CBSE Class 12 Chemistry Question Paper 2024 with Solution PDF-Set 56-4-2

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 Mg^{2+} and SO_4^{2-} are 106.0 S cm^2 mol^{-1} and 160.0 S cm^2 mol^{-1} respectively. The value of limiting molar conductivity of $MgSO_4$ will be : [1 mark]

(A) 266 S cm^2 mol^{-1}

(B) 622 S cm^2 mol^{-1}

(C) 288 S cm^2 mol^{-1}

(D) 822 S cm^2 mol^{-1}

Correct Answer: (A) 266 S cm^2 mol^{-1}

Solution:

Concept:

- Kohlrausch's law states that the limiting molar conductivity is the sum of the independent ionic contributions at infinite dilution.
- For an electrolyte giving ν_+ cations and ν_- anions per formula unit, $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$, where λ° denotes limiting molar ionic conductivity.

Step 1: Count the ions per formula unit The dissociation is $MgSO_4 \longrightarrow Mg^{2+} + {SO_4}^{2-}$. Thus one mole supplies one mole of each ion, giving $\nu_+ = \nu_- = 1$. The charge magnitude 2 is not an additional stoichiometric multiplier.

Step 2: Add the ionic contributions Substitute the given ionic conductivities directly:

$$\Lambda_m^\circ = 106.0 + 160.0 = 266.0\,\mathrm{S\,cm^2\,mol^{-1}}.$$

The values 622, 288 and 822 do not equal this stoichiometric sum, so options (B), (C) and (D) fail.

Step 3: Conclusion The limiting molar conductivity of $MgSO_4$ is $266\,\mathrm{S\,cm^2\,mol^{-1}}$. Hence, the correct option is (A).

Quick Tip to Solve: In Kohlrausch's law, multiply by the number of each ion in the formula, not by its ionic charge.

2. 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:

- Transition elements show variable oxidation states because their $3d$ and $4s$ electrons have comparable energies and can participate in bonding.
- Manganese has the electronic configuration $[\mathrm{Ar}]\,3d^5 4s^2$, providing seven valence electrons and a broad range of oxidation states.

Step 1: Identify manganese's range In the usual chemistry of the first transition series, manganese exhibits oxidation states from $+2$ to $+7$. Examples include $+2$ in $\mathrm{MnCl_2}$, $+4$ in $\mathrm{MnO_2}$ and $+7$ in $\mathrm{KMnO_4}$. Its five $3d$ and two $4s$ electrons account for this wide range.

Step 2: Compare the other listed elements Scandium predominantly shows $+3$. Titanium commonly shows $+2, +3, +4$, while chromium's familiar oxidation states include $+2, +3, +6$. None of these has as many oxidation states as manganese in the standard first-row transition-element comparison.

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

Quick Tip to Solve: In the $3d$ series, remember manganese's $3d^5 4s^2$ configuration when asked for the widest oxidation-state range.

3. 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:

- In an S_N1 reaction, the slow step is ionisation of the carbon–halogen bond to form a carbocation.
- With the same leaving group under comparable conditions, easier formation of a more stable carbocation gives a faster reaction; the usual order is tertiary $>$ secondary $>$ primary.

Step 1: Classify the carbon bearing bromine In (A), bromine is attached to a tertiary carbon, so ionisation produces the tert-butyl cation. Option (B) gives a secondary isopropyl cation, while (C)

Quick Tip to Solve: For S_N1, classify the carbon directly attached to the leaving group; branching on a neighbouring carbon can mislead.

would give a primary ethyl cation.

Step 2: Check the branched distractor In (D), $(CH_3)_3C-CH_2-Br$, bromine is bonded to the terminal CH_2 carbon. The initially formed neopentyl cation is primary, even though the neighbouring carbon is highly branched. A possible subsequent rearrangement does not make this initial ionisation as easy as direct formation of a tertiary carbocation. The tert-butyl cation is stabilised by electron donation and hyperconjugation from its alkyl groups.

Step 3: Conclusion $(CH_3)_3C-Br$ undergoes the fastest S_N1 reaction among the listed halides. Hence, the correct option is (A).

Quick Tip to Solve: For S_N1, classify the carbon directly attached to the leaving group; branching on a neighbouring carbon can mislead.

4. 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 the water-soluble vitamin chemically known as ascorbic acid.
- Ascorbic acid functions as an antioxidant and is required for normal collagen formation; its deficiency causes scurvy.

Step 1: Recall the chemical identity The accepted chemical name of vitamin C is ascorbic acid. This direct identification determines the answer; the mere presence of an acidic group does not make another organic acid vitamin C.

Step 2: Distinguish the other acids Gluconic acid is formed by mild oxidation of glucose's aldehyde group. Saccharic acid is the dicarboxylic acid obtained by stronger oxidation of glucose. Benzoic acid is an aromatic carboxylic acid. These are different compounds and none represents vitamin C.

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

Quick Tip to Solve: Link vitamin C with ascorbic acid and scurvy; gluconic and saccharic acids belong to glucose oxidation chemistry.

5. 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 the corresponding aldehyde by catalytic hydrogenation.
- Palladium supported on barium sulfate, $Pd/BaSO_4$, is used as a deactivated catalyst so that reduction can stop at the aldehyde stage.

Step 1: Write the characteristic conversion The general reaction is

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl.$$

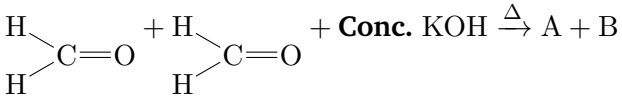
The support lowers catalyst activity, limiting further reduction of the aldehyde to an alcohol; additional catalyst poisons may also be used.

Step 2: Compare the proposed catalysts Anhydrous $AlCl_3$ is a Lewis acid used in Friedel–Crafts reactions. Iron(III) oxide is not the Rosenmund catalyst. $HgSO_4$ is associated with acid-catalysed hydration of alkynes. Thus options (B), (C) and (D) do not supply the required supported palladium catalyst.

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

Quick Tip to Solve: Recognise Rosenmund reduction by the pair acyl chloride to aldehyde and hydrogen over $Pd/BaSO_4$.

6. 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 the Cannizzaro reaction with concentrated alkali.
- This is a disproportionation: one aldehyde molecule is reduced to an alcohol while another is oxidised to a carboxylate salt.

Step 1: Identify why methanal reacts Methanal, $HCHO$, has no carbon adjacent to its carbonyl carbon and therefore no α-hydrogen. In concentrated KOH, it undergoes Cannizzaro disproportionation rather than aldol condensation.

Step 2: Write the balanced products

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

Reduction gives methanol and oxidation gives potassium formate. Both products retain the single carbon atom of a methanal molecule. Ethanol and potassium acetate each contain two carbons and cannot be the corresponding products of this reaction; methanal itself is the starting aldehyde. This rejects (B), (C) and (D).

Step 3: Conclusion A is methanol, CH_3OH, and B is potassium formate, $HCOOK$. Hence, the correct option is (A).

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

7. In effective collisions the colliding molecules must have : [1 mark]

(A) Proper orientation only

(B) A certain minimum amount of activation energy

(C) Threshold energy only

(D) Threshold energy and proper orientation both

Correct Answer: (D) Threshold energy and proper orientation both

Solution:

Concept:

- An effective collision is one that produces a chemical reaction; not every collision between reactant molecules is effective.
- Colliding molecules must have energy at least equal to the threshold energy and must approach with suitable orientation for the required bonds to break and form.

Step 1: Apply the energy condition Molecules need sufficient collision energy to reach the activated configuration. A collision below the threshold energy cannot produce reaction even when orientation is favourable. Therefore proper orientation alone, as in (A), is insufficient.

Step 2: Apply the orientation condition Even energetic molecules may collide at the wrong reactive sites. A favourable orientation is also necessary. Options (B) and (C) mention only an energy condition and omit this requirement. Option (D) includes both conditions and is therefore the complete statement.

Step 3: Conclusion Effective collisions require threshold energy and proper orientation both. Hence, the correct option is (D).

Quick Tip to Solve: In collision-theory MCQs, check for both sufficient energy and correct orientation; either condition alone is incomplete.

8. Identify the secondary amine from the given options : [1 mark]

(A) $(CH_3)_2CHNH_2$

(B) $CH_3NHCH(CH_3)_2$

(C) $(CH_3)_3CNH_2$

(D) $CH_3(CH_2)_2NH_2$

Correct Answer: (B) $CH_3NHCH(CH_3)_2$

Solution:

Concept:

- Amines are classified by the number of carbon groups bonded directly to the nitrogen atom.
- A primary amine has the form RNH_2; a secondary amine has the form R_2NH; a tertiary amine has three carbon groups bonded to nitrogen and no nitrogen-bound hydrogen.

Step 1: Count the groups attached to nitrogen In $CH_3NHCH(CH_3)_2$, nitrogen is bonded to a methyl group and an isopropyl group, as well as one hydrogen. Thus its nitrogen has two carbon substituents,

Quick Tip to Solve: Circle nitrogen first and count its directly attached carbon groups; ignore branching farther along the carbon chain.

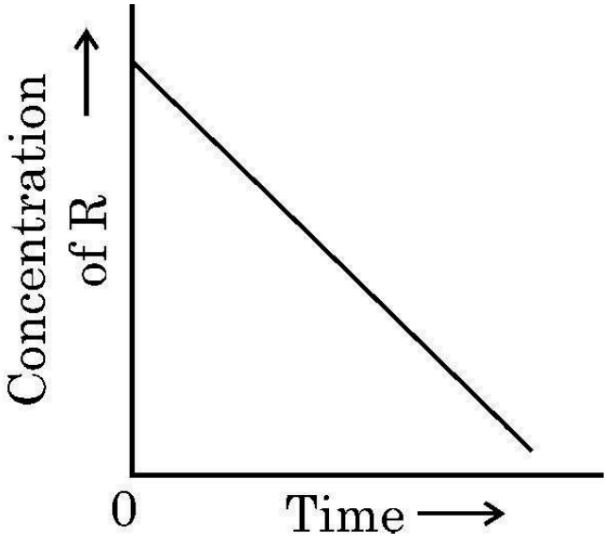
the defining feature of a secondary amine.

Step 2: Check the remaining structures Options (A), (C) and (D) each contain an $-NH_2$ group attached to only one carbon group. They are all primary amines. In particular, the branched carbon skeleton in (C) does not make its amino group tertiary: the classification concerns nitrogen, not the adjacent carbon.

Step 3: Conclusion $CH_3NHCH(CH_3)_2$ is the secondary amine. Hence, the correct option is (B).

Quick Tip to Solve: Circle nitrogen first and count its directly attached carbon groups; ignore branching farther along the carbon chain.

9. 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 the rate is constant: $-d[R]/dt = k$, where $[R]$ is reactant concentration and k is the rate constant.
- Its integrated rate equation is $[R] = [R]_0 - kt$, where $[R]_0$ is the initial concentration and t is elapsed time.

Step 1: Compare with the straight-line equation The graph plots concentration directly against time. Comparing $[R] = -kt + [R]_0$ with $y = mx + c$, the coefficient of time is the gradient and the constant term is the vertical intercept. The descending line agrees with reactant consumption.

Quick Tip to Solve: Read the vertical-axis quantity before using a rate-law graph: concentration itself gives slope $-k$ for zero order.

Step 2: Eliminate the incorrect forms Option (A) has a positive slope, inconsistent with the falling concentration. Options (C) and (D) include logarithmic intercepts and a factor of 2.303, neither of which arises when concentration itself is plotted for a zero order reaction. At $t = 0$, the concentration equals its initial value.

Step 3: Conclusion The slope is $-k$ and the intercept is $[\mathrm{R}]_0$. Hence, the correct option is (B).

Quick Tip to Solve: Read the vertical-axis quantity before using a rate-law graph: concentration itself gives slope $-k$ for zero order.

10. 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 the d-block, electrons progressively occupy the $(n-1)d$ subshell, where n denotes the outermost principal shell.
- Five d orbitals can accommodate ten electrons in total. The usual general configuration is written as $(n-1)d^{1-10}ns^{1-2}$, allowing for individual exceptional configurations.

Step 1: Identify the required occupancy range Across a d-block series the d-electron count varies, so a general expression must include the range from one to ten d electrons. The outer s subshell can contain at most two electrons; the printed general form in (A) expresses the usual range.

Step 2: Compare all alternatives Option (B) fixes the d occupancy at ten, so it cannot represent the full series. Option (C) also fixes that occupancy and even allows three electrons in an s subshell, which is impossible. Option (D) fixes the d occupancy at zero and therefore does not describe progressive d filling. Some actual atoms have exceptional s occupancies, but these do not make any of the other printed options a suitable general form.

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

Quick Tip to Solve: A general d-block formula must allow changing d occupancy; reject fixed d^{10}, fixed d^{0}, and any s^{3} term.

11. 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 adds to the electrophilic carbonyl carbon.
- A ketone already has two carbon groups attached to its carbonyl carbon. Acidic hydrolysis protonates the alkoxide oxygen to form an alcohol.

Step 1: Follow addition at the carbonyl carbon Write the ketone as R_2CO. Its carbonyl carbon is bonded to two carbon groups. Addition of the R group creates a third carbon-carbon bond at that same carbon, while the carbonyl oxygen becomes an alkoxide oxygen.

Step 2: Classify the alcohol after hydrolysis Hydrolysis changes the oxygen group to $-OH$; it does not remove any of the three attached carbon groups. The carbon bearing $-OH$ therefore has three carbon neighbours. Formaldehyde would give a primary alcohol, and other aldehydes give secondary alcohols, so (B) and (D) do not apply to ketones. Alkene formation requires an elimination step, which is not the stated process.

Step 3: Conclusion A ketone reacts with a Grignard reagent and then undergoes acidic hydrolysis to give a tertiary alcohol. Hence, the correct option is (C).

Quick Tip to Solve: Count carbon groups on the carbonyl carbon and add one for the Grignard group: a ketone goes from two to three.

12. 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:

- PCC is a mild oxidising reagent that converts primary alcohols to aldehydes under suitable anhydrous conditions; $NaBH_4$ reduces a ketone to a secondary alcohol.
- Phenol reacts readily with bromine water, while heating an alcohol with phosphoric acid promotes dehydration to an alkene.

Step 1: Match oxidation and reduction Reaction I requires controlled oxidation without further oxidation to a carboxylic acid, so it uses PCC, reagent (r). Reaction II changes a carbonyl group in butan-2-one to the alcohol group of butan-2-ol; the reducing reagent $NaBH_4$, labelled (p), performs this change.

Step 2: Match bromination and dehydration The strongly activated phenol ring gives 2,4,6-tribromophenol with bromine water, so III matches (s). Propan-2-ol loses water on heating with 85% phosphoric acid at $440\,K$, producing propene, so IV matches (q). Among the alternatives only (A) keeps all four assignments; (B), (C) and (D) already assign an unsuitable reagent to oxidation I.

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

Quick Tip to Solve: Match the distinctive transformations first: PCC means aldehyde formation, and bromine water means tribromination of phenol.

13. Two statements are given - one labelled Assertion (A) and the other labelled Reason (R).
Assertion (A) : Bromination of Phenol can be carried out even in the absence of Lewis acid.
Reason (R) : –OH group of Phenol has the high activation effect. [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:

- The $-OH$ group activates the benzene ring of phenol towards electrophilic substitution by donating an oxygen lone pair through resonance.
- This donation increases electron density especially at the ortho and para positions, making bromination easier than in benzene.

Step 1: Judge the assertion Phenol undergoes bromination without a Lewis acid catalyst such as $FeBr_3$. For example, bromine water gives 2,4,6-tribromophenol. Thus Assertion (A) is true.

Step 2: Judge the reason The hydroxyl group has a strong activating effect because its resonance donation supplies electron density to the aromatic ring. This outweighs its opposing inductive effect for electrophilic substitution. Thus Reason (R) is also true.

Step 3: Check the explanatory link The activated ring reacts readily with bromine without requiring Lewis-acid-assisted electrophile formation. The reason therefore explains why the catalyst is unnecessary. Option (B) misses this direct link; (C) and (D) incorrectly declare one true statement false.

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

Quick Tip to Solve: For phenol bromination, connect the oxygen lone-pair donation directly to rapid substitution without a Lewis acid.

14. 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 mild oxidising agents such as Fehling's solution and Tollens' reagent.
- Although fructose is a ketose, the alkaline test conditions allow it to rearrange through an enediol intermediate into aldoses such as glucose and mannose.

Step 1: Judge the assertion Fructose behaves as a reducing sugar. In the alkaline medium used for these tests, its interconversion with aldoses makes reducing aldehyde forms available. Assertion (A) is therefore true.

Step 2: Judge the reason Fructose does reduce Fehling's solution, producing a red precipitate of Cu_2O, and it also reduces Tollens' reagent, depositing metallic silver. The reason denies both reactions and is therefore false.

Step 3: Relate the two statements A false reason cannot explain the true assertion. Options (A) and (B) both require a true reason, while (D) incorrectly calls the assertion false. The apparent objection that fructose contains a ketone overlooks its rearrangement in the alkaline test medium.

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

Quick Tip to Solve: Do not reject fructose as a reducing sugar merely because it is a ketose; check its aldose interconversion in alkaline medium.

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15. 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 converts chemical energy into electrical energy; its spontaneous electron flow is from Zn to Cu.

Quick Tip to Solve: Compare the opposing voltage with the cell emf first: above 1.1 V, both the electrode reactions and the electron-flow direction reverse.

- An opposing external potential greater than the cell emf forces the reverse, non-spontaneous reaction and makes the cell electrolytic.

Step 1: Evaluate the assertion The cell emf under the stated conditions is $1.1\,\text{V}$. An opposing potential greater than this value overcomes the spontaneous reaction. Copper is then oxidised, $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\,\text{e}^-$, and zinc ions are reduced, $\text{Zn}^{2+} + 2\,\text{e}^- \longrightarrow \text{Zn}$. Thus electrons flow through the external circuit from copper towards zinc, so A is true.

Step 2: Evaluate the reason The reverse reaction requires electrical energy supplied from outside. Consequently, the cell now functions as an electrolytic cell, not as a galvanic cell. R is false.

Step 3: Check the explanation and alternatives A false reason cannot explain the true assertion. Options (A) and (B) wrongly treat R as true, while option (D) wrongly treats A as false. The direction must be judged after applying the opposing potential, rather than from the usual spontaneous Daniell-cell reaction.

Step 4: Conclusion Assertion is true, but Reason is false. Hence, the correct option is (C).

Quick Tip to Solve: Compare the opposing voltage with the cell emf first: above $1.1\,\text{V}$, both the electrode reactions and the electron-flow direction reverse.

16. 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 substitution reactions that require a sufficiently reactive aromatic ring and an available Lewis-acid catalyst.
- The $-\text{COOH}$ group withdraws electron density from the benzene ring by its inductive and resonance effects, thereby deactivating the ring.

Step 1: Evaluate the assertion Benzoic acid does not undergo the usual Friedel–Crafts alkylation or acylation. Its carboxyl group strongly reduces the ring's reactivity towards electrophiles. Assertion A is therefore true.

Step 2: Evaluate the reason In addition to deactivating the ring, the carboxyl group coordinates with the Lewis acid AlCl_3 through oxygen. This ties up the catalyst needed for the Friedel–Crafts reaction. Both statements in R are chemically correct, so R is true.

Step 3: Test the causal connection Ring deactivation and complex formation with the catalyst directly

Quick Tip to Solve: For Friedel–Crafts reactions, check both ring deactivation by $-\text{COOH}$ and its coordination with AlCl_3.

account for the failure of the reaction. Thus R explains A. Option (B) misses this causal link, while options (C) and (D) wrongly reject one of the true statements.

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

Quick Tip to Solve: For Friedel–Crafts reactions, check both ring deactivation by $-\mathrm{COOH}$ and its coordination with $\mathrm{AlCl_3}$.

Section B (10 marks)

17. Define the following terms :

(a) Molecularity of reaction

(b) Complex reaction [2 marks]

Solution:

Concept:

- An elementary reaction occurs in a single step; its molecularity counts the reacting species participating in that step.
- A reaction mechanism is the sequence of elementary steps by which the overall reaction takes place. The overall balanced equation need not represent a single molecular event.

Step 1: Define molecularity of reaction Molecularity is the number of reacting species (atoms, ions or molecules) that participate simultaneously in an elementary reaction. It is a positive whole number, usually one, two or three. For example, an elementary step $\mathrm{A} + \mathrm{B} \longrightarrow \text{products}$ is bimolecular because two reacting species participate. Molecularity is assigned to an elementary step, rather than to a multistep overall reaction.

Step 2: Define a complex reaction A complex reaction is a reaction that takes place through a sequence of two or more elementary steps. These steps together constitute its mechanism, and adding their equations gives the overall balanced equation after intermediates cancel. Each elementary step may have its own molecularity; simply adding the coefficients of the overall reaction does not give a meaningful molecularity for the complex reaction.

Step 3: Conclusion (a) Molecularity counts the reacting species participating in a single elementary step. (b) A complex reaction proceeds through two or more elementary steps.

Quick Tip to Solve: Before counting species for molecularity, check that the equation represents one elementary step, not an overall complex reaction.

18. Calculate the molar mass of a compound when 6.3 g of it is dissolved in 27 g of chloroform to form a solution that has a boiling point of 68.04 °C. The boiling point of pure chloroform is 61.04 °C and K_b for chloroform is 3.63 °C kg mol^{-1}. [2 marks]

Solution:

Concept:

- For a non-volatile solute with no association or dissociation, boiling-point elevation obeys $\Delta T_b = K_b m$, where K_b is the ebullioscopic constant and m is molality.
- Molality is moles of solute per kilogram of solvent: $m = (w_2/M_2)/(w_1/1000)$, where w_1, w_2 are the solvent and solute masses in grams and M_2 is the solute molar mass.

Step 1: Calculate the boiling-point elevation Subtract the boiling point of pure chloroform from that of the solution, because the colligative relation uses the increase in temperature:

$$\Delta T_b = 68.04 - 61.04 = 7.00\,^\circ\text{C}.$$

The solvent mass is $27\,\text{g} = 0.027\,\text{kg}$; use this mass, rather than the total solution mass, in the molality.

Step 2: Substitute into the molar-mass relation Combining the two relations and rearranging gives

$$M_2 = \frac{K_b w_2 \times 1000}{\Delta T_b w_1}.$$

With $w_2 = 6.3\,\text{g}$, $w_1 = 27\,\text{g}$ and $K_b = 3.63\,^\circ\text{C}\,\text{kg mol}^{-1}$,

$$M_2 = \frac{3.63 \times 6.3 \times 1000}{7.00 \times 27} = \frac{22869}{189}\,\text{g mol}^{-1}.$$

The temperature units cancel, and the factor of 1000 converts the solvent mass from grams to kilograms.

Step 3: Conclusion The molar mass of the compound is $\boxed{121\,\text{g mol}^{-1}}$.

Quick Tip to Solve: Use the temperature difference $7.00\,^\circ\text{C}$ and the solvent mass $27\,\text{g}$; neither the final boiling point nor the solution mass belongs in the formula.

19. (a) Which of the following compounds will react more rapidly by S_N2 reaction and why ?
$(CH_3)_3C–Br$ or $CH_3–CH_2–CHBr–CH_3$
(b) Arrange the following compounds in the increasing order of their boiling points :
$CH_3CH_2CH_2CH_2Br$, $(CH_3)_2CHCH_2Br$, $(CH_3)_3CBr$ [2 marks]

Solution:

Concept:

- An S_N2 reaction involves a single concerted step with backside attack of the nucleophile at the carbon bearing the leaving group. Steric crowding slows this attack.
- For isomeric haloalkanes of the same molar mass, increased branching reduces the effective surface

Quick Tip to Solve: For S_N2, inspect crowding at the carbon bonded to bromine; for boiling points of these isomers, compare branching of the whole carbon skeleton.

area and weakens intermolecular dispersion forces, lowering the boiling point.

Step 1: Compare steric hindrance in part (a) In $(CH_3)_3CBr$, the carbon bonded to bromine is tertiary and is surrounded by three alkyl groups. These groups strongly hinder the nucleophile's approach from the back. In $CH_3CH_2CHBrCH_3$, the bromine-bearing carbon is secondary and has less steric crowding. Thus backside attack is more accessible in the secondary compound. The ease of formation of a tertiary carbocation is irrelevant here, because S_N2 does not proceed through a carbocation.

Step 2: Compare branching in part (b) The three bromides are isomers and hence have the same molar mass. The compound $(CH_3)_3CBr$ is the most compact and most branched; $(CH_3)_2CHCH_2Br$ is less branched; and $CH_3CH_2CH_2CH_2Br$ has an unbranched chain. Increasing the exposed surface area strengthens intermolecular dispersion attractions, so a higher temperature is needed to separate the molecules into vapour.

Step 3: Conclusion (a) $CH_3CH_2CHBrCH_3$ reacts more rapidly by S_N2 because it is less sterically hindered. (b) The increasing order of boiling points is

$$(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br.$$

Quick Tip to Solve: For S_N2, inspect crowding at the carbon bonded to bromine; for boiling points of these isomers, compare branching of the whole carbon skeleton.

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

[2 marks]

Solution:

Concept:

- In a carbonyl group, oxygen is more electronegative than carbon. The bond is polarised as $C^{\delta+} = O^{\delta-}$, so a nucleophile attacks the electrophilic carbon atom.
- Let Nu^- represent a nucleophile. In $R{-}C(=O){-}R'$, R' may be hydrogen for an aldehyde or an alkyl group for a ketone.

Step 1: Step 1: Nucleophilic attack The nucleophile donates an electron pair to the carbonyl carbon. At the same time, the π-electron pair of the $C = O$ bond shifts to oxygen:

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

This produces a tetrahedral alkoxide intermediate. The carbonyl carbon changes from planar sp^2 hybridisation to tetrahedral sp^3 hybridisation.

Step 2: Step 2: Protonation of the alkoxide The negatively charged oxygen accepts a proton from a proton donor, represented by H^+:

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

The oxygen therefore becomes an $-OH$ group while the nucleophile remains bonded to the former

Quick Tip to Solve: Put the nucleophile on carbon and the negative charge on oxygen first; protonate that oxygen in the next step.

carbonyl carbon. No carbon atom is removed during this addition.

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

Quick Tip to Solve: Put the nucleophile on carbon and the negative charge on oxygen first; protonate that oxygen in the next step.

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 an alkyl side chain containing a benzylic hydrogen to a carboxylate group. Acidification then gives the corresponding carboxylic acid.
- An aldehyde with an α-hydrogen undergoes aldol addition in cold dilute alkali, forming a β-hydroxy aldehyde. Ethanal is obtained from ethanol by dehydrogenation.

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

$$\mathrm{C_6H_5CH_3} \xrightarrow[\text{heat}]{\text{alkaline } \mathrm{KMnO_4}} \mathrm{C_6H_5COOK} \xrightarrow{\text{dilute HCl}} \mathrm{C_6H_5COOH}.$$

The benzene ring remains intact, while its methyl side chain becomes a carboxyl group. The final acidification is essential to obtain benzoic acid from its salt.

Step 2: (ii) Ethanol to 3-hydroxybutanal Pass ethanol vapour over heated copper at $573\,\mathrm{K}$ to obtain ethanal:

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

Treat ethanal with cold dilute NaOH. Two molecules undergo aldol addition:

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

Numbering from the aldehyde carbon places the hydroxyl group at carbon 3. Avoid heating the aldol product, since dehydration would give an unsaturated aldehyde instead of the required hydroxy aldehyde.

Step 3: Conclusion (i) Hot alkaline $\mathrm{KMnO_4}$, followed by acidification, converts toluene to benzoic acid. (ii) Ethanol gives ethanal with Cu at $573\,\mathrm{K}$; cold dilute NaOH then gives 3-hydroxybutanal.

Quick Tip to Solve: For 3-hydroxybutanal, first make ethanal, then join two ethanal molecules by a cold aldol addition without dehydration.

21. (a) What happens when Glucose reacts with HI ? Write chemical equation.

(b) Which type of bond holds a DNA double helix together ? [2 marks]

Solution:

Concept:

- Prolonged heating with hydroiodic acid, HI, reduces glucose to the corresponding straight-chain hydrocarbon by removing its oxygen-containing groups.
- In double-stranded DNA, complementary nitrogenous bases on opposite strands form hydrogen bonds: adenine pairs with thymine, and guanine pairs with cytosine.

Step 1: (a) Reaction of glucose with HI On prolonged heating with excess HI, glucose is reduced to n-hexane. The balanced overall chemical equation is

$$C_6H_{12}O_6 + 14HI \xrightarrow{\text{prolonged heating}} CH_3(CH_2)_4CH_3 + 6H_2O + 7I_2.$$

All six carbon atoms remain in one unbranched chain. Thus formation of n-hexane provides evidence that the six carbon atoms of glucose are connected in a straight chain. Iodide is oxidised to iodine during this reduction.

Step 2: (b) Bonds holding the DNA double helix together The two DNA strands are held together by hydrogen bonds between complementary bases. An adenine–thymine pair has two hydrogen bonds, whereas a guanine–cytosine pair has three. These bonds join bases across the two strands; the sugar–phosphate backbone within each individual strand is linked by covalent phosphodiester bonds.

Step 3: Conclusion (a) Glucose gives n-hexane on prolonged heating with HI. (b) Hydrogen bonds between complementary base pairs hold the two DNA strands together.

Quick Tip to Solve: Remember HI reduction as the straight-chain test for glucose; for DNA, distinguish hydrogen bonds across strands from phosphodiester links along a strand.

Section C (21 marks)

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

$[Co(en)_2Cl_2]^+$

(b) Write the electronic configuration of d^4 ion if $\Delta_0 > P$.

(c) What is a didentate ligand ? Give one example. [3 marks]

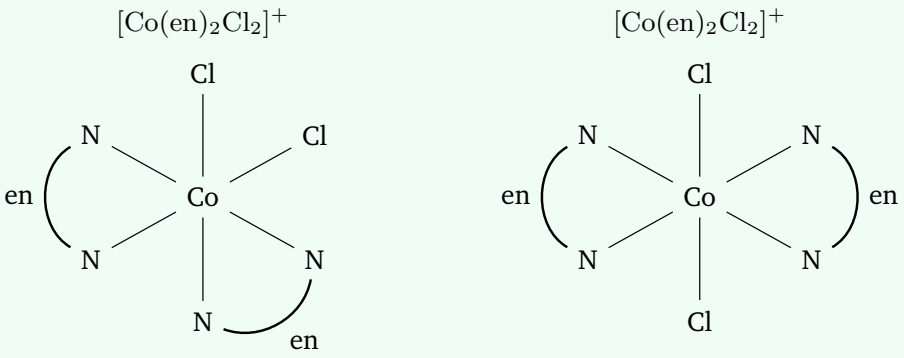
Solution:

Concept:

- In an octahedral complex, geometrical isomers differ in the relative positions of ligands: two identical ligands are adjacent in the cis form and opposite in the trans form.
- The octahedral crystal field splits the five d orbitals into lower-energy t_{2g} and higher-energy e_g sets. When $\Delta_o > P$, pairing in t_{2g} is energetically preferred to promotion into e_g.
- A didentate ligand coordinates to the same metal ion through two donor atoms, forming two coordinate bonds.

Quick Tip to Solve: Compare the two chloride positions to name cis or trans; count donor atoms, not ligand molecules, to find the coordination number.

Step 1: (a) Arrange the ligands in the two geometrical isomers Each ethane-1,2-diamine ligand, abbreviated en, supplies two nitrogen donor atoms. Thus two en ligands and two chloride ligands occupy the six coordination positions around cobalt. The two chlorides can have a 90° separation (cis) or a 180° separation (trans). In the drawings, each curved link joins the two nitrogen donors belonging to one en ligand; the straight lines are metal–ligand bonds.



cis: adjacent Cl ligands trans: opposite Cl ligands

Geometrical isomers of $[Co(en)_2Cl_2]^+$; curved links identify the two en chelates.

Step 2: (b) Fill the split d orbitals Since $\Delta_o > P$, the fourth electron pairs in a lower-energy t_{2g} orbital after the first three electrons occupy those orbitals singly. The occupation is therefore $t_{2g}^4 e_g^0$: the three t_{2g} orbitals have occupations $(\uparrow\downarrow), (\uparrow), (\uparrow)$, while both e_g orbitals are empty. This is the low-spin configuration, with two unpaired electrons.

Step 3: (c) Identify a didentate ligand A didentate ligand has two donor atoms that attach simultaneously to one metal ion. Ethane-1,2-diamine, $H_2NCH_2CH_2NH_2$, is an example: the lone pair on each nitrogen forms a coordinate bond to the metal, producing a chelate ring. Its denticity is two even though it is counted as one ligand.

Step 4: Conclusion (a) The complex has cis and trans geometrical isomers, as drawn. (b) The configuration is $\boxed{t_{2g}^4 e_g^0}$. (c) A didentate ligand binds through two donor atoms; en is an example.

Quick Tip to Solve: Compare the two chloride positions to name cis or trans; count donor atoms, not ligand molecules, to find the coordination number.

23. (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:

- Carboxylic acids liberate carbon dioxide from aqueous sodium hydrogencarbonate; phenol is too weak an acid to give this reaction.
- Tollens' reagent oxidises aldehydes to carboxylate ions while its silver(I) ions are reduced to metallic silver. Ordinary ketones do not give this test.
- Fluorine exerts an electron-withdrawing inductive effect ($-I$ effect), stabilising a carboxylate ion. The effect decreases as its distance from the carboxyl group increases.

Step 1: (a)(i) Distinguish phenol from benzoic acid Add aqueous $NaHCO_3$ separately to the samples. Benzoic acid produces brisk effervescence of CO_2, whereas phenol gives no effervescence. The gas may be confirmed by passing it through limewater, which turns milky. The reaction is

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

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

Step 2: (a)(ii) Distinguish propanal from propanone Warm each sample gently with freshly prepared Tollens' reagent. Propanal forms a silver mirror on the test-tube wall; propanone gives no silver mirror. Propanal's aldehyde group is oxidised to propanoate in the alkaline reagent:

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

Propanone is a ketone and resists oxidation by this mild oxidising reagent.

Step 3: (b) Compare the positions of fluorine Number the carbon chain from the carboxyl carbon. In CH_3CHFCH_2COOH, fluorine is at the beta position; in $CH_2FCH_2CH_2COOH$, it is at the gamma position. Fluorine therefore withdraws electron density more strongly from the carboxyl group in the former. Its conjugate carboxylate ion is more stabilised, so loss of H^+ is more favourable.

Step 4: Conclusion Benzoic acid gives CO_2 with $NaHCO_3$, while phenol does not. Propanal gives a Tollens' silver mirror, while propanone does not. The stronger acid is $\boxed{CH_3CHFCH_2COOH}$, because its fluorine is closer to COOH.

Quick Tip to Solve: For acids with the same electron-withdrawing substituent, count bonds from that substituent to COOH: a shorter distance gives the stronger inductive effect.

24. 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, $k = \dfrac{2.303}{t}\log\dfrac{[A]_0}{[A]_t}$, where k is the rate constant, $[A]_0$ the initial reactant concentration and $[A]_t$ the concentration remaining after time t. Here log denotes the base-ten logarithm.
- The half-life is the time required for the concentration to fall to half its initial value: $t_{1/2} = \dfrac{2.303\log 2}{k}$. Both this time and any fixed-percentage completion time are independent of the initial concentration for a first-order reaction.

Step 1: Express the concentration remaining after 99.9 percent completion If 99.9% has reacted, the percentage remaining is $100 - 99.9 = 0.1\%$. Hence

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

The integrated rate law uses the amount remaining, not the amount that has reacted.

Step 2: Obtain the time for this extent of reaction Rearranging the first-order integrated rate equation gives

$$\begin{aligned} t_{99.9\%} &= \frac{2.303}{k}\log\frac{[A]_0}{[A]_0/1000} \\ &= \frac{2.303}{k}\log 1000 = \frac{2.303\times 3}{k}, \end{aligned}$$

since $\log 1000 = \log 10^3 = 3\log 10 = 3$.

Step 3: Compare with the half-life At half-life, $[A]_t = [A]_0/2$. Therefore

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

Dividing the two time expressions cancels both the common conversion factor and the rate constant:

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

Thus the statement in the question is the usual rounded relation. As a check, ten half-lives leave $2^{-10} = 1/1024$ of the initial amount, corresponding to about 99.902% completion, very close to 99.9%.

Step 4: Conclusion $\boxed{t_{99.9\%} \simeq 10\,t_{1/2}}$. More precisely, the given logarithm yields $t_{99.9\%} = 9.97\,t_{1/2}$ to three significant figures.

Quick Tip to Solve: Convert completion to the fraction remaining first: 99.9 percent completion leaves 0.001, so the logarithm needed is log 1000, not log 99.9.

25. Calculate emf of the following cell at $25\,^\circ$C:

$$\mathrm{Sn/Sn^{2+}\,(0.001\,M)\,\|\,H^+\,(0.01\,M)\,|\,H_2(g)\,(1\,bar)/Pt\,(s)}$$

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

Solution:

Concept:

- For the cell written from left to right, the anode undergoes oxidation and the cathode undergoes reduction. Standard cell potential is $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$, using both electrode potentials as reduction potentials.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0591/n)\log Q$. Here n is the number of electrons transferred and Q is the reaction quotient; pure solids have unit activity.

Step 1: Write the balanced cell reaction Tin is oxidised at the left electrode and hydrogen ions are reduced at the right electrode:

$$\begin{aligned}\text{Anode: } &\mathrm{Sn\,(s) \longrightarrow Sn^{2+}(aq) + 2\,e^-}\\ \text{Cathode: } &\mathrm{2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)}\\ \text{Overall: } &\mathrm{Sn\,(s) + 2\,H^+(aq) \longrightarrow Sn^{2+}(aq) + H_2(g).}\end{aligned}$$

Two electrons are transferred per balanced reaction, so $n = 2$. The coefficient of $\mathrm{H^+}$ also makes its concentration squared in the reaction quotient.

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

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

With concentrations expressed relative to 1 M and gas pressure relative to 1 bar,

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

Neither solid tin nor the inert platinum electrode contributes a concentration factor to Q.

Step 3: Apply the Nernst correction Substitute $n = 2$, $Q = 10$ and the supplied $\log 10 = 1$:

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

Since $Q > 1$, the concentration correction lowers the emf relative to its standard value, as expected from the sign in the Nernst equation.

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

Quick Tip to Solve: Balance the tin–hydrogen cell reaction first: it gives both $n = 2$ and the square on $[\mathrm{H^+}]$ in Q.

26. Define the following terms :

(a) Non essential amino acids

(b) Monosaccharides

(c) Anomers [3 marks]

Solution:

Concept:

- Amino acids are classified nutritionally according to whether the human body can synthesise them in adequate amounts.
- Carbohydrates are classified by their hydrolysis products. The simplest carbohydrate units are monosaccharides.
- Cyclisation of a monosaccharide creates an anomeric carbon from its carbonyl carbon; the two possible configurations at that centre give anomers.

Step 1: Define non-essential amino acids Non-essential amino acids are amino acids that can be synthesised by the human body, so their supply need not depend entirely on dietary intake. Examples include glycine and alanine. The term refers to the body's ability to make them; these amino acids are still needed for protein synthesis and normal biological functions.

Step 2: Define monosaccharides Monosaccharides are the simplest carbohydrates that cannot be hydrolysed into smaller carbohydrate units. They are polyhydroxy aldehydes or ketones, or exist in cyclic forms derived from these structures. Glucose is an example of an aldose monosaccharide, while fructose is a ketose monosaccharide. In contrast, a disaccharide yields monosaccharides on hydrolysis.

Step 3: Define anomers Anomers are cyclic stereoisomers of a carbohydrate that differ in configuration only at the anomeric carbon. This carbon is the former carbonyl carbon of the open-chain sugar. For example, α-D-glucopyranose and β-D-glucopyranose differ only in the configuration of the hydroxyl group at carbon 1; all their other stereocentres have the same configurations. For an aldose the anomeric carbon is generally C-1, while in fructose it is C-2.

Step 4: Conclusion Non-essential amino acids can be made by the body; monosaccharides cannot be hydrolysed into simpler carbohydrates; anomers differ only at the anomeric carbon of a cyclic sugar.

Quick Tip to Solve: In defining anomers, specify the anomeric carbon: a difference at any other stereocentre does not make a pair anomers.

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

(b) Why are haloalkanes more reactive towards nucleophilic substitution reactions than haloarenes ?

(c) What happens when ethyl chloride is treated with aqueous KOH ? [3 marks]



Solution:

Concept:

- Disubstituted benzene derivatives are numbered to give the lowest set of locants; alphabetical order breaks a numbering tie between substituents.
- The ease of nucleophilic substitution depends on carbon–halogen bond strength and the substitution pathway.
- Aqueous alkali supplies OH^-, which replaces the halogen of a suitable haloalkane to form an alcohol.

Step 1: Name the printed compound in part (a) The benzene ring has bromine and chlorine on opposite carbon atoms, so their locants are 1 and 4. Either numbering direction gives the same set of locants. Since bromo precedes chloro alphabetically, bromine receives locant 1. The IUPAC name is therefore **1-bromo-4-chlorobenzene**.

Step 2: Explain the reactivity difference in part (b) In a haloarene, a lone pair on the halogen is delocalised into the benzene ring by resonance. Consequently, the carbon–halogen bond acquires partial double-bond character and is harder to break. The halogen-bearing carbon is also sp^2-hybridised; its greater s-character makes the bond shorter and stronger than the corresponding bond to an sp^3 carbon in a haloalkane. Also, a phenyl carbocation is unstable and backside attack at the ring carbon is difficult. Haloalkanes lack this resonance-strengthened bond and undergo ordinary nucleophilic substitution more readily.

Step 3: Write the reaction in part (c) Ethyl chloride undergoes hydrolysis with aqueous potassium hydroxide to form ethanol. Hydroxide acts as a nucleophile and replaces chloride:

$$CH_3CH_2Cl + KOH\,(aq) \longrightarrow CH_3CH_2OH + KCl.$$

Aqueous alkali favours substitution to an alcohol; alcoholic alkali with heat instead favours elimination.

Step 4: Conclusion (a) 1-Bromo-4-chlorobenzene. (b) The stronger carbon–halogen bond makes haloarenes less reactive. (c) Aqueous KOH gives ethanol.

Quick Tip to Solve: For the para-disubstituted ring, give bromo locant 1 by alphabetical order; for ethyl chloride, check whether KOH is aqueous or alcoholic before choosing the product.

28. 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 alkaline peroxide oxidation converts an alkene into an alcohol with anti-Markovnikov orientation: the hydroxyl group enters the less substituted carbon.
- Williamson synthesis couples an alkoxide with a primary alkyl halide by nucleophilic substitution. In anisole, the methoxy group directs electrophilic substitution to the ortho and para positions.
- The Reimer–Tiemann reaction introduces a formyl group into phenol, mainly ortho to the hydroxyl group, using chloroform and aqueous alkali followed by acidification.

Step 1: Write hydroboration and oxidation of propene Borane adds across the double bond in dry tetrahydrofuran (THF). Oxidation of the trialkylborane gives propan-1-ol:

$$3\,CH_3CH{=}CH_2 + BH_3 \xrightarrow{THF} (CH_3CH_2CH_2)_3B$$

$$(CH_3CH_2CH_2)_3B + 3\,H_2O_2 \xrightarrow{OH^-} 3\,CH_3CH_2CH_2OH + B(OH)_3$$

Boron attaches to the terminal carbon and is subsequently replaced by hydroxyl.

Step 2: Write a Williamson ether synthesis Sodium ethoxide reacts with the primary alkyl halide bromoethane to give ethoxyethane:

$$C_2H_5ONa + C_2H_5Br \longrightarrow C_2H_5OC_2H_5 + NaBr$$

The alkoxide displaces bromide by nucleophilic substitution.

Step 3: Alkylate anisole at the ortho and para positions Methyl chloride in the presence of anhydrous aluminium chloride introduces a methyl group into the aromatic ring:

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

Here $CH_3C_6H_4OCH_3$ represents 2-methylanisole and 4-methylanisole. The para isomer predominates due to lower steric hindrance.

Step 4: Write the Reimer–Tiemann reaction of phenol Phenol is heated with chloroform and aqueous sodium hydroxide and the mixture is then acidified. The overall equation for the main organic product is:

$$C_6H_5OH + CHCl_3 + 3\,NaOH \longrightarrow o\text{-}HOC_6H_4CHO + 3\,NaCl + 2\,H_2O$$

The main product is 2-hydroxybenzaldehyde (salicylaldehyde); a little para isomer also forms.

Step 5: Conclusion The respective products are propan-1-ol, ethoxyethane, ortho- and para-methylanisole, and salicylaldehyde. Any three reactions may be written.

Quick Tip to Solve: Pair each named reaction with its signature reagent: borane/peroxide, alkoxide/primary halide, alkyl chloride/anhydrous aluminium chloride, or chloroform/aqueous alkali.

Section D (8 marks)

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

29. 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]

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

Solution:

Concept:

- A galvanic cell produces a sustained current only when both the external electronic path and the internal ionic path are complete.
- A salt bridge contains an inert electrolyte whose ions migrate to maintain electrical neutrality in the two half-cells.

Step 1: Identify charge accumulation in each half-cell At the zinc anode, oxidation produces Zn^{2+}, so positive charge would accumulate. At the copper cathode, reduction consumes Cu^{2+}, leaving excess negative charge in solution. This separation of charge would soon stop the cell reaction.

Step 2: Explain the movement of salt-bridge ions Anions from the bridge migrate towards the anode compartment and cations towards the cathode compartment. Their movement balances the developing charges and completes the internal circuit. Electrons travel through the external wire, not through the salt bridge.

Step 3: Conclusion A salt bridge completes the circuit and maintains electrical neutrality in both half-cells by allowing ion migration; it also limits direct mixing of the two solutions.

Quick Tip to Solve: Remember anions to the anode and cations to the cathode: the bridge transports ions, while the wire transports electrons.

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

Solution:

Concept:

- A galvanic cell operates by a spontaneous redox reaction that produces an emf, E_{cell}.
- An external voltage applied in opposition to this emf can drive the reverse, non-spontaneous reaction if its magnitude exceeds the cell emf.

Quick Tip to Solve: Distinguish equality from reversal: an equal opposing voltage stops current, whereas a greater opposing voltage drives electrolysis.

Step 1: Oppose the spontaneous current Connect an external source with its positive terminal to the positive terminal of the galvanic cell and its negative terminal to the negative terminal of the cell. This connection applies a potential opposing the cell's own emf.

Step 2: Increase the applied opposing potential At an opposing voltage equal to E_{cell}, the net driving potential is zero and current stops in the ideal case. When the applied opposing voltage becomes greater than E_{cell}, current reverses and electrical energy drives the reverse chemical reaction.

Step 3: Conclusion A galvanic cell behaves like an electrolytic cell when an external opposing potential greater than its emf is applied: $E_{\text{external}} > E_{\text{cell}}$.

Quick Tip to Solve: Distinguish equality from reversal: an equal opposing voltage stops current, whereas a greater opposing voltage drives electrolysis.

29(c). Can copper sulphate solution be stored in a pot made of zinc? Explain with the help of the value of E°_{cell}.

$E^{\circ}(\text{Cu}^{2+}/\text{Cu}) = 0.34\,\text{V}$

$E^{\circ}(\text{Zn}^{2+}/\text{Zn}) = -0.76\,\text{V}$ [2 marks]

Solution:

Concept:

- To test whether a metal container reacts with a salt solution, calculate the standard cell potential for oxidation of the container metal and reduction of the dissolved metal ion.
- Using reduction potentials, $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$. A positive value implies a spontaneous forward reaction under standard conditions because $\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}}$.

Step 1: Write the possible displacement reaction Zinc from the pot would be oxidised while copper(II) ions from solution would be reduced:

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

Adding these gives $\text{Zn}\,(\text{s}) + \text{Cu}^{2+}(\text{aq}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}\,(\text{s})$. Sulphate ions are spectators.

Step 2: Calculate the standard cell potential Copper is the cathode and zinc is the anode for the proposed reaction. Both given values are reduction potentials, so subtract the zinc value without changing its sign first:

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

Since this value is positive, $\Delta G^{\circ} < 0$; zinc can spontaneously reduce copper(II) ions to copper. The zinc wall dissolves as zinc ions enter solution and copper is deposited.

Step 3: Conclusion Copper sulphate solution cannot be stored in a zinc pot: $E^{\circ}_{\text{cell}} = +1.10\,\text{V}$ for $\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$, so the pot reacts with the solution and corrodes.

Quick Tip to Solve: For a storage test, oxidise the container metal and reduce the dissolved metal ion; a positive cell potential indicates that this container will react.

OR

29(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 magnitude of charge carried by one mole of electrons. Thus, transfer of n moles of electrons requires charge $Q = nF$.
- Electron transfer is obtained from the change in oxidation number or from a balanced half-reaction. The charge must be calculated for the specified amount of reactant.

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

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

Hence, reduction of one mole of permanganate involves five moles of electrons; its charge requirement is $Q = 5F$.

Step 2: (ii) Oxidation of water to oxygen Oxygen changes from oxidation number -2 in water to 0 in molecular oxygen. The balanced oxidation half-reaction is

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

Two moles of water release four moles of electrons. Therefore, for the specified one mole of water, the electron transfer is $4/2 = 2$ moles and the charge passed is $Q = 2F$. This produces only half a mole of O_2; $4F$ would correspond to one mole of oxygen gas, not one mole of water.

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

Quick Tip to Solve: First balance the electron transfer, then divide by the coefficient of the reactant whose amount is specified; here one mole of water requires half the charge in its half-reaction.

30. 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]

30(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 electron pairing gives diamagnetism.
- Fluoride is a weak-field ligand and does not cause pairing of the cobalt ion's $3d$ electrons in this complex.

Step 1: Find the cobalt ion configuration Each fluoride ligand has charge -1. If cobalt has oxidation state x, then $x-6=-3$, so $x=+3$. Cobalt has atomic number 27 and configuration $[\mathrm{Ar}]3d^7 4s^2$; therefore Co^{3+} has configuration $[\mathrm{Ar}]3d^6$.

Step 2: Count the unpaired electrons The weak-field fluoride ligands leave the six $3d$ electrons in a high-spin arrangement: one orbital contains a pair and the other four each contain one electron. Thus four electrons remain unpaired. In valence bond theory, the complex uses the outer $4d$ orbitals and has sp^3d^2 hybridisation.

Step 3: Conclusion $[CoF_6]^{3-}$ is **paramagnetic** because it has **four unpaired electrons**.

Quick Tip to Solve: Find cobalt's oxidation state before counting d electrons, then use fluoride's weak-field character to retain the high-spin arrangement.

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

Solution:

Concept:

- The coordination number is the number of ligand donor atoms directly bonded to the central metal ion.
- Ethane-1,2-diamine, abbreviated en, is bidentate: each molecule coordinates through its two nitrogen atoms. A chlorido ligand is monodentate.

Step 1: Count the donor atoms from en The complex $[Co(en)_2Cl_2]^+$ contains two en molecules. Each

Quick Tip to Solve: Count donor atoms, not ligand molecules: multiply the two en ligands by their denticity of two, then add the two chlorido donors.

provides two nitrogen donor atoms, so these ligands form $2 \times 2 = 4$ coordinate bonds to cobalt. Count both donor atoms of each en molecule, rather than counting each molecule as a single coordinating unit.

Step 2: Include the chlorido ligands Both chlorido ligands lie inside the square brackets, so each is directly bonded to cobalt and contributes one donor atom. Their contribution is $2 \times 1 = 2$. The total number of donor atoms is therefore $4 + 2$. The overall charge of the ion is used to find oxidation state, and does not change this donor-atom count.

Step 3: Conclusion The coordination number of cobalt is $\boxed{2(2) + 2(1) = 6}$.

Quick Tip to Solve: Count donor atoms, not ligand molecules: multiply the two en ligands by their denticity of two, then add the two chlorido donors.

30(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 a complex ion, ligand names precede the metal name in alphabetical order, ignoring multiplicative prefixes. The metal oxidation state is written in Roman numerals.
- An octahedral inner orbital complex uses two inner $(n-1)d$ orbitals, one ns orbital and three np orbitals, giving d^2sp^3 hybridisation.

Step 1: (i) Name the platinum complex In $[Pt(NH_3)_2Cl_2]^{2+}$, each ammine ligand is neutral and each chlorido ligand has charge -1. If the oxidation state of platinum is x, then

$$x + 2(0) + 2(-1) = +2 \quad \Rightarrow \quad x = +4.$$

Ammine comes before chlorido alphabetically, and there are two of each ligand. Since the complex is cationic, the metal retains the name platinum. Its IUPAC name is **diamminedichloridoplatinum(IV) ion**. The printed overall $2+$ charge must be included in finding the oxidation state.

Step 2: (ii) Determine the orbitals used by the cobalt complex In $[Co(NH_3)_6]^{3+}$, ammonia is neutral, so cobalt is in the $+3$ oxidation state. Cobalt has atomic number 27; Co^{3+} has the configuration $[Ar]3d^6$. In this complex, the ligand field causes the six $3d$ electrons to pair in three orbitals, leaving two inner $3d$ orbitals vacant. These combine with the $4s$ and three $4p$ orbitals to form six d^2sp^3 hybrid orbitals for octahedral bonding. Thus, the complex uses inner orbitals and is low spin; all electrons are paired, making it diamagnetic.

Step 3: Conclusion (i) **Diamminedichloridoplatinum(IV) ion**. (ii) $[Co(NH_3)_6]^{3+}$ is an **inner orbital**, octahedral complex with $\boxed{d^2sp^3}$ hybridisation.

Quick Tip to Solve: Keep the overall complex charge when finding platinum's oxidation state; for cobalt(III) with ammonia, paired inner 3d electrons leave two orbitals available for hybridisation.

OR

30(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 metal ion provides vacant orbitals equal in number to its coordination number; ligands donate electron pairs into the resulting hybrid orbitals.
- Six equivalent sp^3d^2 hybrid orbitals use one s, three p and two outer d orbitals and point towards the vertices of an octahedron.

Step 1: Determine the electronic configuration of the metal ion Ammonia, NH_3, is neutral, so nickel has oxidation state $+2$ in $[Ni(NH_3)_6]^{2+}$. Nickel has atomic number 28. Removing the two $4s$ electrons gives

$$Ni : [Ar]\, 3d^8 4s^2,$$
$$Ni^{2+} : [Ar]\, 3d^8.$$

Eight electrons occupy the five $3d$ orbitals. Even complete pairing cannot provide two empty $3d$ orbitals, so inner-orbital d^2sp^3 hybridisation is unavailable.

Step 2: Choose the orbitals for six ligand pairs The six ammonia ligands each donate one lone pair, giving coordination number 6. The vacant $4s$, three $4p$ and two $4d$ orbitals mix to form six sp^3d^2 hybrid orbitals. Their directions minimise repulsion between the six bonds and produce an octahedral arrangement around the nickel ion. Since the $4d$ orbitals are used, this is an outer-orbital complex.

Step 3: Conclusion $[Ni(NH_3)_6]^{2+}$ has $\boxed{sp^3d^2}$ hybridisation and an $\boxed{\text{octahedral}}$ shape.

Quick Tip to Solve: For octahedral nickel(II), first count the eight $3d$ electrons: they cannot leave two inner d orbitals empty, so use the outer $4d$ orbitals.

Section E (15 marks)

31(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 solvent flow through a semipermeable membrane towards the concentrated solution. Applying pressure greater than the osmotic pressure reverses this flow.
- The solubility of gases such as oxygen in water generally decreases with rising temperature at a fixed gas pressure. Dissolved oxygen supports respiration by aquatic organisms.

Quick Tip to Solve: Convert both glucose and water masses into moles first; then multiply 32.8 by the water mole fraction $500/501$, which is just below one.

- For a solution of a non-volatile solute, Raoult's law gives $p = x_{\text{water}} p^0$, where p^0 is the vapour pressure of pure water and x_{water} is its mole fraction in the solution.

Step 1: Define reverse osmosis for part (i) Reverse osmosis is the passage of solvent through a semipermeable membrane from a solution to the pure-solvent side when pressure greater than the solution's osmotic pressure is applied on the solution side. The membrane passes solvent but retains solute, so the imposed pressure reverses spontaneous osmosis.

Step 2: Explain the temperature effect for part (ii) Oxygen is more soluble in cold water than in warm water under comparable conditions. The greater availability of dissolved oxygen for respiration makes aquatic species more comfortable in cold water.

Step 3: Calculate the mole fraction for part (iii) Glucose, $C_6H_{12}O_6$, is a non-volatile solute. Using its given molar mass and the molar mass $18\,\text{g mol}^{-1}$ of water, H_2O, gives

$$\begin{aligned} n_{\text{glucose}} &= \frac{2}{180} = \frac{1}{90}\,\text{mol}, \\ n_{\text{water}} &= \frac{100}{18} = \frac{50}{9}\,\text{mol}, \\ x_{\text{water}} &= \frac{n_{\text{water}}}{n_{\text{water}} + n_{\text{glucose}}} = \frac{500}{501}. \end{aligned}$$

Use moles of both components in the denominator, not their masses.

Step 4: Apply Raoult's law at the stated temperature At $303\,\text{K}$, the given pure-water vapour pressure is $p^0 = 32.8\,\text{mm Hg}$. Thus

$$p = x_{\text{water}} p^0 = \frac{500}{501} \times 32.8 = 32.7345\,\text{mm Hg}.$$

The pressure is slightly below the pure-water value, as expected for this dilute solution of a non-volatile solute.

Step 5: Conclusion (i) Reverse osmosis requires applied pressure greater than osmotic pressure. (ii) Cold water offers more dissolved oxygen for respiration. (iii) The vapour pressure is approximately $\boxed{32.73\,\text{mm Hg}}$ at $303\,\text{K}$.

Quick Tip to Solve: Convert both glucose and water masses into moles first; then multiply 32.8 by the water mole fraction $500/501$, which is just below one.

OR

31(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 is $i =$ actual number of solute particles/number of formula units introduced. Association lowers the particle count, whereas dissociation raises it.
- An ideal solution obeys Raoult's law, $p_j = x_j p_j^\circ$, for every component over the entire composition range at a given temperature. Here x_j is mole fraction and p_j° is pure-component vapour pressure.
- Freezing-point depression is $\Delta T_f = iK_f m$, where K_f is the solvent's cryoscopic constant and m is moles of solute per kilogram of solvent.

Step 1: (i) Account for association of ethanoic acid In benzene, ethanoic acid molecules associate to form hydrogen-bonded dimers:

$$2\mathrm{CH_3COOH} \rightleftharpoons (\mathrm{CH_3COOH})_2.$$

Two individual molecules thereby contribute only one solute particle. Consequently the observed colligative effect is smaller than the value calculated without association, so $i < 1$. If a fraction α of the molecules associates, the particle count changes from n to $n(1-\alpha) + n\alpha/2$, giving $i = 1 - \alpha/2$. Complete dimerisation would give $i = 1/2$; completeness is not specified here.

Step 2: (ii) State the definition of an ideal solution An ideal solution is a solution that obeys Raoult's law over the entire range of composition at a given temperature. For a binary solution,

$$p_A = x_A p_A^\circ, \qquad p_B = x_B p_B^\circ, \qquad p_{\text{total}} = p_A + p_B.$$

Such mixing has $\Delta H_{\text{mix}} = 0$ and $\Delta V_{\text{mix}} = 0$, consistent with unlike-molecule interactions being similar to the like-molecule interactions in the pure components.

Step 3: (iii) Find the particle factor for calcium chloride Complete dissociation gives

$$\mathrm{CaCl_2(aq)} \longrightarrow \mathrm{Ca^{2+}(aq)} + 2\mathrm{Cl^-(aq)}.$$

Each formula unit produces three ions, so $i = 3$. The solvent mass is $500\,\text{g} = 0.500\,\text{kg}$. Molality uses this mass of water, rather than the mass of the final solution.

Step 4: (iii) Substitute in the freezing-point depression equation With $\Delta T_f = 2\,\text{K}$ and $K_f = 1.86\,\text{K kg mol}^{-1}$, the required molality is

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

Quick Tip to Solve: Count the ions before substituting: complete dissociation of calcium chloride gives $i = 3$, and the $500\,\text{g}$ of water must be converted to $0.500\,\text{kg}$.

Hence the amount of calcium chloride is

$$n = m \times 0.500 = 0.1792\,\text{mol}.$$

Using its molar mass $M = 111\,\text{g mol}^{-1}$,

$$w = nM = \frac{2 \times 0.500 \times 111}{3 \times 1.86} = 19.89\,\text{g}.$$

Step 5: Conclusion (i) $\boxed{i < 1}$ because ethanoic acid associates in benzene. (ii) An ideal solution obeys Raoult's law throughout the composition range. (iii) The required mass is $\boxed{19.9\,\text{g of } CaCl_2}$.

Quick Tip to Solve: Count the ions before substituting: complete dissociation of calcium chloride gives $i = 3$, and the $500\,\text{g}$ of water must be converted to $0.500\,\text{kg}$.

32(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:

- Hofmann bromamide degradation converts a primary amide, $RCONH_2$, into the primary amine RNH_2, with loss of the carbonyl carbon. Bromine and aqueous alkali are used.
- A primary aromatic amine undergoes diazotisation with nitrous acid in mineral acid at 273–278 K.
- The carbylamine reaction converts a primary amine into an isocyanide using chloroform and alcoholic potassium hydroxide.

Step 1: Identify the amide and apply Hofmann degradation The amide with molecular formula C_7H_7ON that yields an aromatic primary amine is benzamide, $C_6H_5CONH_2$. Thus, A is benzamide. The product B is aniline, $C_6H_5NH_2$:

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

Step 2: Diazotise aniline to identify C Nitrous acid is generated in situ from sodium nitrite and dilute hydrochloric acid. At 273–278 K, aniline forms benzenediazonium chloride, C. With hydrochloric acid as the mineral acid, the equation is

$$C_6H_5NH_2 + NaNO_2 + 2\,HCl \longrightarrow C_6H_5N_2^{+}\,Cl^{-} + NaCl + 2\,H_2O.$$

Step 3: Apply the carbylamine reaction to identify D On heating a separate portion of aniline with

Quick Tip to Solve: Track carbon atoms first: Hofmann degradation changes the seven-carbon amide into a six-carbon amine. Then distinguish the two branches from aniline: cold nitrous acid gives a diazonium salt, while chloroform with alcoholic alkali gives an isocyanide.

chloroform and ethanolic potassium hydroxide, phenyl isocyanide, D, is formed:

$$C_6H_5NH_2 + CHCl_3 + 3\,KOH \longrightarrow C_6H_5NC + 3\,KCl + 3\,H_2O.$$

This reaction confirms that B is a primary amine. The product contains the connectivity $C_6H_5{-}NC$, so it is an isocyanide, not the nitrile $C_6H_5{-}CN$.

Step 4: Reduce the diazonium salt to identify E Ethanol replaces the diazonium group of C by hydrogen, liberating nitrogen gas. Ethanol is simultaneously oxidised to ethanal:

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

Step 5: Conclusion A is benzamide, $C_6H_5CONH_2$; B is aniline, $C_6H_5NH_2$; C is benzenediazonium chloride, $C_6H_5N_2{}^+\,Cl^-$; D is phenyl isocyanide, C_6H_5NC; and E is benzene, C_6H_6.

Quick Tip to Solve: Track carbon atoms first: Hofmann degradation changes the seven-carbon amide into a six-carbon amine. Then distinguish the two branches from aniline: cold nitrous acid gives a diazonium salt, while chloroform with alcoholic alkali gives an isocyanide.

OR

32(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 act as bases by donating the nitrogen lone pair to a proton. Alkyl groups increase its availability through their electron-releasing inductive effect.
- Resonance delocalisation of the nitrogen lone pair in aniline reduces basicity but increases electron density at the ortho and para positions of its benzene ring.
- Intermolecular hydrogen bonding requires a suitable donor bond, such as $N{-}H$, and a lone-pair acceptor. It raises the boiling point by strengthening intermolecular attraction.

Step 1: (i)(1) Identify Hinsberg's reagent Hinsberg's reagent is benzenesulphonyl chloride, $C_6H_5SO_2Cl$. It is used in the Hinsberg test to distinguish primary, secondary and tertiary amines by their different reactions and the solubility of the resulting products in alkali. Its functional group is sulphonyl chloride, $-SO_2Cl$, attached to a phenyl group.

Step 2: (i)(2) Compare the gaseous basic strengths In the gaseous phase, hydration of the protonated amines is absent. The electron-releasing effect of the ethyl groups therefore gives the expected

Quick Tip to Solve: Check the phase before ranking amine basicity. For boiling points of pure amines, count nitrogen-bound hydrogens; for aniline bromination, mark both ortho sites and the para site.

order: tertiary amine is more basic than secondary amine, which is more basic than primary amine. Increasing the number of ethyl groups raises the electron density on nitrogen and stabilises the protonated cation. Hence the increasing order is

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

The aqueous order must not be substituted here, because solvation can change the relative strengths in water.

Step 3: (ii)(1) Explain the basicity of methyl amine and aniline In methyl amine, CH_3NH_2, the methyl group's positive inductive effect increases the electron density on nitrogen. Its localised lone pair is readily available to accept a proton. In aniline, $C_6H_5NH_2$, this lone pair is delocalised into the benzene ring by resonance. It is consequently less available for protonation; the phenyl group's electron-withdrawing inductive effect also lowers the electron density on nitrogen. Methyl amine is therefore more basic than aniline.

Step 4: (ii)(2) Explain rapid bromination of aniline The $-NH_2$ group donates its nitrogen lone pair into the ring by resonance. It strongly activates the ring towards electrophilic substitution and directs incoming electrophiles to the ortho and para positions. Thus bromine water readily substitutes at both ortho positions and the para position without a Lewis-acid catalyst, forming a white precipitate of 2,4,6-tribromoaniline:

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

The three bromine atoms in the product occupy positions 2, 4 and 6 relative to the amino group.

Step 5: (ii)(3) Compare intermolecular forces and boiling points For amines of comparable molecular masses, primary amines have $N-H$ bonds and a lone pair on nitrogen, so their molecules associate through intermolecular $N-H\cdots N$ hydrogen bonds. Tertiary amines have no hydrogen directly bonded to nitrogen and cannot form such hydrogen bonds between their own molecules. More energy is therefore required to separate the molecules of a primary amine during boiling, giving it a higher boiling point. Tertiary amines can accept hydrogen bonds from water, but that does not supply hydrogen bonding in the pure tertiary amine.

Step 6: Conclusion Hinsberg's reagent is $C_6H_5SO_2Cl$. The gaseous basicity order is $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$. Lone-pair availability explains methyl amine's greater basicity; resonance activation explains aniline's 2,4,6-tribromination; intermolecular hydrogen bonding explains the higher boiling points of comparable primary amines.

Quick Tip to Solve: Check the phase before ranking amine basicity. For boiling points of pure amines, count nitrogen-bound hydrogens; for aniline bromination, mark both ortho sites and the para site.

33. 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 :

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow$$

[5 marks]

Solution:

Concept:

- A transition element has an incompletely filled d subshell in its atom or in at least one of its oxidation states. Electronic configurations explain ionisation, magnetism and many colour trends.
- Poor shielding by $4f$ electrons causes the gradual decrease in lanthanoid radii as nuclear charge increases. Unpaired electrons cause paramagnetism.
- Transition-metal catalysts provide an alternative reaction pathway of lower activation energy through intermediate formation or surface adsorption. In acidic redox equations, balance oxygen with H_2O, hydrogen with H^+, and charge with electrons.

Step 1: (a) Apply the definition of a transition element Zinc has the ground-state configuration $[Ar]3d^{10}4s^2$, and its usual ion Zn^{2+} has configuration $[Ar]3d^{10}$. Both have a completely filled $3d$ subshell. Thus, although zinc belongs to the d-block, neither its atom nor its usual ion satisfies the incomplete-d-subshell criterion for a transition element.

Step 2: (b) Define lanthanoid contraction and its cause Lanthanoid contraction is the gradual decrease in atomic and ionic radii, especially the radii of Ln^{3+} ions, with increasing atomic number across the lanthanoid series. The added $4f$ electrons shield the increasing nuclear charge poorly. Consequently, effective nuclear attraction increases and pulls the electron cloud closer to the nucleus.

Step 3: (c) Compare electron removal from chromium and zinc Chromium has configuration $[Ar]3d^5 4s^1$. Removing its outer $4s$ electron gives Cr^+ with a stable half-filled $3d^5$ subshell. Zinc has configuration $[Ar]3d^{10}4s^2$; its greater effective nuclear attraction holds the outer electrons more strongly, and its filled $3d$ and $4s$ subshells confer additional stability. Hence less energy is needed for the first electron removal from chromium than from zinc.

Step 4: (d) Explain catalytic activity Transition elements can exhibit variable oxidation states because their $(n-1)d$ and ns orbitals have comparable energies. They can form intermediates with reactants and then return to their original state, offering a pathway with lower activation energy. Transition metals also adsorb reactants on their surfaces, increasing contact and weakening bonds. These features explain their good catalytic activity.

Step 5: (e) Relate colour to electronic transitions In many transition-metal compounds, the surrounding ligands split the metal ion's d orbitals into different energy levels. An electron can absorb

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state before counting d electrons: $+7$ gives d^0, while $+6$ gives d^1. Do not use colour alone to decide paramagnetism.

light of a suitable visible wavelength and move from a lower to a higher d level. The remaining transmitted or reflected light gives the observed complementary colour. This explains the general colour of compounds containing partially filled d subshells; d^0 and d^{10} ions do not undergo these d-d transitions.

Step 6: (f) Find the oxidation states and unpaired electrons Potassium is $+1$ and oxygen is -2. If x is the oxidation state of manganese, then

$$\begin{aligned} \mathrm{KMnO_4}: &\quad 1 + x + 4(-2) = 0, \quad x = +7, \\ \mathrm{K_2MnO_4}: &\quad 2 + x + 4(-2) = 0, \quad x = +6. \end{aligned}$$

Manganese is $[\mathrm{Ar}]3d^5 4s^2$. Thus Mn(VII) is $3d^0$, with no unpaired d electron, whereas Mn(VI) is $3d^1$, with one unpaired electron. Therefore $\mathrm{K_2MnO_4}$ is paramagnetic and $\mathrm{KMnO_4}$ is diamagnetic. The intense colour of permanganate is due to charge transfer, so colour alone cannot identify an unpaired electron.

Step 7: (g) Complete and check the reduction half-equation Each chromium atom is reduced from $+6$ to $+3$, so two chromium atoms gain a total of six electrons. The seven oxygen atoms form seven water molecules using the fourteen hydrogen ions:

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

Both sides contain two chromium atoms, seven oxygen atoms and fourteen hydrogen atoms. The total charge on the left is $-2 + 14 - 6 = +6$, equal to the charge of the two $\mathrm{Cr^{3+}}$ ions on the right.

Step 8: Conclusion The answers are: (a) zinc and $\mathrm{Zn^{2+}}$ have filled $3d^{10}$ subshells; (b) lanthanoid radii gradually decrease across the series; (c) electron removal from chromium is favoured by formation of a half-filled $3d^5$ ion and weaker effective attraction; (d) variable oxidation states, intermediate formation and adsorption promote catalysis; (e) visible-light absorption in d-d transitions commonly causes colour; (f) $\mathrm{K_2MnO_4}$ is paramagnetic because manganese has one unpaired electron; (g) the products are $\mathrm{2\,Cr^{3+} + 7\,H_2O}$. Any five of these may be attempted.

Quick Tip to Solve: For manganese oxyanions, calculate the oxidation state before counting d electrons: $+7$ gives d^0, while $+6$ gives d^1. Do not use colour alone to decide paramagnetism.