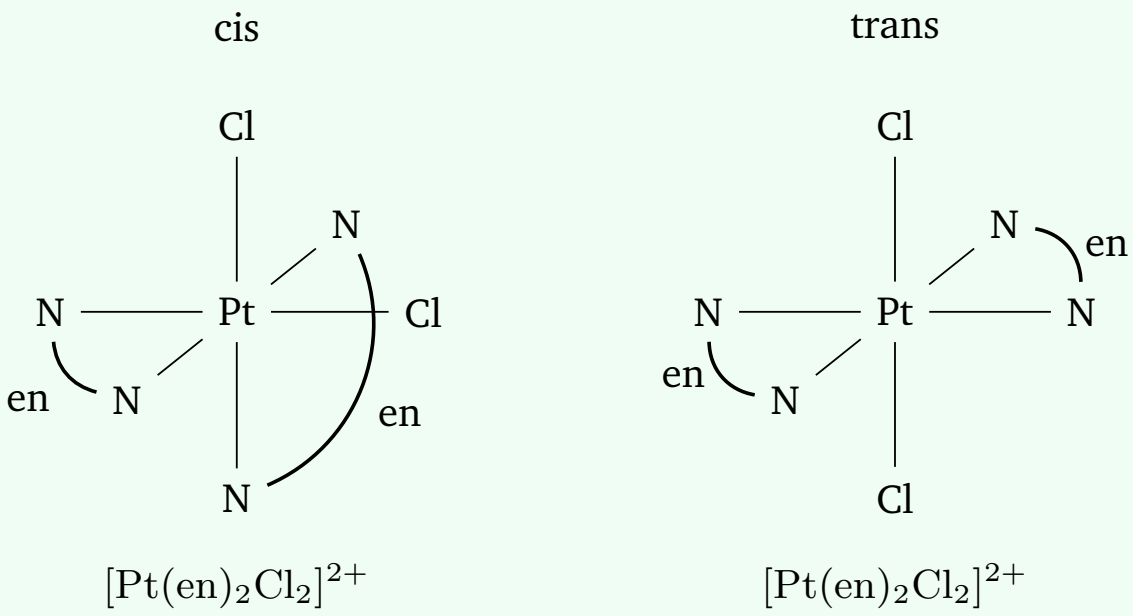
(c) What is meant by a unidentate ligand ? Give an example. [3 marks]

Solution:

Concept:

- Geometrical isomerism depends on the relative positions of ligands. In an octahedral complex, two identical ligands can be adjacent (cis, $90°$) or opposite (trans, $180°$).
- The ligand en is ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, and binds through two nitrogen donors. Two en ligands and two chloride ligands give coordination number six.
- An octahedral field splits five d orbitals into lower t_{2g} and higher e_g sets. When splitting Δ_0 is less than pairing energy P, electrons occupy higher orbitals before pairing.

Step 1: (a) Place the chloride ligands in the two arrangements The sketches show the two geometrical isomers of $[Pt(en)_2Cl_2]^{2+}$. Each curved connection marked en joins two nitrogen atoms of one chelating ligand. In the cis form the chloride ligands are adjacent; in the trans form they occupy the two opposite axial positions. Rotation cannot change one arrangement into the other without changing coordination bonds.



Octahedral cis and trans forms; linked N donors belong to one en ligand.

Step 2: (b) Check the printed electron count The printed question specifies d^{14}. A d subshell contains five orbitals and each holds at most two electrons, so its maximum capacity is ten electrons. Thus a d^{14} ion has no physically possible d-orbital configuration; the condition $\Delta_0 < P$ cannot remove this restriction. If the intended electron count is d^4, the weak-field, high-spin arrangement would be $t_{2g}^3 e_g^1$,

Quick Tip to Solve: Count donor atoms first: two en ligands contribute four sites. Place the two chlorides adjacent for cis and opposite for trans; always check that a d-electron count does not exceed ten.

with all four electrons unpaired: one electron in each lower orbital and the fourth in a higher orbital.

Step 3: (c) Define a unidentate ligand A unidentate ligand has one donor atom through which it forms one coordinate bond to a central metal ion. For example, NH_3 donates the lone pair on its single nitrogen donor atom. Chloride, Cl^-, is another example. The term describes the number of donor atoms used for attachment, not the charge or the total number of atoms in the ligand.

Step 4: Conclusion (a) The two geometrical forms are cis and trans. (b) The printed d^{14} configuration is impossible; for d^4 under $\Delta_0 < P$, the configuration is $t_{2g}^3 e_g^1$. (c) A unidentate ligand binds through one donor atom, for example NH_3.

Quick Tip to Solve: Count donor atoms first: two en ligands contribute four sites. Place the two chlorides adjacent for cis and opposite for trans; always check that a d-electron count does not exceed ten.

23. Calculate emf of the following cell at 25 °C :

Sn / Sn^{2+}(0.001 M) || H^+(0.01 M) | $H_{2(g)}$(1 bar) / $Pt_{(s)}$

Given : $E^\circ(Sn^{2+}/Sn)$ = –0.14 V, $E^\circ(H^+/H_2)$ = 0.00 V (log 10 = 1) [3 marks]

Solution:

Concept:

- The cell is written with oxidation at the left electrode and reduction at the right electrode. Its standard emf is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- At 25 °C, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$, where n is the number of electrons exchanged and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Write the electrode reactions and standard emf Tin is oxidised at the left electrode and hydrogen ions are reduced at the right electrode:

$$\mathrm{Sn(s)} \longrightarrow \mathrm{Sn^{2+}(aq)} + 2\,\mathrm{e^-},$$
$$2\,\mathrm{H^+(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2(g)}.$$

Adding gives $\mathrm{Sn(s)} + 2\,\mathrm{H^+(aq)} \longrightarrow \mathrm{Sn^{2+}(aq)} + \mathrm{H_2(g)}$, so $n = 2$.

$$E^\circ_{\text{cell}} = 0.00 - (-0.14) = 0.14\,\mathrm{V}.$$

Step 2: Calculate the reaction quotient The hydrogen gas has pressure 1 bar, so its activity relative to the standard pressure is one. Tin metal does not appear in the quotient. Using the given molar concentrations as dilute-solution activities,

$$Q = \frac{[\mathrm{Sn^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

The hydrogen-ion concentration is squared because two hydrogen ions occur in the balanced reaction; overlooking that exponent would give a wrong emf.

Quick Tip to Solve: Balance the cell reaction before writing Q: the coefficient two on hydrogen ions means its concentration must be squared, while the 1 bar hydrogen gas contributes a factor of one.

Step 3: Substitute in the Nernst equation Since $\log 10 = 1$,

$$\begin{aligned} E_{\text{cell}} &= 0.14 - \frac{0.0591}{2} \log 10 \\ &= 0.14 - 0.02955 \\ &= 0.11045\,\text{V}. \end{aligned}$$

The correction decreases the standard emf because $Q > 1$. The calculated positive sign also agrees with the direction of the cell reaction as written.

Step 4: Conclusion The emf of the given cell at $25\,^{\circ}\text{C}$ is $E_{\text{cell}} \approx 0.110\,\text{V}$.

Quick Tip to Solve: Balance the cell reaction before writing Q: the coefficient two on hydrogen ions means its concentration must be squared, while the 1 bar hydrogen gas contributes a factor of one.

24. Write chemical equations for the following reactions (Do any three) :

(a) Hydroboration - oxidation reaction

(b) Williamson Synthesis

(c) Friedel-Crafts Alkylation of Anisole

(d) Reimer-Tiemann Reaction [3 marks]

Solution:

Concept:

- Hydroboration followed by oxidation adds water across an alkene in the anti-Markovnikov orientation; the hydroxyl group appears on the less substituted carbon.
- Williamson synthesis forms an ether by the reaction of an alkoxide with a suitable alkyl halide, preferably a primary halide.
- The methoxy group of anisole activates its ring and directs electrophilic substitution to ortho and para positions. Reimer-Tiemann reaction introduces a formyl group mainly ortho to the hydroxyl group of phenol.

Step 1: (a) Write hydroboration followed by oxidation Using propene as the example, hydroboration gives a trialkylborane and alkaline hydrogen peroxide oxidises it to propan-1-ol:

$$3\,\text{CH}_3\text{CH}{=}\text{CH}_2 + \text{BH}_3 \xrightarrow{\text{THF}} \text{B}(\text{CH}_2\text{CH}_2\text{CH}_3)_3$$

$$\text{B}(\text{CH}_2\text{CH}_2\text{CH}_3)_3 + 3\,\text{H}_2\text{O}_2 \xrightarrow{\text{OH}^-} 3\,\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{B}(\text{OH})_3$$

Boron attaches at the less substituted carbon, and oxidation replaces the carbon-boron bond by a carbon-oxygen bond. Hence the terminal alcohol is formed rather than propan-2-ol.

Step 2: (b) Write Williamson ether synthesis A specific balanced example is sodium ethoxide reacting with bromoethane:

$$\text{C}_2\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Br} \longrightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{NaBr}.$$

The ethoxide ion acts as the nucleophile and displaces bromide from the primary alkyl halide in an

Quick Tip to Solve: For these named reactions, pair each reagent with its diagnostic product: borane/peroxide gives terminal alcohol, alkoxide/primary halide gives ether, and chloroform/base gives ortho-formylated phenol.

S_N2 reaction. The organic product is ethoxyethane. A primary halide is chosen to favour substitution over elimination.

Step 3: (c) Write Friedel-Crafts alkylation of anisole Anisole reacts with chloromethane in the presence of anhydrous aluminium chloride:

$$C_6H_5OCH_3 + CH_3Cl \xrightarrow{\text{anhyd} \cdot AlCl_3} CH_3C_6H_4OCH_3 + HCl.$$

Here $CH_3C_6H_4OCH_3$ represents the ortho and para isomers, namely 2-methylanisole and 4-methylanisole. The para product is generally major because it has less steric crowding. The methoxy substituent supplies electron density to the ring and directs the incoming methyl group to these two positions.

Step 4: (d) Write the Reimer-Tiemann reaction Phenol is heated with chloroform and aqueous sodium hydroxide, followed by acidification. The net balanced reaction, expressing the neutral organic product after work-up, is

$$C_6H_5OH + CHCl_3 + 3\,NaOH \xrightarrow[\text{then } H^+]{\text{heat}} \text{o-}HOC_6H_4CHO + 3\,NaCl + 2\,H_2O.$$

The main product is 2-hydroxybenzaldehyde (salicylaldehyde). A small amount of the para isomer may also form. Under the alkaline reaction conditions the phenolic product is present as its salt; acid work-up restores the hydroxyl group.

Step 5: Conclusion Any three of the four equations satisfy the question: hydroboration-oxidation gives propan-1-ol, Williamson synthesis gives ethoxyethane, anisole alkylation gives ortho/para methylanisole, and Reimer-Tiemann reaction gives mainly salicylaldehyde.

Quick Tip to Solve: For these named reactions, pair each reagent with its diagnostic product: borane/peroxide gives terminal alcohol, alkoxide/primary halide gives ether, and chloroform/base gives ortho-formylated phenol.

25. (a) Give chemical tests to distinguish between the following pairs of compounds :

(i) Phenol and Benzoic acid

(ii) Propanal and Propanone

(b) Which one of the given compounds is a stronger acid and why ?

$CH_2FCH_2CH_2COOH$ or CH_3CHFCH_2COOH [3 marks]

Solution:

Concept:

- A distinguishing test must give different observable results for the two compounds under the same conditions. Carboxylic acids liberate carbon dioxide from sodium hydrogen carbonate; phenol is too weak an acid to do so.
- Aldehydes reduce Tollens' reagent, whereas simple ketones do not. An electron-withdrawing fluorine atom increases carboxylic-acid strength by its negative inductive effect, which decreases with distance.

Quick Tip to Solve: Count carbon positions from the carboxyl carbon before comparing the distance-dependent inductive effect.

Step 1: (a)(i) Distinguish phenol and benzoic acid Add aqueous sodium hydrogen carbonate to separate samples. Benzoic acid produces brisk effervescence of carbon dioxide, while phenol gives no effervescence. The gas turns limewater milky. The reaction is

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + H_2O + CO_2 \uparrow.$$

Benzoic acid is sufficiently acidic to displace carbonic acid from its salt, whereas phenol is not.

Step 2: (a)(ii) Distinguish propanal and propanone Warm the samples separately with freshly prepared Tollens' reagent. Propanal gives a silver mirror because its aldehyde group is oxidised to propanoate while silver(I) is reduced to silver metal. Propanone gives no silver mirror under these conditions.

$$CH_3CH_2CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3CH_2COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Step 3: (b) Compare the positions of fluorine In CH_3CHFCH_2COOH, fluorine is on the beta carbon; in $CH_2FCH_2CH_2COOH$, it is on the gamma carbon. The nearer fluorine atom withdraws electron density more effectively through sigma bonds and stabilises the carboxylate conjugate base more strongly. Thus dissociation of the beta-fluoro acid is more favourable.

Step 4: Conclusion Benzoic acid gives effervescence with $NaHCO_3$, while phenol does not; propanal gives Tollens' silver mirror, while propanone does not. CH_3CHFCH_2COOH is the stronger acid because fluorine is closer to the carboxyl group.

Quick Tip to Solve: Count carbon positions from the carboxyl carbon before comparing the distance-dependent inductive effect.

26. Explain the following terms :

(a) Essential amino acids

(b) Peptide bond

(c) Denaturation [3 marks]

Solution:

Concept:

- Proteins are polymers of alpha-amino acids linked by peptide bonds. Amino acids required in the diet are classified according to whether the human body can synthesise them.
- Protein activity depends on its specific three-dimensional structure. Disruption of this structure can destroy biological activity even when the amino-acid sequence remains intact.

Step 1: (a) Essential amino acids Essential amino acids are amino acids that the human body cannot synthesise and therefore must obtain through food. They are needed for normal protein synthesis, growth and tissue repair. Valine and leucine are examples. The word essential refers to their dietary requirement; non-essential amino acids are also needed by the body, but can be synthesised within it.

Step 2: (b) Peptide bond A peptide bond is the amide linkage $-CO-NH-$ formed between the

Quick Tip to Solve: In denaturation distinguish unfolding from hydrolysis: unfolding preserves the peptide-linked amino-acid sequence.

carboxyl group of one amino acid and the amino group of another, with elimination of a water molecule. For two alpha-amino acids, the condensation may be represented as

$$\mathrm{H_2NCH(R)COOH + H_2NCH(R')COOH} \longrightarrow \mathrm{H_2NCH(R)CONHCH(R')COOH + H_2O.}$$

The product is a dipeptide; repetition of this linkage forms a polypeptide chain.

Step 3: (c) Denaturation Denaturation is the loss of a protein's native conformation and biological activity on exposure to heat or a change in pH, for example. The interactions maintaining its secondary and tertiary structures are disrupted, while its primary structure, namely the sequence of amino acids joined by peptide bonds, remains intact. Coagulation of egg white on boiling is a familiar example: the proteins unfold and aggregate, producing a solid mass.

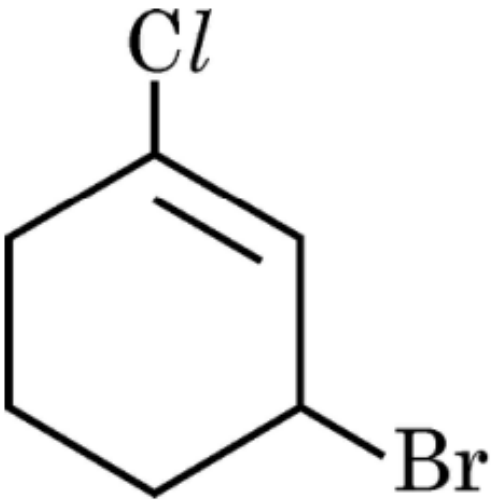
Step 4: Conclusion Essential amino acids must be supplied in the diet; a peptide bond is the $-\mathrm{CO}-\mathrm{NH}-$ linkage joining amino acids; denaturation destroys the native protein structure and activity without changing its primary amino-acid sequence.

Quick Tip to Solve: In denaturation distinguish unfolding from hydrolysis: unfolding preserves the peptide-linked amino-acid sequence.

27. (a) Write the IUPAC name of the given compound :

(b) The presence of $-NO_2$ group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution reactions. Give reason to explain the above statement.

(c) What happens when ethyl chloride is treated with alcoholic potassium hydroxide ? [3 marks]



Solution:

Concept:

- A cycloalkene is numbered so that its double-bond carbons receive positions 1 and 2, followed by the lowest possible locants for substituents. Substituent prefixes are written alphabetically.
- An ortho or para nitro group withdraws electron density and stabilises the anionic intermediate of nucleophilic aromatic substitution by resonance.
- Alcoholic potassium hydroxide on heating promotes beta-elimination of hydrogen halide from a haloalkane to give an alkene.

Step 1: (a) Number and name the ring The parent is cyclohex-1-ene because the six-membered ring contains one double bond. Assign carbon 1 to the double-bond carbon bearing chlorine and carbon 2 to the adjacent double-bond carbon. Bromine is then on carbon 3. The substituent locants are 1 and 3; numbering in the other direction would give 2 and 6, so it is rejected. Writing bromo before chloro alphabetically gives 3-bromo-1-chlorocyclohex-1-ene.

Step 2: (b) Explain activation by the nitro group During nucleophilic attack on the carbon bearing halogen, an anionic intermediate is formed. Its negative charge is delocalised to the ortho and para positions of the aromatic ring. A $-NO_2$ group at either of these positions accepts electron density by resonance, allowing the negative charge to be further delocalised onto its oxygen atoms. This stabilises the intermediate and makes substitution easier. Its electron-withdrawing inductive effect also assists nucleophilic attack. A meta nitro group cannot provide this same resonance stabilisation of the intermediate.

Step 3: (c) Reaction with alcoholic potassium hydroxide On heating ethyl chloride with alcoholic potassium hydroxide, dehydrohalogenation occurs. Hydrogen is removed from the beta carbon and chlorine from the adjacent carbon, forming a carbon-carbon double bond. Ethene is produced:

$$CH_3CH_2Cl + KOH \xrightarrow[\Delta]{\text{alcohol}} CH_2{=}CH_2 + KCl + H_2O.$$

Thus the specified alcoholic medium favours elimination, whereas aqueous potassium hydroxide would favour substitution to form ethanol.

Step 4: Conclusion (a) The compound is 3-bromo-1-chlorocyclohex-1-ene. (b) An ortho or para nitro group stabilises the anionic substitution intermediate by resonance. (c) Ethyl chloride gives ethene on heating with alcoholic KOH.

Quick Tip to Solve: Fix the double bond at positions 1 and 2 first; only then minimise substituent locants and alphabetise the prefixes.

28. Show that the time required for 99.9% completion in a first order reaction is 10 times of half-life ($t_{1/2}$) of the reaction. [log 2 = 0.3010, log 10 = 1] [3 marks]

Solution:

Concept:

- For a first order reaction, the rate constant k and elapsed time t satisfy $kt = 2.303 \log\big([A]_0/[A]_t\big)$, where $[A]_0$ and $[A]_t$ are the initial and remaining reactant concentrations. Here $\log$ denotes the common logarithm.
- The half-life $t_{1/2}$ is the time for the concentration to fall to half its initial value. For first order kinetics it is independent of the initial concentration because the ratio of initial to remaining concentration is always 2.

Step 1: Calculate the half-life At half-life, $[A]_t = [A]_0/2$. Substitution into the integrated rate equation gives

$$t_{1/2} = \frac{2.303}{k} \log 2 = \frac{2.303 \times 0.3010}{k} = \frac{0.693203}{k}.$$

The same units of time must be used here and in the completion-time calculation; the rate constant then has the corresponding inverse-time unit.

Step 2: Find the time for 99.9 percent completion Completion refers to the fraction consumed, so the fraction remaining is $100 - 99.9 = 0.1$ percent. Thus

$$[A]_t = \frac{0.1}{100}[A]_0 = \frac{[A]_0}{1000}.$$

Hence the required time is

$$t_{99.9\%} = \frac{2.303}{k} \log 1000 = \frac{2.303}{k} (3 \log 10) = \frac{6.909}{k}.$$

Using 99.9 percent as the remaining concentration would instead describe only 0.1 percent completion and give the wrong time.

Step 3: Compare the two times Divide the completion time by the half-life. Both the rate constant and the common factor 2.303 cancel:

$$\frac{t_{99.9\%}}{t_{1/2}} = \frac{3}{0.3010} = 9.9668 \simeq 10.$$

The comparison therefore applies to any first order reaction under fixed conditions. With the supplied logarithm, the ratio is approximately ten; the statement in the question uses this usual rounding.

Step 4: Conclusion The time for 99.9% completion is approximately ten half-lives: $\boxed{t_{99.9\%} \simeq 10 t_{1/2}}$.

Quick Tip to Solve: Convert percent completion to the fraction remaining first; 99.9% completion leaves 1/1000, so the logarithm in the time formula is 3.

Section D (8 marks)

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

29. The nature of bonding, structure of the coordination compound can be explained to some extent by valence bond theory. The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number. The appropriate atomic orbitals (s, p and d) of the metal hybridise to give a set of equivalent orbitals of definite geometry such as square planar, tetrahedral, octahedral and so on. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. The d-orbitals involved in the hybridisation may be either inner d-orbitals i.e. (n–1)d or outer d-orbitals i.e. nd. The complexes formed are called inner orbital complex (low spin complex) and outer orbital complex (high spin complex) respectively. Further, the complexes can be paramagnetic or diamagnetic in nature. The drawbacks of this theory are that this involves number of assumptions and also does not explain the colour of the complex.

Answer the following questions : [4 marks]

29(a). Predict whether $[CoF_6]^{3-}$ is diamagnetic or paramagnetic and why ? [Atomic number : Co = 27] [1 mark]

Solution:

Concept:

- A complex is paramagnetic when its metal ion has unpaired electrons; complete pairing gives diamagnetism.
- Fluoride is a weak-field ligand and does not force pairing of the cobalt ion's 3d electrons in this complex.

Step 1: Determine cobalt's oxidation state and configuration Each fluoride ion has charge -1. If cobalt has oxidation state x, then $x - 6 = -3$, giving $x = +3$. Cobalt has atomic number 27 and configuration $[\mathrm{Ar}]3d^7 4s^2$. Removing the two 4s electrons and one 3d electron gives $\mathrm{Co}^{3+} : [\mathrm{Ar}]3d^6$.

Step 2: Count the unpaired electrons The six weak-field fluoride ligands form a high-spin octahedral complex. The 3d electrons are not forced to pair; their octahedral arrangement is $t_{2g}^4 e_g^2$, containing four unpaired electrons. These unpaired electrons produce a magnetic moment, so complete-pairing diamagnetism does not apply.

Step 3: Conclusion $[\mathrm{CoF_6}]^{3-}$ is paramagnetic because the weak-field fluoride ligands leave four unpaired electrons in the high-spin $3d^6$ cobalt(III) ion.

Quick Tip to Solve: First calculate the metal oxidation state, then use ligand strength to decide whether the d electrons pair.

29(b). What is the coordination number of Co in $[Co(en)_2Cl_2]^+$? [1 mark]

Solution:

Concept:

- Coordination number counts the ligand donor atoms directly bonded to the central metal, not simply the number of ligand molecules.
- Ethane-1,2-diamine, abbreviated en, is bidentate: each molecule coordinates through both nitrogen atoms. Chlorido is monodentate.

Step 1: Count the donors from ethane-1,2-diamine The formula $[\mathrm{Co(en)_2Cl_2}]^+$ contains two en molecules. Each has two nitrogen lone pairs that form two coordinate bonds to cobalt, so their combined contribution is $2 \times 2 = 4$ donor atoms. Counting each en as only one ligand donor would miss its bidentate character.

Step 2: Add the chlorido donors Each of the two coordinated chloride ions contributes one donor atom and one coordinate bond. Thus their contribution is $2 \times 1 = 2$. The total number of donor atoms bonded to cobalt is $4 + 2 = 6$; the overall charge on the complex does not change this count.

Step 3: Conclusion The coordination number of Co in $[\mathrm{Co(en)_2Cl_2}]^+$ is $\boxed{6}$.

Quick Tip to Solve: Multiply each ligand's count by its denticity before adding the donor atoms around the metal.

29(c). (i) Write the IUPAC name of the given complex : $[Pt(NH_3)_2Cl_2]^{2+}$
(ii) Explain whether $[Co(NH_3)_6]^{3+}$ is an inner orbital or outer orbital complex. [2 marks]

Solution:

Concept:

- In naming coordination compounds, neutral ammonia is called ammine and coordinated chloride is chlorido. Ligands are named alphabetically, ignoring numerical prefixes.
- Inner-orbital octahedral complexes use two $(n-1)d$ orbitals along with one s and three p orbitals, giving d^2sp^3 hybridisation.

Step 1: (i) Name the platinum complex as printed In $[\mathrm{Pt(NH_3)_2Cl_2}]^{2+}$, ammonia is neutral and each chloride has charge -1. Therefore $x + 2(0) + 2(-1) = +2$, so platinum is in oxidation state $+4$. There are two ammine and two chlorido ligands; ammine precedes chlorido alphabetically. As the coordination entity is a cation, the metal retains the name platinum. Its name is diamminedichlorido-platinum(IV). The printed $2+$ charge must be included in the oxidation-state calculation.

Step 2: (ii) Explain the cobalt complex's orbital character The six neutral ammonia ligands leave cobalt in oxidation state $+3$. Thus Co^{3+} has configuration $[\mathrm{Ar}]3d^6$. In this cobalt(III) complex, ammonia produces pairing of the 3d electrons, leaving two 3d orbitals vacant. These two inner 3d orbitals, one 4s orbital and three 4p orbitals hybridise to form six equivalent d^2sp^3 orbitals. They accept the six ligand lone pairs and give octahedral geometry. Use of 3d rather than 4d orbitals makes it an inner-orbital, low-spin complex, with no unpaired electrons.

Step 3: Conclusion (i) Diamminedichloridoplatinum(IV). (ii) $[\mathrm{Co(NH_3)_6}]^{3+}$ is an inner-orbital octa-

Quick Tip to Solve: Use the printed complex charge to name the metal oxidation state; for inner-orbital character, identify which d shell hybridises.

hedral complex with d^2sp^3 hybridisation.

Quick Tip to Solve: Use the printed complex charge to name the metal oxidation state; for inner-orbital character, identify which d shell hybridises.

OR

29(c). Using valence bond theory, deduce the shape and hybridisation of $[Ni(NH_3)_6]^{2+}$. [Atomic number of Ni = 28] [2 marks]

Solution:

Concept:

- In valence bond theory, the coordination number is the number of ligand donor atoms bonded to the metal; six donors require six equivalent hybrid orbitals.
- Nickel loses its two outer 4s electrons to form Ni^{2+}, whose configuration is $[Ar]3d^8$.

Step 1: Find the metal-ion configuration Ammonia is neutral, so the oxidation state of Ni in $[Ni(NH_3)_6]^{2+}$ is $+2$. Neutral Ni has configuration $[Ar]3d^84s^2$; removal of the two 4s electrons gives $3d^8$. The five 3d orbitals contain eight electrons, with three orbitals doubly occupied and two singly occupied.

Step 2: Identify the hybrid orbitals and geometry Six ammonia ligands donate six lone pairs. A $3d^8$ ion cannot provide two vacant 3d orbitals, even by pairing its electrons: eight electrons require at least four 3d orbitals. Therefore inner-orbital d^2sp^3 hybridisation is unavailable. One empty 4s, three empty 4p and two empty 4d orbitals hybridise to form six sp^3d^2 orbitals directed towards the six vertices of an octahedron. Each accepts an ammonia lone pair to form a coordinate bond.

Step 3: Conclusion The complex $[Ni(NH_3)_6]^{2+}$ is octahedral with sp^3d^2 hybridisation (an outer-orbital complex).

Quick Tip to Solve: For a six-coordinate d^8 ion, count vacant inner d orbitals before choosing octahedral hybridisation.

30. Case Study : In a galvanic cell, chemical energy of a redox reaction is converted into electrical energy, whereas in an electrolytic cell the redox reaction occurs on passing electricity. The simplest galvanic cell is in which Zn rod is placed in a solution of $ZnSO_4$ and Cu rod is placed in a solution of $CuSO_4$. The two rods are connected by a metallic wire through a voltmeter. The two solutions are joined by a salt bridge. The difference between the two electrode potentials of the two electrodes is known as electromotive force. In the process of electrolysis, the decomposition of a substance takes place by passing an electric current. One mole of electric charge when passed through a cell will discharge half a mole of a divalent metal ion such as Cu^{2+}. This was first formulated by Faraday in the form of laws of electrolysis.

Answer the following questions : [4 marks]

30(a). What is the function of a salt bridge in a galvanic cell ? [1 mark]

Solution:

Concept:

- A galvanic cell requires a complete electrical circuit: electrons flow in the external wire and ions carry current within the electrolyte.
- Each half-cell must remain approximately electrically neutral for the redox reaction to continue.

Step 1: Track the charge imbalance At the zinc anode, $\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^{-}$ adds positive ions to solution. At the copper cathode, consumption of Cu^{2+} leaves an excess of negative charge. Without compensation, this charge separation opposes further electron flow.

Step 2: Explain ion migration The salt bridge supplies mobile, nonreacting ions: its anions migrate towards the anode compartment and its cations towards the cathode compartment. This maintains electrical neutrality and completes the internal circuit while limiting direct mixing of the two electrolytes.

Step 3: Conclusion A salt bridge completes the circuit by ionic conduction and maintains electrical neutrality in both half-cells.

Quick Tip to Solve: Remember: electrons move in the wire; salt-bridge ions restore charge balance in the solutions.

30(b). When does galvanic cell behave like an electrolytic cell ? [1 mark]

Solution:

Concept:

- A galvanic cell drives a spontaneous redox reaction using its own emf E_{cell}.
- An electrolytic cell uses an external source to drive the reverse, nonspontaneous reaction.

Step 1: Apply an opposing external voltage Connect an external source so that its voltage opposes the galvanic cell emf. For the Daniell cell, this source opposes the normal electron flow from Zn to Cu. If its voltage merely equals the cell emf, the net driving voltage is zero and no current flows.

Step 2: Exceed the cell emf When the opposing applied voltage is greater than E_{cell}, the direction of current and the cell reaction reverse. The external source now supplies electrical energy: copper

Quick Tip to Solve: Distinguish equality from excess: equal opposing voltage stops current; greater opposing voltage reverses it.

oxidises and zinc ions are reduced. Thus the cell operates electrolytically rather than supplying electrical energy.

Step 3: Conclusion A galvanic cell behaves as an electrolytic cell when an external opposing voltage greater than its emf is applied.

Quick Tip to Solve: Distinguish equality from excess: equal opposing voltage stops current; greater opposing voltage reverses it.

30(c). Can copper sulphate solution be stored in a pot made of zinc ? Explain with the help of the value of E°_{cell}.
(E° Cu^{2+}/Cu = 0.34 V)
(E° Zn^{2+}/Zn = –0.76 V) [2 marks]

Solution:

Concept:

- The standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using reduction potentials for both electrodes.
- A positive E°_{cell} corresponds to a spontaneous reaction under standard conditions because $\Delta G^\circ = -nFE^\circ_{\text{cell}}$.

Step 1: Write the possible reaction If copper sulphate contacts a zinc pot, zinc can oxidise and copper ions can reduce:

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

The overall reaction is $\text{Zn(s)} + \text{Cu}^{2+}\text{(aq)} \rightarrow \text{Zn}^{2+}\text{(aq)} + \text{Cu(s)}$, or $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$.

Step 2: Calculate the standard cell potential Copper is the cathode and zinc is the anode for this proposed reaction. Using the given reduction potentials,

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10\,\text{V}.$$

The positive value means that zinc reduces copper ions spontaneously under standard conditions. Copper is deposited while zinc dissolves, corroding the wall of the pot; the solution also changes as zinc sulphate forms.

Step 3: Conclusion No. Copper sulphate solution cannot be stored in a zinc pot because $E^\circ_{\text{cell}} = +1.10\,\text{V}$ for the reaction that dissolves zinc and deposits copper.

Quick Tip to Solve: For a metal container, test whether its oxidation coupled with solution-ion reduction gives a positive cell potential.

OR

30(c). How much charge in terms of Faraday is required for the following :

(i) 1 mol of MnO_4^- to Mn^{2+}

(ii) 1 mol of H_2O to O_2 [2 marks]

Solution:

Concept:

- One Faraday, F, is the charge carried by one mole of electrons. Thus a reaction consuming or releasing n moles of electrons requires a charge of magnitude nF.
- Balance the redox half-reaction for the amount of substance specified. The electron coefficient must be referred to one mole of the stated reactant, rather than automatically to one mole of product.

Step 1: (i) Reduction of one mole of permanganate In MnO_4^-, manganese has oxidation number $+7$; in Mn^{2+}, it is $+2$. Each manganese atom therefore gains five electrons. The balanced acidic half-reaction is

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O.$$

One mole of permanganate consumes five moles of electrons, so the required charge is $Q = 5F$.

Step 2: (ii) Oxidation of one mole of water Oxygen changes from oxidation number -2 in water to zero in molecular oxygen. The oxidation half-reaction is

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-.$$

This releases four moles of electrons for two moles of water. Hence one mole of water releases $4/2 = 2$ moles of electrons and forms half a mole of oxygen. The corresponding charge magnitude is $Q = 2F$, not $4F$, which would correspond to two moles of water.

Step 3: Conclusion The required charges are $\boxed{5F}$ for (i) and $\boxed{2F}$ for (ii).

Quick Tip to Solve: Divide the electron coefficient by the coefficient of the specified reactant before expressing charge in Faradays.

Section E (15 marks)

31. Attempt any five of the following :

(a) Why Zinc is not regarded as a transition element ?

(b) What is Lanthanoid contraction ?

(c) Why is first ionization enthalpy of chromium lower than that of Zn ?

(d) Why are transition elements good catalysts ?

(e) Compounds of transition metals are generally coloured. Give reason.

(f) Out of $KMnO_4$ and K_2MnO_4, which one is paramagnetic and why ?

(g) Complete the following ionic equation : $Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightarrow$ _____ [5 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its usual ions. Electronic configuration governs many transition-metal properties.
- Poor shielding by $4f$ electrons produces lanthanoid contraction. Unpaired electrons cause paramagnetism, while absorption of visible light during electronic transitions can produce colour.
- In balancing an ionic redox equation, conserve both atoms and total charge. Variable oxidation states and surface adsorption help transition metals catalyse reactions.

Step 1: (a) Why zinc is not a transition element Zinc has configuration $[\mathrm{Ar}]3d^{10}4s^2$, and its usual ion Zn^{2+} has configuration $[\mathrm{Ar}]3d^{10}$. Both have a completely filled $3d$ subshell. Thus zinc does not satisfy the condition of a partially filled d subshell in the atom or a usual ion, even though it belongs to the d block.

Step 2: (b) Lanthanoid contraction Lanthanoid contraction is the gradual decrease in atomic and ionic radii, especially those of Ln^{3+} ions, from lanthanum to lutetium as atomic number increases. The added electrons enter the $4f$ subshell and shield the increasing nuclear charge poorly. Consequently, effective nuclear attraction increases and the electron cloud contracts.

Step 3: (c) First ionization enthalpies of chromium and zinc Chromium is $[\mathrm{Ar}]3d^5 4s^1$, whereas zinc is $[\mathrm{Ar}]3d^{10}4s^2$. Removal of chromium's single $4s$ electron leaves the stable half-filled $3d^5$ configuration. Across the series, the increasing nuclear charge also holds zinc's outer electrons more strongly. Therefore less energy is required to remove the first electron from chromium than from zinc.

Step 4: (d) Catalytic activity Transition elements show variable oxidation states, so they can form intermediate compounds and participate in electron transfer during a reaction. Their metal surfaces can also adsorb reactants and bring them together in a favourable orientation. These effects provide an alternative reaction path of lower activation energy; the catalyst is regenerated.

Step 5: (e) Colour of transition-metal compounds In many transition-metal ions, the d subshell is partially filled. The surrounding ligands split the d orbitals into groups of different energies. Absorption of suitable visible wavelengths promotes electrons between these levels, giving d-d transitions. The remaining transmitted or reflected light gives the observed colour. This explains the general trend; d^0 and d^{10} ions do not show such transitions.

Step 6: (f) Paramagnetism of manganate and permanganate In $KMnO_4$, $1 + x + 4(-2) = 0$ gives

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state first, then count the remaining d electrons to decide magnetism.

manganese oxidation state $+7$, with configuration $3d^0$. It has no unpaired d electron and is diamagnetic. In K_2MnO_4, $2 + x + 4(-2) = 0$ gives $+6$, with configuration $3d^1$. Its one unpaired electron makes potassium manganate paramagnetic. Colour alone is not a test for paramagnetism.

Step 7: (g) Complete the dichromate half-reaction Each chromium atom is reduced from $+6$ to $+3$, so two chromium atoms accept six electrons. The balanced ionic equation is

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

There are two chromium, seven oxygen and fourteen hydrogen atoms on each side. The charge on the left is $-2 + 14 - 6 = +6$, matching the charge of $2Cr^{3+}$ on the right.

Step 8: Conclusion Any five of the seven responses above may be used. Zinc has a filled d subshell; lanthanoid radii decrease across the series; chromium loses its first electron more readily; variable oxidation states and adsorption explain catalysis; electronic transitions explain colour; K_2MnO_4 is paramagnetic; and the products in (g) are $\boxed{2Cr^{3+} + 7H_2O}$.

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state first, then count the remaining d electrons to decide magnetism.

32(a). (i) Define reverse osmosis.

(ii) Why are aquatic species more comfortable in cold water in comparison to warm water ?

(iii) A solution containing 2 g of glucose (M = 180 g mol^{-1}) in 100 g of water is prepared at 303 K. If the vapour pressure of pure water at 303 K is 32.8 mm Hg, what would be the vapour pressure of the solution ? [5 marks]

Solution:

Concept:

- Osmosis is the passage of solvent through a semipermeable membrane from pure solvent or a dilute solution into a more concentrated solution. Osmotic pressure is the minimum pressure needed on the solution side to stop this flow.
- The solubility of oxygen in water decreases on warming. Aquatic organisms depend on dissolved oxygen for respiration.
- For an ideal solution containing a non-volatile solute, Raoult's law gives $p = x_{\text{water}} p^0$, where p^0 is the pure solvent's vapour pressure and x_{water} is its mole fraction.

Step 1: (i) Define reverse osmosis Reverse osmosis is the process in which solvent is forced through a semipermeable membrane from the solution side to the pure-solvent side by applying a pressure greater than the osmotic pressure on the solution side. The membrane permits the solvent to pass but retains the dissolved solute. Thus the applied pressure reverses the direction of the natural osmotic flow; this principle is used in water purification.

Step 2: (ii) Explain the preference for cold water Oxygen, like most gases, dissolves to a greater extent in cold water than in warm water at the same gas pressure. Warming favours the escape of dissolved gas, so warm water contains less dissolved oxygen. Aquatic species therefore obtain oxygen

Quick Tip to Solve: Convert both masses to moles before finding the solvent mole fraction; the non-volatile solute must make the final pressure slightly less than 32.8 mm Hg.

for respiration more readily in cold water and are more comfortable there.

Step 3: (iii) Calculate the amounts of solvent and solute Glucose is a non-volatile molecular solute. Using the molar mass of water as $18\,\text{g mol}^{-1}$, the numbers of moles are

$$n_{\text{glucose}} = \frac{2}{180} = \frac{1}{90}\,\text{mol},$$
$$n_{\text{water}} = \frac{100}{18} = \frac{50}{9}\,\text{mol}.$$

The mole fraction uses moles of both components, rather than the solvent mass or the glucose mass fraction:

$$x_{\text{water}} = \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{glucose}}} = \frac{500}{501} = 0.998004.$$

Step 4: Apply Raoult's law at the stated temperature Since glucose contributes negligibly to the vapour pressure, the solution vapour pressure is the partial pressure of water. At $303\,\text{K}$, substitute the given pure-water vapour pressure:

$$p = 32.8 \times \frac{500}{501} = 32.7345\,\text{mm Hg}.$$

As a check, the relative lowering is

$$\frac{p^0 - p}{p^0} = x_{\text{glucose}} = \frac{1}{501},$$

so the lowering is only $0.06547\,\text{mm Hg}$. This small positive lowering is consistent with the dilute glucose solution.

Step 5: Conclusion (i) Reverse osmosis forces solvent from solution to pure solvent through a semipermeable membrane under pressure exceeding the osmotic pressure. (ii) Cold water has more dissolved oxygen available for aquatic respiration. (iii) The solution vapour pressure is $\boxed{32.73\,\text{mm Hg}}$ at $303\,\text{K}$.

Quick Tip to Solve: Convert both masses to moles before finding the solvent mole fraction; the non-volatile solute must make the final pressure slightly less than 32.8 mm Hg.

OR

32(b). (i) Predict whether Van't Hoff factor will be less or greater than one, when Ethanoic acid is dissolved in benzene.

(ii) Define ideal solution.

(iii) Calculate the mass of $CaCl_2$ (molar mass = 111 g mol^{-1}) to be dissolved in 500 g of water to lower its freezing point by 2 K, assuming that $CaCl_2$ undergoes complete dissociation. (K_f for water = 1.86 K kg mol^{-1}) [5 marks]

Solution:

Concept:

- The van't Hoff factor i is the ratio of the observed colligative property to its value calculated for an undissociated solute. Association reduces the number of solute particles, so $i < 1$; dissociation increases it.
- An ideal solution obeys Raoult's law over the entire range of composition: $p_A = x_A p_A^\circ$ and $p_B = x_B p_B^\circ$, where x denotes liquid-phase mole fraction and p° the vapour pressure of the pure component.
- Freezing-point depression is $\Delta T_f = iK_f m$, where K_f is the solvent's molal depression constant and m is moles of solute formula units per kilogram of solvent.

Step 1: (i) Account for association in benzene Ethanoic acid molecules associate in benzene through intermolecular hydrogen bonding to form dimers:

$$2\,CH_3COOH \rightleftharpoons (CH_3COOH)_2.$$

Two individual acid molecules then behave as one solute particle. Thus the effective number of particles is reduced and the observed colligative effect is smaller than that calculated without association. Accordingly, the van't Hoff factor is less than one. Complete dimerisation would give $i = \frac{1}{2}$; partial dimerisation gives a value between $\frac{1}{2}$ and 1.

Step 2: (ii) Define an ideal solution An ideal solution is a solution that obeys Raoult's law for each component throughout the entire range of composition at a given temperature. Thus the partial vapour pressure of each component is proportional to its mole fraction in the solution. Its total vapour pressure is

$$p = x_A p_A^\circ + x_B p_B^\circ.$$

For ideal mixing, $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$. The interactions between unlike molecules are approximately the same as those between like molecules, so mixing produces neither heat change nor volume change.

Step 3: (iii) Determine the particle factor and required molality Complete dissociation produces three ions from each formula unit:

$$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-.$$

Therefore $i = 3$. The specified decrease in freezing point is $\Delta T_f = 2\,K$, and $K_f = 1.86\,K\,kg\,mol^{-1}$.

Quick Tip to Solve: For complete dissociation of calcium chloride, count three ions and use $i = 3$; convert the 500 g of water to 0.500 kg before applying molality.

Hence

$$m = \frac{\Delta T_f}{iK_f} = \frac{2}{3 \times 1.86} = 0.3584\,\text{mol kg}^{-1}.$$

Molality counts moles of calcium chloride before dissociation; the factor i separately accounts for the resulting ions.

Step 4: Convert molality into mass of calcium chloride The mass of solvent is $500\,\text{g} = 0.500\,\text{kg}$. The required amount and mass of calcium chloride are therefore

$$\begin{aligned} n(\text{CaCl}_2) &= m \times 0.500 = 0.1792\,\text{mol}, \\ w = nM &= \frac{2 \times 0.500 \times 111}{3 \times 1.86} \\ &= 19.89\,\text{g}. \end{aligned}$$

As a check, $3 \times 1.86 \times [(19.89/111)/0.500]$ gives approximately $2.00\,\text{K}$, the required freezing-point depression.

Step 5: Conclusion (i) Ethanoic acid associates into dimers in benzene, so $i < 1$. (ii) An ideal solution obeys Raoult's law over the entire composition range and has $\Delta H_{\text{mix}} = \Delta V_{\text{mix}} = 0$. (iii) The required mass of CaCl_2 is $\boxed{19.89\,\text{g}}$, approximately $19.9\,\text{g}$.

Quick Tip to Solve: For complete dissociation of calcium chloride, count three ions and use $i = 3$; convert the 500 g of water to 0.500 kg before applying molality.

33(a). An amide 'A' with molecular formula C_7H_7ON undergoes Hoffmann Bromamide degradation reaction to give amine 'B'. 'B' on treatment with nitrous acid at 273-278 K forms 'C' and on treatment with chloroform and ethanolic potassium hydroxide forms 'D'. 'C' on treatment with ethanol gives 'E'. Identify 'A', 'B', 'C', 'D' and 'E' and write the sequence of chemical equations. [5 marks]

Solution:

Concept:

- In Hofmann bromamide degradation, a primary amide RCONH_2 gives the primary amine RNH_2, with one carbon atom fewer. The carbonyl carbon is removed as carbonate in alkaline medium.
- A primary aromatic amine undergoes diazotisation with nitrous acid at 273–278 K. Nitrous acid is generated in situ from sodium nitrite and hydrochloric acid; the cold conditions preserve the diazonium salt.
- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide. Ethanol reduces an aromatic diazonium group to hydrogen and is itself oxidised to ethanal.

Step 1: Identify the amide and its degradation product The amide must be benzamide, $C_6H_5CONH_2$, whose molecular formula is C_7H_7ON. Removal of its carbonyl carbon by Hofmann bromamide degradation produces aniline, $C_6H_5NH_2$. This primary aromatic amine also satisfies both subsequent

Quick Tip to Solve: Track the reagent branches: Hofmann degradation removes one carbon, carbylamine gives an N-linked isocyanide, and ethanol replaces the diazonium group by H.

reactions in the question. Thus the balanced first transformation is

$$C_6H_5CONH_2 + Br_2 + 4KOH \longrightarrow C_6H_5NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Hence A is benzamide and B is aniline. The benzene ring remains intact during this degradation.

Step 2: Diazotise aniline to identify C Treat aniline with freshly generated nitrous acid in hydrochloric acid at 273–278 K. Its amino group becomes the diazonium group, giving benzenediazonium chloride:

$$C_6H_5NH_2 + NaNO_2 + 2HCl \xrightarrow{273\text{–}278\ K} C_6H_5N_2^+Cl^- + NaCl + 2H_2O.$$

Thus C is benzenediazonium chloride. Hydrochloric acid supplies the acidic medium and chloride counter-ion; sodium nitrite supplies nitrous acid in situ. Keeping the reaction cold prevents premature decomposition of the diazonium salt.

Step 3: Apply the carbylamine reaction to identify D The separate treatment of B, aniline, with chloroform and ethanolic potassium hydroxide gives phenyl isocyanide:

$$C_6H_5NH_2 + CHCl_3 + 3KOH \xrightarrow[\text{ethanol}]{\Delta} C_6H_5NC + 3KCl + 3H_2O.$$

Therefore D is phenyl isocyanide, C_6H_5NC. Its ring is attached to nitrogen in the $-NC$ group. It is consequently different from benzonitrile, C_6H_5CN, where the ring is attached to carbon. This reaction is characteristic of primary amines.

Step 4: Reduce the diazonium salt with ethanol to identify E Ethanol replaces the diazonium group of C by hydrogen, with evolution of nitrogen. At the same time ethanol is oxidised to ethanal:

$$C_6H_5N_2^+Cl^- + C_2H_5OH \longrightarrow C_6H_6 + N_2 + CH_3CHO + HCl.$$

Thus E is benzene. The equation accounts for the reducing action of ethanol and balances the carbon, hydrogen, oxygen, nitrogen and chlorine atoms. Notice that ethanol is applied to the diazonium salt, whereas the carbylamine reagents are applied directly to aniline.

Step 5: Conclusion $A = C_6H_5CONH_2$ (benzamide), $B = C_6H_5NH_2$ (aniline), $C = C_6H_5N_2^+Cl^-$ (benzenediazonium chloride), $D = C_6H_5NC$ (phenyl isocyanide), and $E = C_6H_6$ (benzene). The transformations are $A \to B \to C \to E$, with the separate branch $B \to D$.

Quick Tip to Solve: Track the reagent branches: Hofmann degradation removes one carbon, carbylamine gives an N-linked isocyanide, and ethanol replaces the diazonium group by H.

OR

33(b). (i) (1) What is Hinsberg's reagent ?

(2) Arrange the following compounds in the increasing order of their basic strength in gaseous phase :

$C_2H_5NH_2$, $(C_2H_5)_3N$, $(C_2H_5)_2NH$

(ii) Give reasons for the following :

(1) Methyl amine is more basic than aniline.

(2) Aniline readily reacts with bromine water to give 2, 4, 6-tribromoaniline.

(3) Primary amines have higher boiling points than tertiary amines. [5 marks]

Solution:

Concept:

- Amines are Lewis bases: the lone pair on nitrogen accepts a proton. Electron-releasing alkyl groups increase its availability by the positive inductive effect.
- In the gaseous phase, solvation is absent; for the ethylamines here the basic strength increases from primary to secondary to tertiary amine.
- In aniline, the nitrogen lone pair is delocalised into the benzene ring. This reduces basicity but activates the ortho and para positions towards electrophilic substitution.
- Intermolecular hydrogen bonding needs a hydrogen attached to nitrogen as a donor. Primary amines have such bonds; tertiary amines do not.

Step 1: (i)(1) Identify Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It is used to distinguish primary, secondary and tertiary amines through their different behaviour towards sulphonamide formation and alkali. A primary amine forms a sulphonamide containing an acidic $N-H$ bond, which dissolves in alkali. A secondary amine forms a sulphonamide without an $N-H$ bond, insoluble in alkali; a tertiary amine does not form a sulphonamide under this test.

Step 2: (i)(2) Compare the gaseous-phase basic strengths Each ethyl group releases electron density towards nitrogen by its $+I$ effect and helps stabilise the conjugate ammonium ion formed on protonation. The number of ethyl groups increases from one in ethylamine to two in diethylamine and three in triethylamine. Since the question specifies the gaseous phase, differential hydration of the conjugate acids does not enter the comparison. Thus the increasing order follows the increasing electron-releasing effect:

$$C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N.$$

Step 3: (ii)(1) Explain the higher basicity of methylamine In methylamine, CH_3NH_2, the methyl group has a $+I$ effect that increases electron density on nitrogen, making its localised lone pair more available to accept H^+. In aniline, $C_6H_5NH_2$, this lone pair participates in resonance with the benzene ring and is consequently less available for protonation. The phenyl group's negative inductive effect also reduces electron density at nitrogen. Therefore methylamine is more basic than aniline.

Step 4: (ii)(2) Explain bromination of aniline The $-NH_2$ group donates its lone pair into the ring by resonance, strongly increasing electron density at the two ortho positions and the para position. It is therefore a powerful activating, ortho/para-directing group. With bromine water, substitution occurs

Quick Tip to Solve: First check whether the basicity comparison is in gas or water: in gas, use the alkyl +I effect; for boiling points, check for an N-H hydrogen-bond donor.

readily at all three activated positions, without a Lewis-acid catalyst, producing a white precipitate of 2,4,6-tribromoaniline:

$$C_6H_5NH_2 + 3Br_2 \longrightarrow C_6H_2Br_3NH_2 + 3HBr.$$

Step 5: (ii)(3) Compare the boiling points For amines of comparable molar mass, primary amines have higher boiling points than tertiary amines because primary amines contain $N - H$ bonds and form intermolecular $N - H \cdots N$ hydrogen bonds. Additional energy is required to overcome these attractions on boiling. Tertiary amines have no hydrogen bonded directly to nitrogen, so they cannot form such hydrogen bonds between their own molecules, although they can accept hydrogen bonds from water. Their weaker intermolecular attractions give lower boiling points in this comparison.

Step 6: Conclusion Hinsberg's reagent is $C_6H_5SO_2Cl$; the gaseous-phase order is ethylamine $<$ diethylamine $<$ triethylamine. Methylamine has a more available nitrogen lone pair than aniline; aniline's $-NH_2$ group strongly activates the ortho and para positions; and primary amines form intermolecular hydrogen bonds that tertiary amines cannot form with one another.

Quick Tip to Solve: First check whether the basicity comparison is in gas or water: in gas, use the alkyl $+I$ effect; for boiling points, check for an N-H hydrogen-bond donor.