CBSE 12 Chemistry (56/4/3) Question Paper with Solutions

Time Allowed :3 hours	**Maximum Marks :**70	**Total questions :**33

General Instructions

Read the following instructions very carefully and strictly follow them :

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

(ii) This question paper is divided into five sections — Section A, B, C, D and E.

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

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

(v) Section C - questions number 22 to 28 are short answer type questions. Each q ype q question carries 8 marks.

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

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

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

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

(x) Use of calculators is not allowed.

1. The molar ionic conductivities of Al^{3+} and SO_4^{2-} are 189 S cm^2 mol^{-1} and 160 S cm^2 mol^{-1} respectively. The value of limiting molar conductivity of $Al_2(SO_4)_3$ will be:

(A) 198 S cm^2 mol^{-1}

(B) 858 S cm^2 mol^{-1}

(C) 588 S cm^2 mol^{-1}

(D) 891 S cm^2 mol^{-1}

Correct Answer: (B) 858 S cm^2 mol^{-1}

Solution: Step 1: The molar conductivity for $Al_2(SO_4)_3$ is the sum of the molar conductivities of Al^{3+} and SO_4^{2-}. Using the given data, the limiting molar conductivity can be calculated as:

$$\Lambda_m = 2 \times \Lambda_{Al^{3+}} + 3 \times \Lambda_{SO_4^{2-}} = 2 \times 189 + 3 \times 160 = 858\,\mathrm{S\ cm^2\ mol^{-1}}.$$

Quick Tip

When calculating the limiting molar conductivity, add the ionic conductivities of the individual ions in the compound, accounting for the number of ions per formula unit.

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2. Which of the following acids represents Vitamin C?

(A) Saccharic acid

(B) Gluconic acid

(C) Ascorbic acid

(D) Benzoic acid

Correct Answer: (C) Ascorbic acid

Solution: Vitamin C is chemically known as ascorbic acid ($C_6H_8O_6$). It is a water-soluble vitamin that plays an important role in the body as an antioxidant and in collagen synthesis. The other acids listed, such as saccharic acid, gluconic acid, and benzoic acid, do not represent Vitamin C.

Step 1: Ascorbic acid is widely known as Vitamin C. **Step 2:** It is essential for the proper functioning of the immune system and collagen formation.

Quick Tip

Ascorbic acid (Vitamin C) is an essential nutrient for humans, playing a role in tissue repair and antioxidant activity.

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3. Rosenmund reduction is used for the preparation of aldehydes. The catalyst used in this reaction is:

(A) Pd – $BaSO_4$

(B) Anhydrous $AlCl_3$

(C) Iron (III) oxide

(D) $HgSO_4$

Correct Answer: (A) Pd – $BaSO_4$

Solution: The Rosenmund reduction is used to reduce acyl chlorides (RCOCl) to aldehydes. The catalyst used in this reaction is palladium on barium sulfate (Pd – $BaSO_4$). The presence of barium sulfate acts as a poison to the catalyst, which prevents over-reduction to the corresponding alcohol, allowing the selective formation of the aldehyde.

Step 1: Palladium (Pd) is the catalyst that facilitates the reduction of acyl chlorides. **Step 2:** Barium sulfate ($BaSO_4$) is used to poison the palladium and prevent over-reduction.

Quick Tip

Rosenmund reduction requires Pd – $BaSO_4$ as the catalyst to selectively reduce acyl chlorides to aldehydes.

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4. From the elements of 3d series given below, which element shows the maximum number of oxidation states?

(A) Scandium

(B) Manganese

(C) Chromium

(D) Titanium

Correct Answer: (B) Manganese

Solution:

Manganese (Mn) has the highest number of oxidation states among the given elements of the 3d series. Manganese can exhibit oxidation states from $+2$ to $+7$ in its compounds, giving it a total of 7 possible oxidation states. These oxidation states include $+2, +3, +4, +5, +6, +7$, and sometimes 0 (in its elemental form).

- Scandium (Sc) shows a maximum oxidation state of $+3$,
- Chromium (Cr) shows a maximum oxidation state of $+6$,
- Titanium (Ti) shows a maximum oxidation state of $+4$.

Therefore, Manganese has the most oxidation states among the 3d transition elements in this group.

Quick Tip

Manganese exhibits the maximum number of oxidation states in the 3d transition series, ranging from $+2$ to $+7$.

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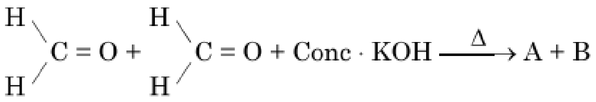
5. Consider the following reaction:



$$\mathrm{H_2C=O + H_2C=O + Conc \cdot KOH \xrightarrow{\Delta} A + B}$$

Identify A and B from the given options:

(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: The reaction described is a Formose reaction, where two molecules of formaldehyde (HCHO) react with concentrated KOH under heat to form methanol (CH_3OH) and potassium formate (HCOOK). The formose reaction typically involves the condensation of formaldehyde in the presence of an alkaline catalyst, producing methanol and potassium formate.

Step 1: Two molecules of formaldehyde undergo condensation. **Step 2:** Methanol and potassium formate are the expected products.

Quick Tip

The Formose reaction with formaldehyde and KOH produces methanol and potassium formate.

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6. Which alkyl halide from the given options will undergo S$_N$1 reaction faster?

(A) $(CH_3)_3C–Br$

(B) $(CH_3)_2CH–Br$

(C) $CH_3CH_2–Br$

(D) $(CH_3)_3C–CH_2–Br$

Correct Answer: (A) $(CH_3)_3C–Br$

Solution: S$_N$1 reactions are favored by the formation of a stable carbocation. Among the given options, $(CH_3)_3C–Br$ (tert-butyl bromide) forms a highly stable tertiary carbocation, making it the most reactive towards S$_N$1 reactions. The tertiary carbocation is more stable than the secondary or primary carbocations formed from the other alkyl halides.

Step 1: Stability of carbocations is crucial in S$_N$1 reactions. **Step 2:** Tertiary carbocations are the most stable, thus $(CH_3)_3C–Br$ undergoes the reaction faster.

Quick Tip

S$_N$1 reactions are favored by tertiary carbocations due to their stability.

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7. The fraction of molecules having energy equal to or greater than activation energy is:

(A) A

(B) $e^{-\frac{E_a}{RT}}$

(C) K

(D) $Ae^{-\frac{E_a}{RT}}$

Correct Answer: (B) $e^{-\frac{E_a}{RT}}$

Solution: The fraction of molecules with energy equal to or greater than the activation energy is given by the Arrhenius equation:

$$f = e^{-\frac{E_a}{RT}}$$

Quick Tip

The Arrhenius equation describes the fraction of molecules that have enough energy to overcome the activation energy barrier for a reaction to occur.

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8. Identify the primary amine from the given options:

(A) $C_2H_5NH_3$

(B) $(C_2H_5)_2NH$

(C) $C_2H_5NH_2$

(D) CH_3NH_2

Correct Answer: (C) $C_2H_5NH_2$

Solution: The primary amine contains one alkyl group attached to the nitrogen. Among the options, $C_2H_5NH_2$ (ethanamine) is the primary amine because it has one ethyl group attached to the nitrogen.

Quick Tip

A primary amine has one alkyl group attached to the nitrogen atom, whereas secondary and tertiary amines have two and three alkyl groups, respectively.

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9. The general electronic configuration of d-block elements is:

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

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

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

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

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

Solution: The general electronic configuration of d-block elements is $(n-1)d^{1-10}ns^{1-2}$, where n represents the principal quantum number, and the electrons fill the $(n-1)$ d-orbitals and the n s-orbitals.

Quick Tip

D-block elements fill the $(n-1)$ d-orbitals, and their electronic configuration follows the pattern $(n-1)d^{1-10}ns^{1-2}$.

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10. 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- (r) PCC Tribromophenol

IV. Dehydration of propan-2-ol to (s) Bromine water propene

(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: - The oxidation of primary alcohols to aldehydes is done using PCC Tribromophenol.

- Butan-2-one is reduced to Butan-2-ol using $NaBH_4$.
- Bromination of Phenol to 2, 4, 6-tribromophenol is done using Bromine water propene.
- Dehydration of propan-2-ol leads to propene when treated with 85% phosphoric acid at 440 K

Step 1: Match each reaction with its respective reagent.

Quick Tip

For oxidation reactions, $NaBH_4$ is commonly used, and for reduction reactions, phosphoric acid is often the reagent.

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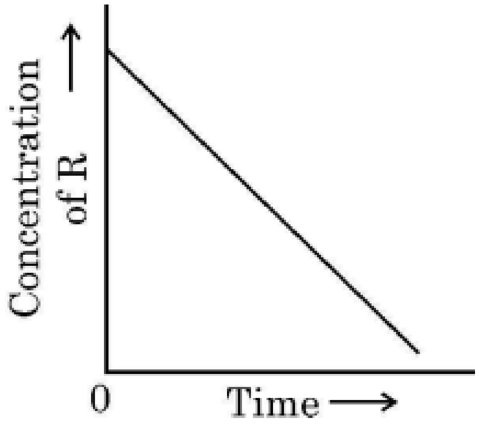
11. In a given graph of zero order reaction, the slope and intercept are:



(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:

For a zero-order reaction, the integrated rate law is given by:

$$[R] = [R]_0 - kt$$

Where:

- $[R]$ is the concentration of the reactant at time t,
- $[R]_0$ is the initial concentration of the reactant,
- k is the rate constant,
- t is the time.

The graph of $[R]$ vs. t is a straight line with a slope of $-k$ and an intercept of $[R]_0$.

Step 1: The slope of the line is the rate constant $-k$.

Step 2: The intercept is the initial concentration of the reactant $[R]_0$.

Quick Tip

For a zero-order reaction, the slope of the plot of [R] vs. time is –k, and the intercept is the initial concentration $[R]_0$.

12. Nucleophilic addition of Grignard reagent to ketones followed by hydrolysis with dilute acids forms:

(A) Alkene

(B) Primary alcohol

(C) Tertiary alcohol

(D) Secondary alcohol

Correct Answer: (C) Tertiary alcohol

Solution: The reaction of a Grignard reagent (RMgX) with a ketone results in the formation of a tertiary alcohol. The mechanism involves the nucleophilic attack of the Grignard reagent on the carbonyl carbon of the ketone, followed by hydrolysis to yield a tertiary alcohol. This is because the Grignard reagent adds a second alkyl group to the carbonyl carbon, resulting in a tertiary alcohol.

Step 1: Grignard reagent attacks the carbonyl carbon of the ketone to form a tetrahedral intermediate.

Step 2: Hydrolysis of the intermediate yields a tertiary alcohol.

Quick Tip

Grignard reagents add to the carbonyl carbon of ketones to form tertiary alcohols after hydrolysis.

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13. Assertion (A): Phenols are stronger acids than alcohols. Reason (R): Alkoxide ion is more stable than phenoxide ion.

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

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

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

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

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

Solution: The Assertion (A) is true because phenols are stronger acids than alcohols due to the ability of the phenoxide ion to stabilize the negative charge through resonance, whereas the alkoxide ion does not have such stabilization. The Reason (R) is false because the phenoxide ion is actually more stable than the alkoxide ion due to resonance stabilization in phenoxide.

Quick Tip

Phenols are stronger acids than alcohols because their conjugate base (phenoxide ion) is stabilized by resonance, whereas alkoxide ions lack this stabilization.

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14. Assertion (A): For a Daniell cell, Zn/Zn^{2+}(1M) —— Cu^{2+}(1M)/Cu with $E_{\text{cell}} = 1.1\,V$, 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.

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

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

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

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

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

Solution:

- Assertion (A) is correct because, in a Daniell cell, when the external opposing potential exceeds 1.1 V, the electron flow is reversed, causing electrons to flow from Cu to Zn.
- Reason (R) is false because a galvanic cell operates without an external opposing potential. A Daniell cell is a type of galvanic cell, but the external potential in this case is artificially introduced, which is not a typical condition for a galvanic cell.

Step 1: In a Daniell cell, electron flow is from the anode (Zn) to the cathode (Cu), but if an external voltage is applied, it can reverse the flow of electrons.

Step 2: A galvanic cell generates electrical energy spontaneously, but external voltages disrupt the normal flow.

Quick Tip

In a Daniell cell, if the external potential is greater than the cell potential, the direction of electron flow is reversed.

15. 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.

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

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

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

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

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

Solution:

- Assertion (A) is correct because benzoic acid does not undergo Friedel – Crafts reactions due to the deactivating effect of the carboxyl group.

- Reason (R) is also true. The carboxyl group (-COOH) is electron-withdrawing, which deactivates the aromatic ring, making it less reactive towards electrophilic substitution reactions, including Friedel – Crafts reactions.

Step 1: The carboxyl group in benzoic acid deactivates the aromatic ring and prevents the reaction with electrophiles.

Step 2: The catalyst, $AlCl_3$, is unable to bond with the deactivated ring for the Friedel – Crafts reaction to occur.

Quick Tip

Electron-withdrawing groups such as carboxyl groups deactivate the aromatic ring, preventing Friedel – Crafts reactions.

16. Assertion (A): Fructose is a reducing sugar.

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

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

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

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

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

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

Solution:

- Assertion (A) is true because fructose is a reducing sugar. It contains a carbonyl group in the form of a ketone, which can reduce Fehling's solution and Tollen's reagent under certain conditions.
- Reason (R) is false because fructose, being a reducing sugar, can reduce Tollen's reagent and Fehling's solution. The statement that fructose does not reduce these reagents is incorrect.

Step 1: Fructose, though a ketose, has reducing properties due to its ability to undergo isomerization into an aldose form.

Step 2: Fructose is a reducing sugar and can reduce Fehling's solution and Tollen's reagent.

Quick Tip

Fructose is a reducing sugar because it can isomerize to an aldose form, which is capable of reducing Tollen's and Fehling's solutions.

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17. Define the following terms:

(a) Half life period ($t_{1/2}$)

(b) Effective collisions

Solution: (a) Half-life period ($t_{1/2}$):

The half-life period is the time required for the concentration of a reactant to decrease to half of its initial value in a chemical reaction. For first-order reactions, the half-life period is constant and independent of the initial concentration. It is given by the formula:

$$t_{1/2} = \frac{\ln 2}{k}$$

where k is the rate constant of the reaction. For reactions of other orders, the half-life varies with concentration.

(b) Effective collisions:

Effective collisions are collisions between reacting particles that result in the formation of products. For a collision to be effective, two conditions must be met:

1. The molecules must collide with proper orientation, so that the reacting atoms can rearrange.
2. The molecules must collide with enough energy to overcome the activation energy barrier of the reaction. This energy is called the activation energy (E).

Only a small fraction of all collisions result in effective collisions, contributing to the rate of the reaction.

Quick Tip

The concept of effective collisions is crucial in understanding the rate of a reaction. Increasing temperature or concentration often increases the number of effective collisions, thus speeding up the reaction.

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18. A solution containing 60 g of a non-volatile solute in 250 g of water freezes at 270.67 K. Calculate the molar mass of the solute. (Kf of water = 1.86 K kg mol^{-1})

Solution: The freezing point depression (ΔT_f) is given by the formula:

$$\Delta T_f = T_f^{\text{pure solvent}} - T_f^{\text{solution}}$$

where $T_f^{\text{pure solvent}}$ is the freezing point of the pure solvent (water) and T_f^{solution} is the freezing point of the solution.

The freezing point of pure water is 273.15 K. Thus,

$$\Delta T_f = 273.15\,\text{K} - 270.67\,\text{K} = 2.48\,\text{K}$$

The freezing point depression is also related to the molality (m) of the solution:

$$\Delta T_f = K_f \times m$$

where K_f is the cryoscopic constant (given as 1.86 K kg mol^{-1}) and m is the molality of the solution.

Rearranging for molality:

$$m = \frac{\Delta T_f}{K_f} = \frac{2.48\,\text{K}}{1.86\,\text{K kg mol}^{-1}} = 1.33\,\text{mol kg}^{-1}$$

Molality is defined as the number of moles of solute per kilogram of solvent. Using the molality, we can calculate the number of moles of solute:

$m = \frac{molesofsolute}{kgofsolvent} \quad \Rightarrow \quad moles\ of\ solute = m \times kg\ of\ solvent = 1.33\,mol\ kg^{-}1 \times 0.250\,\text{kg} = 0.3325\,mol$

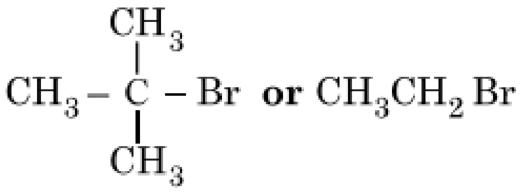
Now, the molar mass of the solute is given by:

$$\text{Molar mass} = \frac{\text{mass of solute}}{\text{moles of solute}} = \frac{60\,\text{g}}{0.3325\,\text{mol}} = 180\,\text{g mol}^{-1}$$

Quick Tip

When solving problems involving freezing point depression, remember to use the relationship $\Delta T_f = K_f \times m$, where molality (m) is the number of moles of solute per kilogram of solvent.

19(a). Which of the following compounds will react more rapidly by S_N1 reaction and why?



$CH_3-C(CH_3)_2-Br$ **or** CH_3CH_2Br

Solution: The first compound, $CH_3C\,Br$ (isopropyl bromide), will react more rapidly in an S_N1 reaction compared to CH_3CH_2Br (ethyl bromide). The key factor that influences this is the stability of the carbocation intermediate that is formed during the reaction.

In an S_N1 reaction, the reaction proceeds in two steps:

1. Formation of the carbocation: The leaving group (Br-) departs, forming a positively charged carbocation. 2. Nucleophilic attack: The nucleophile attacks the carbocation, leading to the formation of the product.

The rate-determining step in the S_N1 reaction is the formation of the carbocation. The more stable the carbocation, the faster the reaction proceeds. This is because a more stable carbocation is less likely to undergo side reactions and can form more easily.

- Isopropyl bromide ($\mathrm{CH_3C\,Br}$) forms a tertiary carbocation when the bromine leaves. Tertiary carbocations are highly stabilized due to two effects: - Inductive effect: The electron-donating nature of the two methyl groups (attached to the central carbon) helps stabilize the positive charge.
- Hyperconjugation: The overlapping of the bonds of the adjacent C-H or C-C groups with the empty p-orbital of the carbocation also provides stabilization.
- Ethyl bromide ($\mathrm{CH_3CH_2Br}$) forms a secondary carbocation when the bromine leaves. Secondary carbocations are less stable than tertiary carbocations because there is less electron donation from neighboring groups to stabilize the positive charge. The secondary carbocation does not benefit as much from inductive and hyperconjugation effects as the tertiary carbocation does.

Thus, the tertiary carbocation formed from isopropyl bromide is more stable than the secondary carbocation formed from ethyl bromide, making the S_N1 reaction faster in the case of isopropyl bromide.

Quick Tip

In S_N1 reactions, the rate of reaction increases with the stability of the carbocation. Tertiary carbocations are the most stable, followed by secondary, and primary carbocations are the least stable.

19(b) Arrange the following compounds in the increasing order of their boiling points:

Bromoform, Dibromomethane, Chloromethane, Bromomethane

Solution: Boiling points are influenced by the type of intermolecular forces present in the compound. The primary factors affecting boiling points are:

1. Molecular size: Larger molecules generally have higher boiling points due to increased Van der Waals forces.
2. Polarity: More polar molecules tend to have higher boiling points due to stronger dipole-dipole interactions.
3. Halogen substituent: The presence of more halogen atoms increases the boiling point due to the increase in molecular weight and the associated Van der Waals forces.

Let's examine the compounds:

- Chloromethane (CH_3Cl) has the lowest boiling point because chlorine is smaller and less electronegative than bromine, leading to weaker Van der Waals forces and dipole-dipole interactions.
- Bromomethane (CH_3Br) has a higher boiling point than chloromethane because bromine is larger, which increases the molecular size and leads to stronger Van der Waals forces. - Dibromomethane (CH_2Br_2) has an even higher boiling point due to the presence of two bromine atoms, which further increase the molecular size and intermolecular forces. - Bromoform $(CHBr_3)$ has the highest boiling point because it contains three bromine atoms, resulting in the largest molecular size and the strongest intermolecular forces.

Thus, the increasing order of boiling points is:

$$\text{Chloromethane} < \text{Bromomethane} < \text{Dibromomethane} < \text{Bromoform}$$

Quick Tip

In general, as the size of the halogen atom increases in a molecule, the boiling point increases due to stronger Van der Waals forces. Additionally, the more halogen atoms present, the higher the boiling point.

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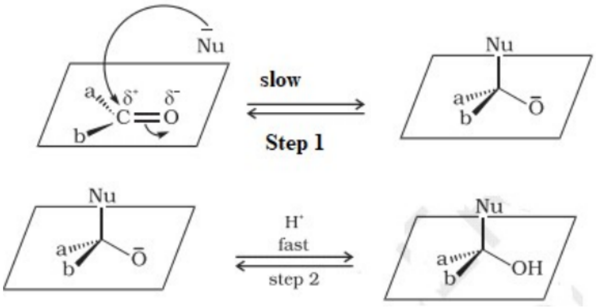
20. (a) Write the stepwise mechanism of nucleophilic addition reactions in the carbonyl compounds.

Solution: Nucleophilic addition reactions occur when a nucleophile attacks the electrophilic carbonyl carbon in aldehydes or ketones. The general mechanism is as follows:

Step 1: The nucleophile (e.g., a hydride ion, alkoxide, or Grignard reagent) attacks the carbonyl carbon of the aldehyde or ketone, breaking the double bond and forming a tetrahedral intermediate.

Step 2: The intermediate is protonated (usually by a water molecule or proton donor) to form the final addition product. For example, if the nucleophile is a hydride (H^-), the product will be an alcohol.

Step 3: The product after protonation is a carbonyl addition product, such as an alcohol.



Quick Tip

In nucleophilic addition reactions, the nucleophile adds to the electrophilic carbonyl carbon, forming a tetrahedral intermediate that is protonated to yield the product.

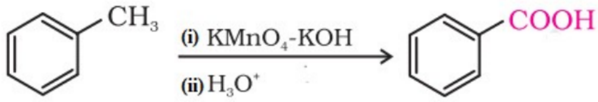
(b) How will you convert the following?

(i) Toluene to benzoic acid.

(ii) Ethanol to 3-Hydroxybutanal.

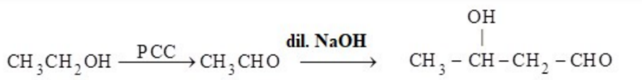
Solution: (i) Toluene to Benzoic acid:

Toluene ($C_6H_5CH_3$) can be oxidized to benzoic acid (C_6H_5COOH) using strong oxidizing agents such as potassium permanganate ($KMnO_4$) or chromic acid (H_2CrO_4). These reagents will oxidize the methyl group ($-CH_3$) into a carboxyl group ($-COOH$), converting toluene into benzoic acid.



(ii) Ethanol to 3-Hydroxybutanal:

Ethanol (CH_3CH_2OH) can be oxidized to acetaldehyde (CH_3CHO) by using an oxidizing agent like PCC (Pyridinium chlorochromate) or mild oxidizers. The acetaldehyde then undergoes a nucleophilic addition with a Grignard reagent (like CH_3MgBr) to form the intermediate 3-hydroxybutanal.



$$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow{\text{dil. NaOH}} CH_3-\overset{OH}{CH}-CH_2-CHO$$

Quick Tip

Toluene can be oxidized using strong oxidizing agents to form benzoic acid, while ethanol can be oxidized to acetaldehyde, which then reacts to form 3-hydroxybutanal.

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

Solution:

When glucose reacts with HI, the reaction produces an alkyl iodide. The hydroxyl group (-OH) of glucose is replaced by iodine. The reaction mechanism involves the cleavage of the -OH group and its substitution with iodine.

$$C_6H_{12}O_6 \xrightarrow{HI} C_6H_{12}I + H_2O$$

Thus, glucose undergoes substitution with iodine, forming an alkyl iodide.

Quick Tip

HI reacts with glucose by replacing the hydroxyl group (-OH) with iodine, forming an alkyl iodide.

21(b) Write one structural difference between DNA and RNA.

Solution: One key structural difference between DNA and RNA lies in the sugar component of their nucleotides:

- DNA (Deoxyribonucleic acid) contains the sugar deoxyribose, which has a hydrogen atom (-H) attached to the 2’ carbon atom of the sugar ring. This absence of an -OH group at the 2’ position is where the name ”deoxyribo-” comes from, signifying ”lacking oxygen.”
- RNA (Ribonucleic acid), on the other hand, contains the sugar ribose, which has a hydroxyl group (-OH) attached to the 2’ carbon atom of the sugar ring.

This structural difference, where DNA contains deoxyribose and RNA contains ribose, is significant because it affects the stability and function of these molecules. The presence of the -OH group in RNA makes it more reactive and less stable than DNA, which is crucial for RNA's role in protein synthesis and other cellular processes where it is required to be more transient.

Quick Tip

The presence of the -OH group in ribose (RNA) makes RNA more prone to hydrolysis, leading to its relatively short lifespan compared to DNA, which is more stable due to the lack of the -OH group at the 2' carbon.

---

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

$$[\mathrm{Pt(NH_3)_2Cl_2}]^{2+}$$

Solution: The complex $[Pt(NH_3)_2Cl_2]^{2+}$ consists of platinum (Pt) as the central metal ion, two ammonia (NH_3) ligands, and two chloride (Cl^-) ligands. This is a square planar complex (since Pt^{2+} is a d^8 ion and typically forms square planar complexes). The two chloride ligands can be arranged in different ways, leading to two possible geometrical isomers:

1. Cis-isomer: In this isomer, the two chloride ions are adjacent to each other (i.e., positioned at 90° to each other), which results in a square planar arrangement where both chloride ions are next to each other. The two ammonia ligands will be on opposite sides of the complex.

$$\text{Cis-}[Pt(NH_3)_2Cl_2]^{2+}$$

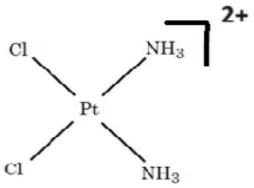
In this form, the chloride ions are placed next to each other in a cis position.

2. Trans-isomer: In this isomer, the two chloride ions are positioned opposite each other (i.e., 180° apart). The ammonia ligands will be adjacent to the chloride ions, forming a linear arrangement.

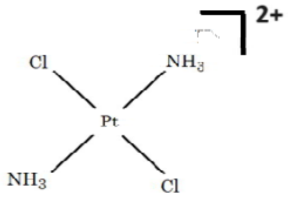
$$\text{Trans-}[Pt(NH_3)_2Cl_2]^{2+}$$

In this form, the chloride ions are placed on opposite sides in a trans position.

These two isomers arise because the ligands are free to rotate about the central metal ion in square planar complexes, which allows them to adopt different spatial arrangements.



Cis isomer



trans isomer

Quick Tip

In coordination complexes, cis and trans isomerism occurs due to different spatial arrangements of ligands around the central metal ion.

(b) Write the electronic configuration of the d^5 ion if $\Delta_0 < P$.

Solution: The electronic configuration of a d^5 ion is influenced by the splitting of the d-orbitals in an octahedral field. In an octahedral crystal field, the five degenerate d-orbitals split into two sets:

- The lower-energy t_{2g} orbitals (which are of lower energy due to the ligand field splitting).
- The higher-energy e_g orbitals (which are of higher energy due to the repulsion from the ligands).

The splitting energy between the two sets of orbitals is represented by Δ_0, and the pairing energy of electrons is denoted by P. If $\Delta_0 < P$ (i.e., the splitting energy is less than the pairing energy), the complex will adopt a high-spin configuration, meaning that the electrons will occupy all the orbitals before any pairing occurs.

For a d^5 configuration with $\Delta_0 < P$, the electronic configuration is:

$$t_{2g}^3 e_g^2$$

In this configuration:

- The three electrons will fill the lower-energy t_{2g} orbitals (3 electrons in 3 orbitals).
- The two remaining electrons will fill the higher-energy e_g orbitals (2 electrons in 2 orbitals).

This configuration corresponds to the high-spin state, which is typical when Δ_0 is smaller than the pairing energy.

Quick Tip

When $\Delta_0 > P$, electrons prefer to pair in the lower-energy t_{2g} orbitals, leading to low-spin configurations.

(c) What is an ambidentate ligand?

Solution: An ambidentate ligand is a ligand that can bind to a metal center through two different donor atoms. The ligand has more than one donor atom, and depending on the reaction conditions, the ligand can attach to the metal through one donor atom or another. The donor atoms are typically different atoms with lone pairs of electrons that can coordinate with the metal ion.

For example: - Thiocyanate (SCN^-) is an ambidentate ligand because it can coordinate through either the sulfur (S) atom or the nitrogen (N) atom.

- When it binds through sulfur, it forms a thiol (S) complex.
- When it binds through nitrogen, it forms a nitrile (N) complex.

Similarly, the cyanate ion (OCN^-) can also act as an ambidentate ligand, coordinating through either the oxygen or the nitrogen atom.

The ability of ambidentate ligands to bind via different donor atoms can lead to different isomeric forms of the complex, and this ability plays a crucial role in the chemistry of coordination compounds.

Quick Tip

Ambidentate ligands can lead to structural isomerism depending on which donor atom is used to bind to the metal. This feature is important in the study of coordination chemistry and the formation of isomers.

23. 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

Solution: (a) Hydroboration – Oxidation reaction:

The hydroboration-oxidation of an alkene results in an alcohol. In this reaction, alkene ($CH_3CH=CH_2$) undergoes hydroboration with diborane (B_2H_6), followed by oxidation with hydrogen peroxide to form an alcohol. The reaction is as follows:

$$\mathrm{CH_3CH = CH_2} + B_2H_6 \xrightarrow{\mathrm{H_2}O_2} \mathrm{CH_3CH_2OH}$$

Here, the alkene is converted to the alcohol with anti-Markovnikov addition.

(b) Williamson Synthesis:

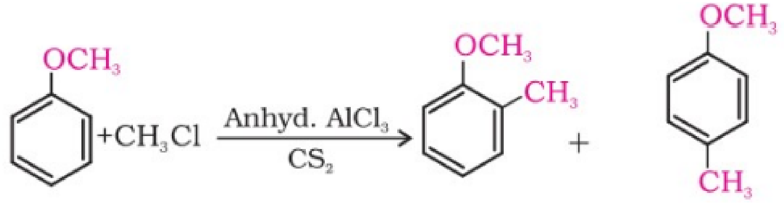
The Williamson synthesis involves the reaction of an alkoxide ion with an alkyl halide to form an ether. The general reaction is:

$$R\text{-}X + \mathrm{R'O^-} \rightarrow R\text{-}R' + \mathrm{Na}X$$

Where R-X is the alkyl halide, R'-O$^-$ is the alkoxide ion, and R-R' is the ether product.

(c) Friedel-Crafts Alkylation of Anisole:

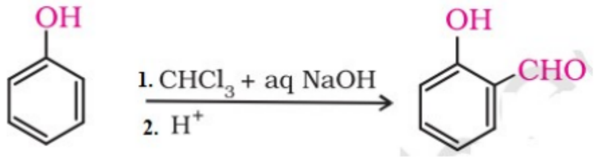
In Friedel-Crafts alkylation, anisole ($C_6H_5OCH_3$) reacts with an alkyl halide (CH_3Cl) in the presence of $AlCl_3$ catalyst to form an alkylated product. The reaction is as follows:



Here, the methyl group is added to the aromatic ring, forming methyl anisole.

(d) Reimer-Tiemann Reaction:

The Reimer-Tiemann reaction involves the reaction of phenol (C_6H_5OH) with chloroform ($CHCl_3$) in the presence of aqueous NaOH, followed by acidification to form salicylaldehyde ($C_7H_6O_2$). The reaction is as follows:



Here, the formyl group (-CHO) is introduced to the phenol to form salicylaldehyde.

Quick Tip

These reactions are classic organic transformations. Hydroboration-oxidation adds alcohol across alkenes, Williamson synthesis forms ethers, Friedel-Crafts alkylation alkylates aromatic rings, and Reimer-Tiemann introduces a formyl group to phenol.

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

(i) Phenol and Benzoic acid

(ii) Propanal and Propanone

Solution: (i) Phenol and Benzoic acid:

- To distinguish phenol and benzoic acid, add neutral $FeCl_3$.
- Phenol: When neutral $FeCl_3$ is added to phenol, a violet color complex is formed due to the coordination of the Fe^{3+} ion with the oxygen of the phenol's hydroxyl group.
- Benzoic acid: Benzoic acid, which is a carboxylic acid, does not form a complex with $FeCl_3$, hence no color change is observed.
- Alternatively, you can add bromine water to each compound:
- Phenol: Phenol reacts with bromine water to form 2,4,6-tribromophenol, a white precipitate.
- Benzoic acid: Benzoic acid does not react with bromine water.

(ii) Propanal and Propanone:

- Tollens' reagent: This reagent is a mild oxidizer used to distinguish aldehydes from ketones. Propanal, being an aldehyde, will reduce Tollens' reagent to silver metal, which forms a silver mirror.
- Propanone: Propanone, a ketone, does not react with Tollens' reagent. Hence, no silver mirror will form.
- Fehling's solution: This is another test to distinguish between aldehydes and ketones.
- Propanal: It will reduce Fehling's solution, which contains Cu^{2+} ions, to a red precipitate of Cu_2O.
- Propanone: Being a ketone, it will not reduce Fehling's solution, and no precipitate will form.

Quick Tip

For distinguishing phenol and benzoic acid, $FeCl_3$ is used to form a violet color with phenol. For distinguishing aldehydes from ketones, Tollens' and Fehling's reagents are useful.

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

$CH_2FCH_2CH_2COOH$ or CH_3CHFCH_2COOH

Solution: The compound CH_3CHFCH_2COOH is the stronger acid. This is because:

- The fluorine atom in CH_3CHFCH_2COOH is more electronegative than hydrogen and pulls electron density away from the carboxyl group (-COOH) through the inductive effect. This results in the stabilization of the conjugate base (carboxylate anion, $RCOO^-$), making the release of a proton (H^+) easier, thus increasing the acidity.

- In contrast, $CH_2FCH_2CH_2COOH$ has the fluorine atom further from the carboxyl group, resulting in a weaker electron-withdrawing effect. Therefore, the carboxyl group is less stabilized, making $CH_2FCH_2CH_2COOH$ a weaker acid than CH_3CHFCH_2COOH.

Quick Tip

Fluorine is a highly electronegative element. The closer it is to the carboxyl group, the stronger the acid due to the electron-withdrawing inductive effect.

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25. 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.

Solution: The integrated rate law for a first-order reaction is:

$$\ln\left(\frac{[R_0]}{[R]}\right) = kt$$

Where:

- $[R_0]$ is the initial concentration,

- $[R]$ is the concentration at time t,

- k is the rate constant,

- t is the time.

Step 1: For 99.9

$$\ln\left(\frac{[R_0]}{0.1[R_0]}\right) = kt_{99.9\%}$$

$$\ln 10 = kt_{99.9\%}$$

$$t_{99.9\%} = \frac{2.303}{k}\log 10 = \frac{2.303}{k}$$

Step 2: For half-life $t_{1/2}$, $[R] = 0.5[R_0]$, so:

$$\ln\left(\frac{[R_0]}{0.5[R_0]}\right) = kt_{1/2}$$

$$\ln 2 = kt_{1/2}$$

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

Step 3: Now, dividing the two expressions:

$$\frac{t_{99.9\%}}{t_{1/2}} = \frac{\frac{2.303}{k}}{\frac{2.303\times 0.3010}{k}} = \frac{1}{0.3010} = 10$$

Final Answer: The time required for 99.9% completion is 10 times the half-life of the reaction.

Quick Tip

For first-order reactions, the time for 99.9% completion is approximately 10 times the half-life ($t_{1/2}$).

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26. Define the following terms:

(a) Glycosidic linkage

(b) Primary structure of protein

(c) Disaccharides

Solution:

(a) Glycosidic linkage: A glycosidic linkage is a covalent bond formed between two monosaccharide units. This bond forms through a dehydration reaction, in which a water molecule is removed when a hydroxyl group from one monosaccharide reacts with the anomeric carbon (the carbon that was part of the carbonyl group in the monosaccharide) of another monosaccharide. The bond formed between the two sugars is typically between the

1st carbon of one sugar and the hydroxyl group attached to another carbon in the second sugar. For example, in disaccharides like sucrose, glucose and fructose are joined by a glycosidic bond.

(b) Primary structure of protein: The primary structure of a protein refers to the unique sequence of amino acids that are linked by peptide bonds to form a polypeptide chain. This sequence is encoded by the genetic information in DNA and determines the specific characteristics of the protein. The primary structure is essential because it dictates how the protein will fold into its higher-order structures (secondary, tertiary, and quaternary structures), ultimately determining its function. A single change in the amino acid sequence can result in a dysfunctional protein, as seen in various genetic disorders like sickle cell anemia.

(c) Disaccharides: Disaccharides are carbohydrates composed of two monosaccharide units that are bonded together by a glycosidic linkage. Common disaccharides include sucrose (table sugar), which is composed of glucose and fructose, and lactose (milk sugar), which consists of glucose and galactose. Disaccharides are important in energy storage and transport. Upon hydrolysis, disaccharides break down into their component monosaccharides, which can then be used by the body for energy.

Quick Tip

The primary structure of a protein is the sequence of amino acids in the polypeptide chain. This sequence directly influences how the protein will fold and function.

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

$$\mathrm{CH_2 = CH - CH_2 - CH_2 - Cl}$$

Solution: The given compound is a simple organic molecule with a chlorine atom attached to a carbon chain. The molecule contains a double bond between the first and second carbon atoms, and a chlorine atom attached to the third carbon.

- The molecule contains four carbon atoms, so it is based on the butane chain (C_4).

- The double bond between the first and second carbon atoms means the name should include ”ene” to indicate the presence of a double bond.
- The chlorine atom is attached to the third carbon, so the prefix ”4-chloro” indicates the position of the chlorine.

Thus, the IUPAC name of the compound is 4-chlorobut-1-ene.

(b) Why is thionyl chloride preferred for preparing alkyl halides from alcohols?

Solution: Thionyl chloride (SOCl) is commonly used for converting alcohols to alkyl chlorides because it offers several advantages:

1. High efficiency: Thionyl chloride reacts with alcohols to form alkyl chlorides in high yield, with minimal side reactions.
2. Volatile by-products: The by-products of the reaction, sulfur dioxide (SO) and hydrogen chloride (HCl), are gaseous, making them easy to remove from the reaction mixture. This reduces the need for further purification steps.
3. Mild reaction conditions: The reaction can be performed under relatively mild conditions, often requiring only a solvent (such as pyridine) and moderate temperatures. This makes it more convenient than some other chlorinating reagents that may require harsher conditions.

Thionyl chloride is particularly preferred for sensitive alcohols or when a clean conversion to alkyl chloride is desired.

(c) What happens when methyl bromide reacts with KCN?

Solution: When methyl bromide (CH_3Br) reacts with potassium cyanide (KCN), a nucleophilic substitution reaction occurs. The cyanide ion (CN^-) from KCN acts as a nucleophile and attacks the electrophilic carbon atom in methyl bromide, which is attached to the bromine atom. This leads to the displacement of the bromine atom, resulting in the formation of methyl cyanide (CH_3CN), also known as acetonitrile.

The reaction proceeds via the S_N2 mechanism, where the cyanide ion directly displaces the bromine atom in a single step, producing the product without any intermediate formation of carbocations.

The overall reaction is:

$$CH_3Br + KCN \rightarrow CH_3CN + KBr$$

Quick Tip

When methyl bromide reacts with KCN, it undergoes an S_N2 substitution to form methyl cyanide (CH_3CN), which is a useful organic compound in synthesis.

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28. 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°(Sn^{2+}/Sn) = -0.14 V, E° H$^+$/H$_2$ = 0.00 V (log 10 = 1)

Solution: We are given the following data:

- The cell consists of two half-reactions:

1. $\text{Sn}^{2+} + 2e^- \rightarrow$ Sn with $E^\circ = -0.14\,\text{V}$

2. $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ with $E^\circ = 0.00\,\text{V}$

- Concentration of Sn^{2+} = 0.001 M

- Concentration of H$^+$ = 0.01 M

- Standard pressure for H$_2$ = 1 bar

Step 1: Write the Nernst equation for the cell:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n}\log Q$$

Where:

- $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$

- n is the number of electrons transferred (in this case, $n = 2$).

- Q is the reaction quotient, which is calculated as:

$$Q = \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

Substitute the given values:

$$Q = \frac{0.001}{(0.01)^2} = \frac{0.001}{0.0001} = 10$$

Step 2: Calculate the standard cell potential E°_{cell}:

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

Step 3: Apply the values to the Nernst equation:

$$E_{\text{cell}} = 0.14\,\text{V} - \frac{0.0592}{2}\log 10$$

Since $\log 10 = 1$, we get:

$$E_{\text{cell}} = 0.14\,\text{V} - \frac{0.0592}{2} \times 1$$

$$E_{\text{cell}} = 0.14\,\text{V} - 0.0296\,\text{V} = 0.1104\,\text{V}$$

Final Answer: The emf of the cell at 25°C is $E_{\text{cell}} = 0.1104\,\text{V}$.

Quick Tip

Use the Nernst equation to calculate the emf of electrochemical cells, considering concentrations and standard electrode potentials.

---

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:

(a) What is the function of a salt bridge in a galvanic cell?

Solution:

Function of a salt bridge in a galvanic cell:

The salt bridge allows the flow of ions between the two half-cells, which maintains electrical neutrality. Without the salt bridge, the flow of electrons in the external circuit would stop as the charges would accumulate in the solutions, thus preventing the redox reactions from continuing. It completes the circuit and ensures the flow of charge, allowing the electrochemical reactions to continue.

Quick Tip

A salt bridge maintains electrical neutrality in the galvanic cell by allowing ions to flow between the two half-cells.

(b) When does a galvanic cell behave like an electrolytic cell?

Solution: A galvanic cell behaves like an electrolytic cell when an external potential greater than the emf (E_{cell}) is applied to the system. This causes the reverse of the natural spontaneous reaction, i.e., a non-spontaneous reaction occurs. In this situation, the cell starts to consume electrical energy rather than produce it. The external voltage must exceed the cell's electromotive force ($E_{\text{ext}} > E_{\text{cell}}$) for the reaction to reverse.

Quick Tip

When $E_{\text{ext}} > E_{\text{cell}}$, a galvanic cell behaves like an electrolytic cell, and the electrochemical reaction is driven in reverse.

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

Solution: To determine if copper sulphate solution can be stored in a pot made of zinc, we need to calculate the E°_{cell} for the cell. The E°_{cell} is given by:

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}$$

Substituting the given values:

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

Since E°_{cell} is positive ($+1.10\,\text{V}$), the reaction will proceed spontaneously, with zinc being oxidized and copper being reduced. This means that copper sulphate solution cannot be stored in a pot made of zinc because zinc will react with the copper ions in the solution, causing zinc to dissolve and copper to deposit on the surface.

Quick Tip

A positive E°_{cell} indicates that the reaction is spontaneous, so zinc will be oxidized in the presence of copper ions, making copper sulphate unsuitable for storage in a zinc pot.

OR

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

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

(ii) 1 mol of H_2O to O_2

Solution: To calculate the charge required, we use Faraday's first law of electrolysis, which states that one mole of electrons corresponds to 1 Faraday (F) of charge, and the amount of charge required for a reaction depends on the number of moles of electrons involved in the reaction.

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

The reaction for the reduction of MnO_4^- to Mn^{2+} involves 5 electrons, so the charge required is:

$$\text{Charge} = 5 \times F = 5F$$

(ii) 1 mol of H_2O to O_2:

The reaction for the oxidation of H_2O to O_2 involves 2 electrons, so the charge required is:

$$\text{Charge} = 2 \times F = 2F$$

Quick Tip

Faraday's law relates the charge passed through a solution to the amount of substance decomposed or deposited. The number of electrons involved in a reaction determines the total charge required.

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 hybridize 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 hybridization 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:

(a) Predict whether $[CoF_6]^{3-}$ **is diamagnetic or paramagnetic and why?**

$[Atomic\ \ number : Co = 27]$

Solution:

(a) Paramagnetic or Diamagnetic Nature of $[CoF_6]^{3-}$**:**

To predict whether $[CoF_6]^{3-}$ is paramagnetic or diamagnetic, let's look at the electronic configuration of Co^{3+}. The electronic configuration of Co is $[Ar]\,3d^7\,4s^2$. For Co^{3+}, the electrons are removed from the 4s and 3d orbitals, leaving the configuration $3d^6$. In the case of $[CoF_6]^{3-}$, fluorine is a weak field ligand and does not cause pairing of the electrons. Therefore, the 6 electrons in the $3d$ orbitals remain unpaired, making $[CoF_6]^{3-}$ paramagnetic.

Step 1: Determine the electron configuration of Co^{3+}

$$Co^{3+} : 3d^6$$

Step 2: The presence of unpaired electrons in the $3d$ orbitals means that the complex is paramagnetic.

Quick Tip

A complex is paramagnetic if it contains unpaired electrons in its metal's d-orbitals. If all electrons are paired, it is diamagnetic.

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

Solution: The coordination number of a metal in a coordination complex is determined by the number of ligand atoms directly bonded to the metal ion. In $[Co(en)_2Cl_2]^+$, ethylenediamine (en) is a bidentate ligand, meaning each en ligand forms two bonds with the metal. Chloride (Cl) is a monodentate ligand, forming one bond with the metal. Therefore, the total coordination number is:

$$\text{Coordination number} = 2 \times 2\,(\text{from two en ligands}) + 2\,(\text{from two Cl ligands}) = 6$$

Quick Tip

The coordination number is determined by counting the number of bonds formed between the metal and the ligands. Bidentate ligands contribute two bonds.

---

c(i) Write the IUPAC name of the given complex:

$[Pt(NH_3)_2Cl_2]^{2+}$

Solution:

In this complex, platinum (Pt) is the central metal ion, and it is surrounded by two ammonia (NH_3) ligands and two chloride (Cl^-) ligands. According to IUPAC nomenclature:

- Ammonia is a neutral ligand and is named as "ammine."
- Chloride is an anionic ligand and is named as "chloro."
- The metal ion (platinum) is named first, followed by the ligands in alphabetical order.

The IUPAC name of the complex is:

$$\text{Diamminedichloroplatinum(IV)\,ion}$$

Step 1: Identify the ligands and their names (ammine and chloro).

Step 2: Name the metal and its oxidation state (Pt(IV)).

Step 3: Put the ligands and metal together following IUPAC naming rules.

Quick Tip

In IUPAC naming, the ligands are named alphabetically before the metal, and the oxidation state of the metal is indicated in parentheses.

---

c(ii) Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital or outer orbital complex.

Solution: The complex $[Co(NH_3)_6]^{3+}$ involves the coordination of six ammine (NH_3) ligands to a Co^{3+} ion. For Co^{3+} (with electron configuration $3d^6$), the hybridization occurs using the inner $3d$, $4s$, and $4p$ orbitals, as NH_3 is a weak field ligand and does not cause significant pairing of electrons. Therefore, the complex uses the inner d-orbitals for hybridization and is considered an inner orbital complex.

Step 1: Consider the electron configuration of Co^{3+} and the ligands involved.

Step 2: Since NH_3 is a weak field ligand, Co^{3+} does not undergo pairing, and the metal uses its inner orbitals for hybridization.

Quick Tip

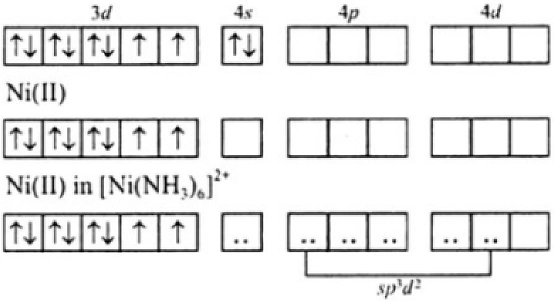
Inner orbital complexes form when the metal ion uses lower energy d-orbitals for bonding. Outer orbital complexes use higher energy d-orbitals.

OR

(c) Using valence bond theory, deduce the shape and hybridisation of $[Ni(NH_3)_6]^{2+}$

$[Atomic\ number\ of\ Ni = 28]$

Solution: For $[Ni(NH_3)_6]^{2+}$, the coordination number is 6, and the ligand is ammine (NH_3), which is a weak field ligand. Thus, the metal ion, Ni^{2+}, will undergo octahedral hybridization using $3d$, $4s$, and $4p$ orbitals. Since the coordination number is 6, the complex must have an octahedral shape.



Step 1: The Ni^{2+} ion has the electron configuration $3d^8 4s^2$, and upon losing two electrons, it forms Ni^{2+} with $3d^8$.

Step 2: The Ni^{2+} ion uses its $3d$, $4s$, and $4p$ orbitals to form six hybrid orbitals, leading to an octahedral shape.

Step 3: The hybridization of the Ni^{2+} ion is sp^3d^2, and the complex adopts an octahedral shape.

Quick Tip

For a coordination number of 6, the complex adopts an octahedral shape with sp^3d^2 hybridization.

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31. (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.

Solution:

Step 1: Identify the structure of 'A' (C_7H_7ON):

The molecular formula C_7H_7ON suggests the compound is a derivative of an amide. A common structure that fits this molecular formula is benzamide ($C_6H_5CONH_2$), which contains a benzene ring attached to a carboxamide group.

Step 2: Hoffmann Bromamide degradation reaction:

In this reaction, benzamide (A) undergoes a degradation when treated with bromine in the presence of alkali (usually NaOH) to give a primary amine. The reaction leads to the loss of one carbon atom from the amide.

- The product 'B' is aniline ($C_6H_5NH_2$), formed after the elimination of CO_2 from the amide group.

$$C_6H_5CONH_2 \xrightarrow{Br_2/NaOH} C_6H_5NH_2 \quad \text{(Aniline)}$$

Step 3: Reaction of 'B' with nitrous acid:

When aniline (B) reacts with nitrous acid (HNO_2) at 273-278 K, it undergoes diazotization followed by deamination to form a phenol derivative.

- The product 'C' is phenol (C_6H_5OH).

$$C_6H_5NH_2 + HNO_2 \rightarrow C_6H_5OH + N_2 \text{ (gas)}$$

Step 4: Reaction of 'B' with chloroform and ethanolic potassium hydroxide:

When aniline (B) is treated with chloroform ($CHCl_3$) and ethanolic potassium hydroxide (KOH), it undergoes the Carbylamine reaction, which produces an isocyanide (or isothiocyanate).

- The product 'D' is phenyl isocyanide (C_6H_5NC).

$$C_6H_5NH_2 + CHCl_3 + KOH \rightarrow C_6H_5NC + KCl + H_2O$$

Step 5: Reaction of 'C' with ethanol:

When phenol (C) reacts with ethanol, it undergoes etherification to form an ethoxy group attached to the benzene ring.

- The product 'E' is ethyl phenyl ether ($C_6H_5OCH_2CH_3$).

$$C_6H_5OH + C_2H_5OH \xrightarrow{HCl} C_6H_5OCH_2CH_3$$

Quick Tip

Hoffmann Bromamide degradation removes the carbonyl group from amides, forming amines. Diazotization of amines with nitrous acid yields phenol derivatives. Carbylamine reaction with chloroform forms isocyanides.

OR

(b) (i) What is Hinsberg's reagent?

Solution: Hinsberg's reagent is benzenesulfonyl chloride ($C_6H_5SO_2Cl$), which is used to differentiate between primary, secondary, and tertiary amines. The reagent reacts with primary amines to form sulfonamides, with secondary amines to form N-alkyl sulfonamides, and with tertiary amines, no reaction occurs due to the lack of an available hydrogen atom for reaction. This test helps distinguish between the different classes of amines.

Quick Tip

Hinsberg's reagent is used to differentiate between primary, secondary, and tertiary amines based on their reactions with the sulfonyl chloride group.

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

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

Solution:

The basic strength of amines in the gaseous phase is determined by the availability of the lone pair of electrons on nitrogen for protonation. The steric and inductive effects of the alkyl groups also influence the basicity.

1. Ethylamine ($C_2H_5NH_2$): This is a simple primary amine where the lone pair on nitrogen is available for protonation.

2. Diethylamine $(C_2H_5)_2NH$: This is a secondary amine. The basicity of secondary amines is lower than primary amines because the nitrogen's lone pair is partially sterically hindered by the two ethyl groups, making it less available for protonation.

3. Triethylamine $(C_2H_5)_3N$: This is a tertiary amine, and the nitrogen atom in tertiary amines is even more sterically hindered than in secondary amines. Furthermore, the inductive effect of the three ethyl groups reduces the availability of the nitrogen lone pair, lowering the basicity further.

Hence, the order of basicity in the gaseous phase is:

$$C_2H_5NH_2 > (C_2H_5)_2NH > (C_2H_5)_3N$$

This indicates that ethylamine is the strongest base, followed by diethylamine, and triethylamine being the weakest.

Quick Tip

Aromatic groups withdraw electron density, reducing basicity, while alkyl groups donate electron density, increasing basicity.

(ii) Give reasons for the following:

(1) Methyl amine is more basic than aniline.

Solution: Methylamine (CH_3NH_2) is more basic than aniline ($C_6H_5NH_2$) because the methyl group is an electron-donating group. It increases the electron density on the nitrogen atom, making it more available to accept a proton. In contrast, the phenyl group in aniline is electron-withdrawing through resonance, decreasing the electron density on the nitrogen atom and thus reducing its basicity.

Step 1: Methyl group donates electrons, increasing basicity.

Step 2: Phenyl group withdraws electrons, decreasing basicity.

Quick Tip

Electron-donating groups (like methyl) increase basicity, while electron-withdrawing groups (like phenyl) decrease basicity.

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

Solution: Aniline reacts with bromine water in an electrophilic aromatic substitution reaction. The amino group (-NH_2) in aniline is an electron-donating group, which activates the benzene ring towards electrophilic substitution. The bromine molecules attack the ortho and para positions relative to the amino group, resulting in the formation of 2, 4, 6-tribromoaniline.

Step 1: Amino group donates electrons to the ring, making it more reactive.

Step 2: Bromine undergoes electrophilic substitution at the activated positions.

Quick Tip

Electron-donating groups like -NH_2 activate the aromatic ring towards electrophilic substitution, leading to products like 2, 4, 6-tribromoaniline.

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(3) Primary amines have higher boiling points than tertiary amines.

Solution: Primary amines have higher boiling points than tertiary amines due to the ability to form hydrogen bonds. In primary amines, the nitrogen atom has a hydrogen atom attached, allowing for hydrogen bonding between molecules. Tertiary amines, on the other hand, do not have a hydrogen atom on the nitrogen, so they cannot form hydrogen bonds as efficiently, leading to lower boiling points.

Step 1: Primary amines form hydrogen bonds, increasing boiling point.

Step 2: Tertiary amines cannot form hydrogen bonds, leading to lower boiling points.

Quick Tip

Hydrogen bonding increases boiling point. Primary amines have higher boiling points than tertiary amines due to the presence of hydrogen atoms on the nitrogen.

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32. Attempt any five of the following:

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

Solution: Zinc is not regarded as a transition element because it does not have an incomplete d-orbital in its ground state or any of its common oxidation states. The electronic configuration of zinc is $[Ar]\,3d^{10}4s^2$, and in its most stable oxidation state of $+2$, the configuration becomes $[Ar]\,3d^{10}$, which is a fully filled d-orbital. For an element to be considered a transition metal, it must have at least one incomplete d-orbital in either its ground state or common oxidation states. Zinc, therefore, does not exhibit the typical characteristics of transition metals such as variable oxidation states and colored complexes.

Quick Tip

Transition metals typically have an incomplete d-orbital in their ground or common oxidation states, which is not the case for zinc.

(b) What is Lanthanoid contraction?

Solution: Lanthanoid contraction refers to the gradual decrease in the size of the lanthanoid ions (from La^{3+} to Lu^{3+}) across the lanthanide series. Despite the increasing nuclear charge, the addition of electrons occurs mainly in the 4f orbitals, which do not effectively shield the increased positive charge. As a result, the effective nuclear charge experienced by the electrons increases, leading to a gradual contraction of the ionic radius. This contraction is particularly significant between elements such as La and Lu and affects the properties of the elements and their compounds, including the stability of their coordination complexes and their atomic size.

Quick Tip

Lanthanoid contraction occurs due to poor shielding by the 4f-electrons, causing a decrease in the size of the ions across the series.

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

Solution: The first ionization enthalpy of chromium is lower than that of zinc because of the electron configuration and the stability of the orbitals. Chromium has an electron configuration of $[Ar]\,3d^5 4s^1$, where one electron from the 4s orbital is promoted to the 3d orbital, leading to a half-filled stable d-subshell. This arrangement provides extra stability to chromium, making it easier to lose an electron compared to zinc, which has a completely filled $3d^{10} 4s^2$ configuration. The completely filled d-subshell in zinc results in higher stability, which makes it harder to ionize. Hence, chromium's first ionization enthalpy is lower.

Quick Tip

Half-filled d-subshells, like in chromium, provide extra stability, making ionization easier compared to elements with completely filled orbitals like zinc.

(d) Why are transition elements good catalysts?

Solution: Transition elements are good catalysts due to several reasons:

1. Variable oxidation states: Transition metals can easily change oxidation states, which helps in facilitating redox reactions by acting as both electron donors and acceptors.
2. Ability to form complexes: Transition metals can coordinate with various ligands, forming complexes that are essential intermediates in catalytic processes.
3. Partial filling of d-orbitals: The presence of partially filled d-orbitals allows transition metals to interact with reactant molecules, lowering activation energies.
4. Surface area: Many transition metals have high surface area, providing more active sites for reactions to occur.

These factors combined make transition metals effective in speeding up reactions without being consumed in the process.

Quick Tip

Transition metals are good catalysts due to their variable oxidation states, ability to form complexes, and partially filled d-orbitals that facilitate reaction mechanisms.

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

Solution: Compounds of transition metals are generally colored because of d-d transitions. In these compounds, the d-orbitals are split into two energy levels due to the ligand field. When electrons in the lower energy d-orbitals absorb visible light, they get excited to the higher energy d-orbitals. The wavelength of light absorbed corresponds to the energy difference between the split d-orbitals, and the remaining transmitted light gives the color of the compound. This phenomenon is common in transition metal complexes, particularly when the metal has an incomplete d-orbital configuration. The presence of ligands and the metal's oxidation state also affect the color.

Quick Tip

Transition metal compounds are colored because of d-d transitions, where electrons absorb visible light and move between split d-orbitals.

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

Solution: $KMnO_4$ has Mn in the +7 oxidation state, meaning that there are no unpaired electrons and it is diamagnetic. However, in K_2MnO_4, Mn is in the +6 oxidation state, and it has unpaired electrons in the d-orbital, making it paramagnetic.

Quick Tip

The magnetic behavior of a compound depends on the number of unpaired electrons. If a compound has unpaired electrons, it is paramagnetic; if all electrons are paired, it is diamagnetic.

(g). Complete the following ionic equation:

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

Solution: The reaction is a reduction half-reaction, where Cr(VI) is reduced to Cr(III). The complete ionic equation is:

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

Quick Tip

In redox reactions, always balance the charges and atoms by adding electrons and water molecules when necessary. Here, Cr(VI) is reduced to Cr(III) with water molecules added to balance the oxygens.

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

Solution:

Step 1: Reverse osmosis is the process in which solvent molecules pass through a semipermeable membrane from a region of low solute concentration to a region of high solute concentration when pressure greater than the osmotic pressure is applied. The solvent moves against the natural osmotic gradient.

Step 2: This process is widely used in water purification and desalination, where solvent (typically water) is purified by removing solutes like salts and other impurities.

Quick Tip

In reverse osmosis, pressure is applied to push the solvent from low concentration to high concentration across a semipermeable membrane.

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

Solution:

Step 1: Cold water has a higher solubility for gases such as oxygen. Since oxygen is crucial for respiration in aquatic species, cold water allows more oxygen to dissolve, making it more available for aquatic species.

Step 2: As temperature increases, the solubility of gases in water decreases. Therefore, warmer water contains less dissolved oxygen, making it less suitable for aquatic life.

Quick Tip

Cold water can hold more dissolved oxygen, making it more suitable for aquatic species, as they rely on dissolved oxygen for respiration.

(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?

Solution: We can calculate the vapour pressure of the solution using Raoult's Law, which states that the vapour pressure of the solvent in the solution is proportional to the mole fraction of the solvent.

$$P = P_0 \times X_{\text{solvent}}$$

Where: - $P_0 = 32.8\,\text{mm Hg}$ is the vapour pressure of pure water,
- X_{solvent} is the mole fraction of water.

Step 1: Calculate the moles of glucose:

$$\text{Moles of glucose} = \frac{2}{180} = 0.0111\,\text{mol}$$

Step 2: Calculate the moles of water:

$$\text{Moles of water} = \frac{100}{18} = 5.56\,\text{mol}$$

Step 3: Calculate the mole fraction of water:

$$X_{\text{water}} = \frac{\text{moles of water}}{\text{moles of water} + \text{moles of glucose}} = \frac{5.56}{5.56 + 0.0111} = 0.998$$

Step 4: Calculate the vapour pressure of the solution:

$$P = 32.8 \times 0.998 = 32.734\,\text{mm Hg}$$

Thus, the vapour pressure of the solution is 32.734 mm Hg.

Quick Tip

Raoult's Law states that the vapour pressure of a solvent in a solution is proportional to the mole fraction of the solvent. The presence of a solute lowers the vapour pressure.

OR

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

Solution: Ethanoic acid (CH_3COOH) is a weak acid and it forms dimers in benzene due to hydrogen bonding between two molecules of ethanoic acid. The formation of dimers reduces the number of particles in the solution. Since Van't Hoff factor i represents the number of particles in solution, for ethanoic acid in benzene, i will be less than 1 due to the dimerization process.

Step 1: Ethanoic acid dissociates into dimers, reducing the total number of particles in the solution.

Step 2: Therefore, the Van't Hoff factor i will be less than 1.

Quick Tip

Van't Hoff factor (i) is less than 1 when solute molecules form complexes or dimers in solution.

(ii) Define ideal solution.

Solution: An ideal solution is one that obeys Raoult's Law completely over the entire range of concentrations. In an ideal solution, the enthalpy of mixing is zero, and the intermolecular forces between the components (solvent-solvent, solute-solute, and solvent-solute) are similar. There is no excess enthalpy change upon mixing, and the vapor pressure of the solution is proportional to the mole fraction of each component. Real solutions that do not follow Raoult's law due to differences in intermolecular interactions are termed non-ideal solutions.

Quick Tip

Ideal solutions obey Raoult's law at all concentrations and have no enthalpy change during mixing, implying similar intermolecular forces between components.

(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 2K, assuming that $CaCl_2$ undergoes complete dissociation.

Solution: We can use the formula for freezing point depression:

$$\Delta T_f = i \times K_f \times m$$

Where:

- $\Delta T_f = 2\,\mathrm{K}$,
- $K_f = 1.86\,\mathrm{K\ kg\ mol^{-1}}$ (given),

- $i = 3$ (for $CaCl_2$ as it dissociates into 3 ions: Ca^{2+} and 2 Cl^-), - m is the molality of the solution.

Step 1: Rearrange the equation to solve for molality:

$$m = \frac{\Delta T_f}{i \times K_f} = \frac{2}{3 \times 1.86} = 0.358\,\text{mol/kg}$$

Step 2: Calculate the moles of $CaCl_2$:

$$\text{moles of CaCl}_2 = m \times \text{mass of solvent} = 0.358 \times 0.5 = 0.179\,\text{mol}$$

Step 3: Calculate the mass of $CaCl_2$:

$$\text{mass of CaCl}_2 = \text{moles} \times \text{molar mass} = 0.179 \times 111 = 19.89\,\text{g}$$

Thus, the mass of $CaCl_2$ required is 19.89 g.

Quick Tip

Freezing point depression depends on the molality and the Van't Hoff factor. For ionic compounds like $CaCl_2$, dissociation increases the number of particles and the effect on the freezing point.