

CBSE 12 Chemistry Set 1 (56/3/1) 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 32 questions. All questions are compulsory.
- (ii) This question paper is divided into five sections — Section A, B, C, D and E.
- (iii) Section A - questions number 1 to 16 are multiple choice type questions. Each question carries 1 mark.
- (iv) Section B - questions number 17 to 21 are very short answer type questions. Each question carries 2 marks.
- (v) Section C - questions number 22 to 28 are short answer type questions. Each question carries 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 32 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.

SECTION A

Questions no. 1 to 16 are Multiple Choice type Questions, carrying 1 mark each

1. Which of the following does *not* show variable oxidation states?

- (A) Fe
- (B) Cu
- (C) Mn
- (D) Sc

Correct Answer: (D) Sc

Solution: Scandium (Sc) has a stable oxidation state of +3 due to its electronic configuration ($[\text{Ar}]3d^14s^2$), and it does not exhibit multiple oxidation states like Fe, Cu, or Mn. Other elements in the list have variable oxidation states due to their partially filled *d*-orbitals, allowing them to lose different numbers of electrons in different compounds.

Quick Tip

Transition elements generally show variable oxidation states due to the availability of vacant *d*-orbitals. However, elements like Scandium, with only one stable oxidation state, are exceptions.

2. The type of isomerism shown by the complex $[\text{CoCl}_2(\text{en})_2]^+$ is:

- (A) Ionisation isomerism
- (B) Geometrical isomerism
- (C) Linkage isomerism
- (D) Coordination isomerism

Correct Answer: (B) Geometrical isomerism

Solution: The given coordination complex $[\text{CoCl}_2(\text{en})_2]^+$ contains two bidentate ethylenediamine (en) ligands and two chloride ligands. The spatial arrangement of these ligands can lead to **cis** and **trans** forms, which exhibit geometrical isomerism. In the **cis**

form, similar ligands are adjacent, whereas in the **trans** form, they are opposite each other, making them distinct non-superimposable structures.

Quick Tip

Geometrical isomerism occurs in octahedral and square planar complexes when ligands have different spatial arrangements around the central metal atom.

3. Which of the following is diamagnetic in nature?

- (A) Co^{3+} , octahedral complex with strong field ligand
- (B) Co^{3+} , octahedral complex with weak field ligand
- (C) Co^{3+} , in a square planar complex
- (D) Co^{3+} , in a tetrahedral complex

[Atomic number: $\text{Co} = 27$]

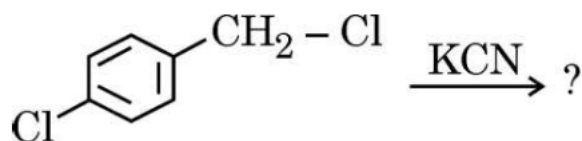
Correct Answer: (A) Co^{3+} , octahedral complex with strong field ligand

Solution: Cobalt (Co) has an atomic number of 27, and Co^{3+} has an electron configuration of $[\text{Ar}]3d^6$. In an octahedral complex with a strong field ligand, the ligand field splits the d -orbitals significantly, leading to a low-spin configuration where all electrons pair up in the lower energy orbitals, making the complex diamagnetic. In contrast, weak field ligands lead to high-spin configurations with unpaired electrons.

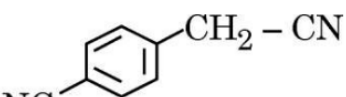
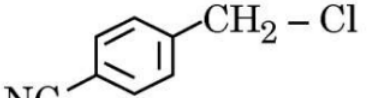
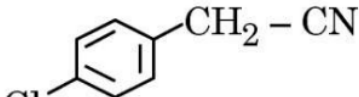
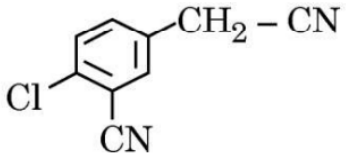
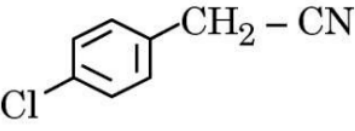
Quick Tip

The magnetic behavior of a transition metal complex depends on the ligand field strength and the electronic configuration of the metal ion.

4. Consider the following reaction:



The major product of the reaction is:

- (A) 
- (B) 
- (C) 
- (D) 
- Correct Answer: (C) 

Solution: The reaction of benzyl chloride ($\text{C}_6\text{H}_5 - \text{CH}_2 - \text{Cl}$) with potassium cyanide (KCN) follows an $\text{S}_\text{N}2$ nucleophilic substitution mechanism. The cyanide ion (CN^-) replaces the chlorine (Cl) group, forming benzyl cyanide ($\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CN}$). Since benzyl chloride has a benzylic carbon, the substitution occurs easily, leading to the formation of the major product.

Quick Tip

$\text{S}_\text{N}2$ reactions occur with a backside attack mechanism, leading to an inversion of configuration at the reaction center.

5. Which one of the following compounds has the lowest pK_a value?

- (A) *p*-Cresol
(B) *p*-Nitrophenol
(C) *m*-Nitrophenol
(D) 2, 4, 6-Trinitrophenol

Correct Answer: (D) 2, 4, 6-Trinitrophenol

Solution: The pK_a value of a compound represents its acidity; a lower pK_a value corresponds to higher acidity. 2, 4, 6-Trinitrophenol (picric acid) is the most acidic due to the presence of three electron-withdrawing nitro (NO_2) groups. These groups stabilize the negative charge on the phenoxide ion formed after deprotonation, significantly reducing its pK_a value compared to other phenols.

Quick Tip

Electron-withdrawing groups ($-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$) increase acidity by stabilizing the conjugate base, thereby lowering the pK_a .

6. $(\text{CH}_3)_2\text{CH} - \text{O} - \text{CH}_3$ when treated with HI gives:

- (A) $(\text{CH}_3)_2\text{CH} - \text{I} + \text{CH}_3\text{OH}$
- (B) $(\text{CH}_3)_2\text{CH} - \text{OH} + \text{CH}_3 - \text{I}$
- (C) $(\text{CH}_3)_2\text{CH} - \text{I} + \text{CH}_3 - \text{I}$
- (D) $(\text{CH}_3)_2\text{CH} - \text{OH} + \text{CH}_3\text{OH}$

Correct Answer: (B) $(\text{CH}_3)_2\text{CH} - \text{OH} + \text{CH}_3 - \text{I}$

Solution: The cleavage of the ether bond in $(\text{CH}_3)_2\text{CH} - \text{O} - \text{CH}_3$ occurs due to the action of hydriodic acid (HI). The more hindered alkyl group $(\text{CH}_3)_2\text{CH}-$ prefers to form an alcohol (OH) rather than an iodide due to steric hindrance, while the less hindered methyl group (CH_3) forms methyl iodide (CH_3I).

Quick Tip

Ethers react with HI to form alkyl iodides and alcohols, where steric hindrance determines which group forms the alcohol.

7. Which of the following compounds on treatment with benzene sulphonyl chloride forms an alkali-soluble precipitate?

- (A) CH_3CONH_2

- (B) $(\text{CH}_3)_3\text{N}$
(C) $(\text{CH}_3)_2\text{NH}$
(D) $\text{CH}_3\text{CH}_2\text{NH}_2$

Correct Answer: (D) $\text{CH}_3\text{CH}_2\text{NH}_2$

Solution: Primary amines, such as ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$), react with benzene sulphonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$) to form sulphonamides, which are soluble in alkali due to the presence of a strong acidic hydrogen. Secondary and tertiary amines either do not form precipitates or are insoluble in alkali.

Quick Tip

The Hinsberg test differentiates primary, secondary, and tertiary amines based on their solubility in alkali after reaction with benzene sulphonyl chloride.

8. The order of increasing basicities of CH_3NH_2 (I), $(\text{CH}_3)_2\text{NH}$ (II), $(\text{CH}_3)_3\text{N}$ (III), and $\text{C}_6\text{H}_5\text{NH}_2$ (IV) in aqueous media is:

- (A) $\text{IV} < \text{III} < \text{I} < \text{II}$
(B) $\text{II} < \text{I} < \text{IV} < \text{III}$
(C) $\text{I} < \text{III} < \text{II} < \text{IV}$
(D) $\text{II} < \text{III} < \text{I} < \text{IV}$

Correct Answer: (A) $\text{IV} < \text{III} < \text{I} < \text{II}$

Solution: Basicity in aqueous medium depends on the electron-donating ability of the nitrogen atom and the solvation effect. Aniline ($\text{C}_6\text{H}_5\text{NH}_2$, IV) is the least basic due to the electron-withdrawing effect of the benzene ring. Trimethylamine ($\text{CH}_3)_3\text{N}$, III) is less basic than methylamine (CH_3NH_2 , I) due to steric hindrance reducing solvation. Dimethylamine ($(\text{CH}_3)_2\text{NH}$, II) is the most basic as it experiences the best balance between electron donation and solvation effects.

Quick Tip

Basicity in aqueous solutions depends on both inductive effects and solvation effects, which influence the availability of the lone pair on nitrogen.

9. The vitamin which plays an important role in coagulating blood is:

- (A) Vitamin A
- (B) Vitamin E
- (C) Vitamin D
- (D) Vitamin K

Correct Answer: (D) Vitamin K

Solution: Vitamin K is essential for the synthesis of clotting factors in the blood, including prothrombin. It plays a crucial role in the blood coagulation process by helping in the activation of proteins required for clot formation. A deficiency in Vitamin K can lead to excessive bleeding disorders.

Quick Tip

Vitamin K is a fat-soluble vitamin, found in leafy greens and is crucial for blood clotting and bone metabolism.

10. When a catalyst increases the rate of a chemical reaction, then the rate constant (k):

- (A) remains constant
- (B) decreases
- (C) increases
- (D) may increase or decrease depending on the order of the reaction

Correct Answer: (A) remains constant

Solution: A catalyst provides an alternative reaction pathway with a lower activation energy, increasing the rate of reaction. However, the rate constant (k) is determined by temperature

and is not affected by the presence of a catalyst. Instead, the catalyst affects the rate by lowering the energy barrier required for the reaction.

Quick Tip

A catalyst speeds up a reaction without altering the equilibrium constant or undergoing permanent chemical change.

11. A 1% solution of solute 'X' is isotonic with a 6% solution of sucrose (molar mass = 342 g mol⁻¹). The molar mass of solute 'X' is:

- (A) 34.2 g mol⁻¹
- (B) 57 g mol⁻¹
- (C) 114 g mol⁻¹
- (D) 3.42 g mol⁻¹

Correct Answer: (B) 57 g mol⁻¹

Solution: For isotonic solutions, the osmotic pressure is the same, meaning the number of solute particles per unit volume is equal. The relation:

$$\frac{1}{\text{Molar Mass of X}} = \frac{6}{342}$$

Solving for the molar mass of X:

$$\text{Molar Mass of X} = \frac{1 \times 342}{6} = 57 \text{ g mol}^{-1}$$

Quick Tip

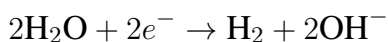
Isotonic solutions have equal osmotic pressure, meaning their solute concentration ratios follow an inverse proportionality with molar mass.

12. During the electrolysis of aqueous NaCl, the cathodic reaction is:

- (A) Oxidation of Cl^- ion
- (B) Reduction of Na^+ ion
- (C) Oxidation of H_2O
- (D) Reduction of H_2O

Correct Answer: (D) Reduction of H_2O

Solution: In the electrolysis of aqueous sodium chloride (NaCl), water competes with sodium ions (Na^+) for reduction at the cathode. Since sodium has a more negative reduction potential than water, water is preferentially reduced. The cathodic reaction is:



This leads to the evolution of hydrogen gas (H_2) at the cathode, while chloride ions (Cl^-) undergo oxidation at the anode to form chlorine gas (Cl_2).

Quick Tip

In aqueous electrolysis, the reduction of water occurs at the cathode instead of alkali metal ions due to their higher reduction potential.

For Questions number 13 to 16, two statements are given — one labelled as Assertion (A) and the other labelled as Reason (R). Select the correct answer to these questions from the codes (A), (B), (C), and (D) as given below.

- (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.

13. Assertion (A): Addition of ethylene glycol to water lowers its freezing point.

Reason (R): Ethylene glycol is insoluble in water due to lack of its ability to form hydrogen bonds with water molecules.

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

Solution: Ethylene glycol is highly soluble in water due to its ability to form hydrogen bonds. The addition of ethylene glycol lowers the freezing point of water because it disrupts the formation of ice, making the solution remain liquid at lower temperatures. Thus, Assertion (A) is correct, but Reason (R) is incorrect.

Quick Tip

Colligative properties like freezing point depression depend on the number of solute particles, not their chemical nature.

14. Assertion (A): Order of reaction and molecularity are always the same for complex reactions.

Reason (R): Order is determined experimentally, and molecularity is applicable only for elementary reactions.

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

Solution: Order of a reaction is determined experimentally and may not always match molecularity, especially in complex reactions where multiple steps occur. Molecularity is defined only for elementary reactions. Since Assertion (A) is incorrect but Reason (R) is correct, the answer is (D).

Quick Tip

Molecularity is always a whole number, whereas the order of a reaction can be fractional or even zero.

15. Assertion (A): The boiling point of ethanol is higher than that of dimethyl ether.

Reason (R): Ethanol molecules are associated through hydrogen bonding, whereas in dimethyl ether, it is not possible.

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

Solution: Ethanol ($\text{C}_2\text{H}_5\text{OH}$) has hydrogen bonding due to the presence of an OH group, which increases its boiling point. Dimethyl ether (CH_3OCH_3) lacks hydrogen bonding and has a lower boiling point. Since Reason (R) correctly explains Assertion (A), the answer is (A).

Quick Tip

Compounds with hydrogen bonding generally have higher boiling points than those without.

16. Assertion (A): Aniline does not undergo Friedel-Crafts reaction.

Reason (R): Friedel-Crafts reaction is an electrophilic substitution reaction.

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

Solution: Aniline ($\text{C}_6\text{H}_5\text{NH}_2$) does not undergo Friedel-Crafts alkylation/acylation because its lone pair on nitrogen forms a complex with the AlCl_3 catalyst, making the reaction ineffective. Although Friedel-Crafts is an electrophilic substitution reaction, this fact does not explain why aniline does not undergo the reaction. Thus, (B) is the correct answer.

Quick Tip

Friedel-Crafts reactions require a neutral or electron-rich benzene ring, but aniline's lone pair interacts with AlCl_3 , deactivating the ring.

SECTION B

17(a). Define molal depression constant. How is it related to enthalpy of fusion?

Solution:

Step 1: Definition of Molal Depression Constant Molal depression constant (K_f) is the depression in freezing point observed when one mole of a non-volatile solute is dissolved in 1 kg (1000 g) of solvent.

Step 2: Relationship with Enthalpy of Fusion The molal depression constant is mathematically expressed as:

$$K_f = \frac{R \times M_{\text{solvent}} \times T_f^0}{1000 \times \Delta_{\text{fus}}H^0}$$

where:

- R is the universal gas constant,
- M_{solvent} is the molar mass of the solvent,
- T_f^0 is the freezing point of the pure solvent,
- $\Delta_{\text{fus}}H^0$ is the enthalpy of fusion of the solvent.

Quick Tip

Molal depression constant helps determine freezing point depression. It depends on the solvent properties, including its enthalpy of fusion and molar mass.

(b) What type of deviation is shown by ethanol and acetone mixture ? Give reason.

What type of azeotropic mixture is formed by that deviation ?

Solution: Ethanol and acetone mixture shows a **positive deviation** from Raoult's law. In this case, the intermolecular forces between ethanol and acetone molecules are weaker than the forces between ethanol molecules and between acetone molecules. This leads to an increase in vapor pressure of the mixture compared to what is predicted by Raoult's law for an ideal solution.

This deviation leads to the formation of an **azeotropic mixture**. In this case, the azeotrope formed is a minimum boiling azeotrope, where the mixture boils at a lower temperature than

either of the pure components. The azeotrope consists of approximately 89

Quick Tip

Positive deviation occurs when the interactions between molecules in the mixture are weaker than those in the pure components, leading to an increase in vapor pressure.

18. (a) In a reaction, if the concentration of reactant X is tripled, the rate of reaction becomes twenty-seven times. What is the order of the reaction?

Solution:

Determining the Order of Reaction The rate law for a reaction is generally given by:

$$\text{Rate} = k[X]^p$$

Given that when $[X]$ is tripled, the rate increases by a factor of 27:

$$27 \times \text{Rate} = k[3X]^p$$

$$(3)^p = 27$$

Since $27 = 3^3$, we get $p = 3$.

Thus, the order of the reaction is **Third order**.

Quick Tip

For determining reaction order, observe how the rate changes with concentration. If a bimolecular reaction has an excess reactant, it behaves like a first-order reaction.

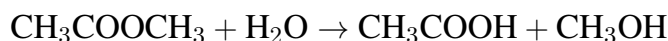
(b) State a condition under which a bimolecular reaction is kinetically a first-order reaction and give an example.

Solution:

Condition for Bimolecular Reaction to Follow First-Order Kinetics A bimolecular reaction follows first-order kinetics when one of the reactants is in excess. In such cases, the

reaction appears to be first-order because the concentration of the excess reactant remains nearly constant.

Example: Hydrolysis of ester:



Here, water is in large excess, making the reaction effectively first-order.

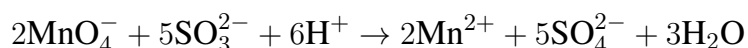
Quick Tip

For determining reaction order, observe how the rate changes with concentration. If a bimolecular reaction has an excess reactant, it behaves like a first-order reaction.

19(a). Complete the following ionic equation:



Solution: This is a redox reaction where permanganate (MnO_4^-) acts as an oxidizing agent. In acidic medium, permanganate ions (MnO_4^-) undergo reduction to form Mn^{2+} , while sulphite ions (SO_3^{2-}) are oxidized to sulphate (SO_4^{2-}). The balanced equation ensures mass and charge conservation.



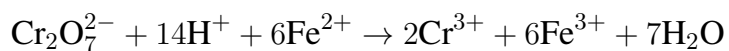
Quick Tip

Redox reactions in acidic medium often involve H^+ ions to balance the charge and ensure electron transfer.

19(b). Complete the following ionic equation:



Solution: Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is a strong oxidizing agent in acidic medium. It undergoes reduction to form chromium (Cr^{3+}), while iron(II) ions (Fe^{2+}) get oxidized to iron(III) (Fe^{3+}). This reaction plays a crucial role in redox titrations where dichromate is commonly used as an oxidizing agent.



Quick Tip

The oxidation number of chromium in $\text{Cr}_2\text{O}_7^{2-}$ changes from +6 to +3 in acidic conditions.

20(a). Which halogen compound in the following pair will react faster in S_N2 reactions and why?



Solution: The S_N2 reaction is a bimolecular nucleophilic substitution mechanism that occurs in a single step with a backside attack. The leaving group plays a critical role in determining the reaction rate. Iodide (I^-) is a much better leaving group than bromide (Br^-) because of its larger atomic size and lower bond dissociation energy. Therefore, ethyl iodide reacts faster in S_N2 reactions compared to ethyl bromide.

$\text{CH}_3 - \text{CH}_2 - \text{I}$, as iodide is a better leaving group due to the larger size of I^- .

Quick Tip

In S_N2 reactions, the rate follows the order of leaving group ability: $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$.

20(b). Why is chloroform stored in closed dark-colored bottles?

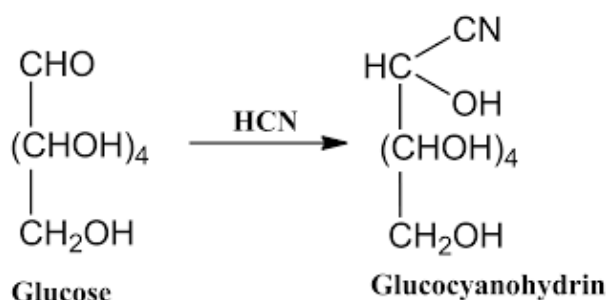
Solution: Chloroform (CHCl_3) is light-sensitive and undergoes photochemical oxidation in the presence of air to form phosgene (COCl_2), a highly toxic gas. Storing chloroform in dark-colored, airtight bottles minimizes its exposure to light and oxygen, preventing decomposition and ensuring safe handling.

Quick Tip

Phosgene, formed from chloroform oxidation, is a toxic gas historically used as a chemical warfare agent.

21(a). Give the reaction of glucose with hydrogen cyanide (HCN).

Solution: Glucose, an aldehyde-containing carbohydrate, reacts with hydrogen cyanide (HCN) via nucleophilic addition to form a cyanohydrin. The cyanide ion (CN^-) attacks the carbonyl carbon, leading to the formation of an additional hydroxyl ($-\text{OH}$) group.



This reaction is significant in organic synthesis as cyanohydrins can be hydrolyzed to carboxylic acids or used to elongate carbohydrate chains.

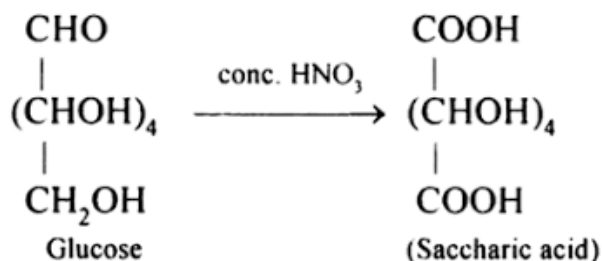
Quick Tip

Cyanohydrin formation is a key step in the Kiliani-Fischer synthesis used to elongate carbohydrate chains.

21(b). Give the reaction of glucose with concentrated nitric acid (HNO_3).

Solution: Glucose undergoes oxidation with concentrated nitric acid (HNO_3) to form

saccharic acid. Both the aldehyde (-CHO) and primary alcohol (-CH₂OH) groups in glucose are converted into carboxyl (-COOH) groups.



This reaction is an example of oxidation using a strong oxidizing agent, producing a dicarboxylic acid.

Quick Tip

Nitric acid (HNO₃) is a strong oxidizing agent and converts both aldehydes and primary alcohols into carboxyl groups.

Section C

22. A solution is prepared by dissolving 5 g of a non-volatile solute in 200 g of water. It has a vapor pressure of 31.84 mm Hg at 300 K. Calculate the molar mass of the solute. (Vapor pressure of pure water at 300 K = 32 mm Hg)

Solution:

We can use Raoult's Law to find the molar mass of the solute. Raoult's Law states:

$$\frac{P_{\text{solvent}}}{P_{\text{solvent, pure}}} = \frac{n_{\text{solute}}}{n_{\text{solution}}}$$

Where: - P_{solvent} is the vapor pressure of the solution, - $P_{\text{solvent, pure}}$ is the vapor pressure of the pure solvent, - n_{solute} is the number of moles of solute, - n_{solution} is the number of moles of the solution.

Step 1: Calculate the mole fraction of the solute:

$$\frac{P_{\text{solvent}}}{P_{\text{solvent, pure}}} = 1 - \frac{31.84}{32} = 0.005$$

Step 2: Use this value to find the moles of solute:

$$\frac{n_{\text{solute}}}{n_{\text{solution}}} = 0.005 \quad \Rightarrow \quad n_{\text{solute}} = 0.005 \times \left(\frac{200}{18}\right)$$

This gives:

$$n_{\text{solute}} = 0.005 \times 11.11 = 0.0555 \text{ mol}$$

Step 3: Calculate the molar mass:

$$\text{Molar mass of solute} = \frac{\text{mass of solute}}{n_{\text{solute}}} = \frac{5 \text{ g}}{0.0555 \text{ mol}} = 90.05 \text{ g/mol}$$

So, the molar mass of the solute is 90.05 g/mol.

Quick Tip

Raoult's Law allows the calculation of molar mass of non-volatile solutes by using vapor pressure lowering. Ensure to use proper unit conversions and balance the mole fraction equations carefully.

23. The conductivity of a 0.2 M solution of KCl is $2.48 \times 10^{-2} \text{ S cm}^{-1}$. Calculate its molar conductivity and degree of dissociation (α).

Given: $\lambda_{\text{K}^+}^0 = 73.5 \text{ S cm}^2 \text{ mol}^{-1}$, $\lambda_{\text{Cl}^-}^0 = 76.5 \text{ S cm}^2 \text{ mol}^{-1}$

Solution:

Step 1: Molar conductivity Λ_m

The molar conductivity Λ_m is given by:

$$\Lambda_m = \frac{k}{C}$$

Where: - $k = 2.48 \times 10^{-2} \text{ S cm}^{-1}$ is the conductivity of the solution, - $C = 0.2 \text{ mol/L}$ is the concentration of the solution.

First, we multiply the conductivity by 1000 to convert the units from S cm^{-1} to S L mol^{-1} :

$$\Lambda_m = \frac{k \times 1000}{C} = \frac{1000 \times 2.48 \times 10^{-2}}{0.2}$$

This gives:

$$\Lambda_m = 124 \text{ S cm}^2 \text{ mol}^{-1}$$

Step 2: Calculate the molar conductivity at infinite dilution Λ^0

The molar conductivity at infinite dilution is the sum of the molar conductivities of the individual ions:

$$\Lambda_m^0 = \lambda_{\text{K}^+}^0 + \lambda_{\text{Cl}^-}^0$$

Substitute the given values:

$$\Lambda_m^0 = 73.5 + 76.5 = 150 \text{ S cm}^2 \text{ mol}^{-1}$$

Step 3: Calculate the degree of dissociation α

The degree of dissociation α is given by the ratio of the observed molar conductivity to the molar conductivity at infinite dilution:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{124}{150} = 0.826$$

Thus, the degree of dissociation is approximately 0.826.

Quick Tip

Molar conductivity can be calculated using the solution's conductivity and concentration. The degree of dissociation can be determined by comparing the observed molar conductivity to the molar conductivity at infinite dilution.

24. A first-order reaction is 25% complete in 40 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

Given: $\log 2 = 0.30$, $\log 3 = 0.48$, $\log 4 = 0.60$, $\log 5 = 0.69$

Solution: Step 1: The integrated rate law for a first-order reaction is given by:

$$\log \left(\frac{[R]_0}{[R]} \right) = \frac{k \cdot t}{2.303}$$

Where: - $[R]_0$ is the initial concentration,

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

- k is the rate constant, and

- t is the time.

We are told that the reaction is 25% complete in 40 minutes, which means that 75% of the reactant remains. Therefore, we calculate:

$$\frac{[R]_0}{[R]} = \frac{1}{0.75} = 1.33$$

Taking the logarithm:

$$\log 1.33 = 0.125$$

Substitute into the rate law:

$$0.125 = \frac{k \cdot 40}{2.303}$$

Solving for k :

$$k = \frac{0.125 \times 2.303}{40} = 0.0069 \text{ min}^{-1}$$

Step 2: To find the time required for the reaction to be 80

$$\log 5 = 0.69$$

Substitute into the rate law:

$$0.69 = \frac{k \cdot t}{2.303}$$

Substituting the value of k :

$$0.69 = \frac{0.0069 \cdot t}{2.303}$$

Solving for t :

$$t = \frac{0.69 \times 2.303}{0.0069} = 230.3 \text{ min}$$

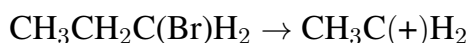
Thus, the time required for the reaction to be 80% complete is 230.3 minutes.

Quick Tip

For first-order reactions, the concentration decreases exponentially over time. Use the integrated rate law to find the rate constant and calculate the time for any given percentage completion.

25. (a) What type of nucleophilic substitution (S_N1 or S_N2) occurs in the hydrolysis of 2-Bromobutane to form (+-)-Butan-2-ol? Give reason.

Solution: Step 1: The reaction follows an S_N1 mechanism. This is due to the formation of a planar carbocation, which can be attacked by the nucleophile from either side. This leads to racemization of the product.



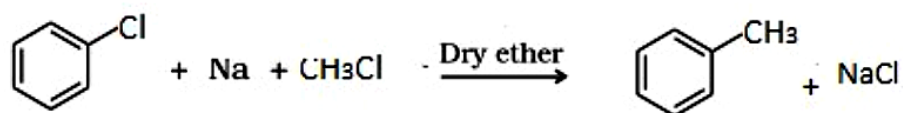
The reaction is accompanied by racemization, and the intermediate carbocation is formed in an S_N1 reaction.

Quick Tip

In S_N1 reactions, the rate-determining step is the formation of a carbocation intermediate. This intermediate can be attacked from either side, leading to racemization of the product.

25. (b) What happens when chlorobenzene and methyl chloride are treated with sodium metal in dry ether?

Solution: When chlorobenzene and methyl chloride are treated with sodium metal in dry ether, a reaction known as the Wurtz-Fittig reaction occurs, leading to the formation of toluene. Sodium metal reduces the chlorine atom in chlorobenzene, and the methyl group from methyl chloride is added to the benzene ring. This results in the formation of toluene ($\text{C}_6\text{H}_5\text{CH}_3$).



Quick Tip

The Wurtz-Fittig reaction is a coupling reaction where sodium metal reduces halides, leading to the formation of new carbon-carbon bonds. The reaction between chlorobenzene and methyl chloride forms toluene.

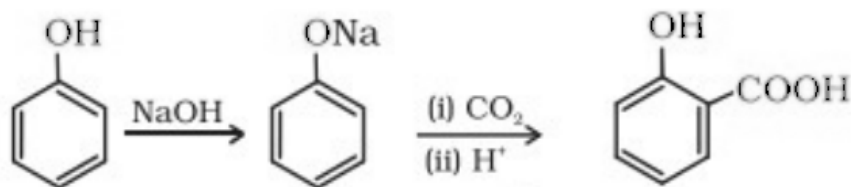
26. (a) Write the reactions involved in the following:

(i) Reimer-Tiemann reaction

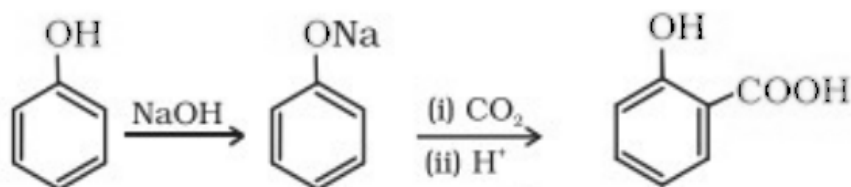
(ii) Kolbe's reaction

Solution:

(i) Reimer-Tiemann Reaction: The Reimer-Tiemann reaction involves the introduction of a formyl group ($-\text{CHO}$) to the aromatic ring using chloroform (CHCl_3) and sodium hydroxide (NaOH):



(ii) Kolbe's Reaction: This reaction involves the carboxylation of sodium phenoxide with carbon dioxide under high pressure, yielding salicylic acid:



26. (b) Name the reagent used in the bromination of phenol to form 2,4,6-Tribromophenol.

Solution:

The reagent used in the bromination of phenol to form 2,4,6-Tribromophenol is Bromine water (Br_2 in water).

1. Electrophilic Aromatic Substitution:

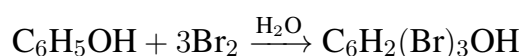
- The bromination of phenol is an example of electrophilic aromatic substitution, where the phenol acts as an electron-rich aromatic compound due to the presence of the hydroxyl group ($-\text{OH}$). The hydroxyl group is an activating group and directs incoming electrophiles to the ortho- and para- positions of the aromatic ring.

2. Action of Bromine:

- Bromine water (a solution of Br_2 in water) acts as the electrophile in this reaction. The bromine molecule (Br_2) is polarized by the electron-rich benzene ring, and one of the bromine atoms becomes highly electrophilic, attacking the ortho- and para- positions relative to the hydroxyl group on the benzene ring.

3. Result:

- The reaction results in the formation of 2,4,6-Tribromophenol, where the three bromine atoms are attached to the ortho- and para- positions of the phenol ring, as shown below:



- The bromine atoms occupy the 2, 4, and 6 positions (relative to the hydroxyl group), making the product 2,4,6-Tribromophenol.

Thus, the reagent used is Bromine water.

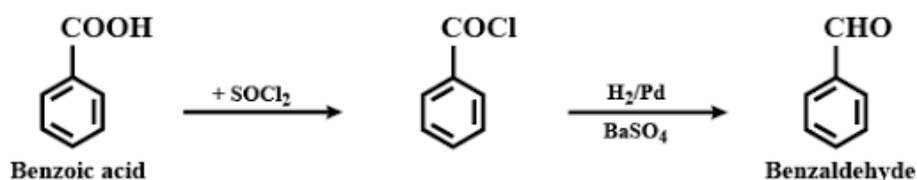
Quick Tip

In electrophilic aromatic substitution reactions such as bromination and formylation, electron-rich aromatic rings are more reactive. The presence of activating groups like hydroxyl ($-\text{OH}$) increases the reactivity of phenol.

27(a). How will you bring about the conversion of Benzoic acid to Benzaldehyde?

Solution: Benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) is first converted into benzoyl chloride ($\text{C}_6\text{H}_5\text{COCl}$) using thionyl chloride (SOCl_2). The resulting benzoyl chloride undergoes Rosenmund reduction using hydrogen and palladium catalyst on barium sulfate ($\text{H}_2/\text{Pd}-\text{BaSO}_4$) to form

benzaldehyde.

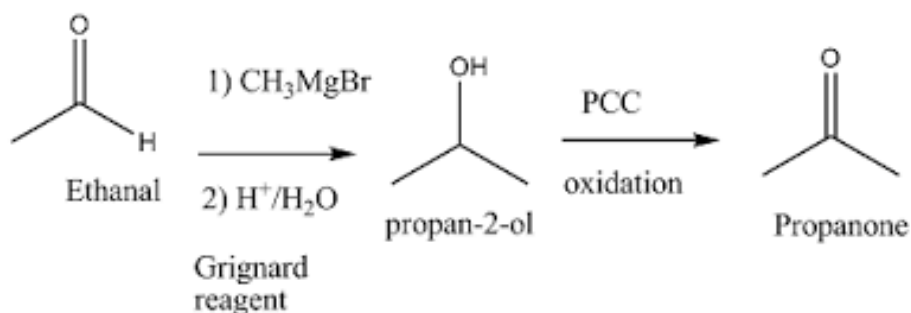


Quick Tip

Rosenmund reduction selectively converts acid chlorides to aldehydes without further reduction to alcohols.

27(b). How will you bring about the conversion of Ethanal to Propanone?

Solution: Ethanal (CH_3CHO) undergoes Grignard addition with methylmagnesium bromide (CH_3MgBr) to form an intermediate alcohol (propan-2-ol). This alcohol is then oxidized using pyridinium chlorochromate (PCC) or another mild oxidizing agent to form propanone (CH_3COCH_3).

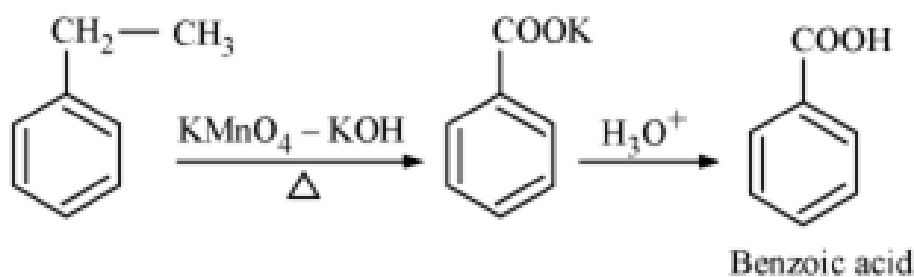


Quick Tip

Grignard reagents add to carbonyl compounds to form alcohols, which can be further oxidized to ketones or aldehydes.

27(c). How will you bring about the conversion of Acetophenone to Benzoic acid?

Solution: Acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) is oxidized using alkaline potassium permanganate (KMnO_4/KOH), which cleaves the methyl ketone group and converts it into benzoate ion ($\text{C}_6\text{H}_5\text{COO}^-$). The solution is then acidified with dilute HCl to yield benzoic acid.

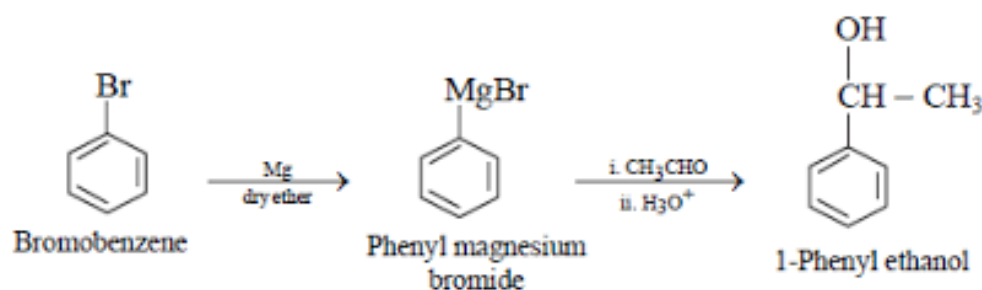


Quick Tip

Strong oxidizing agents like KMnO_4 fully oxidize ketones to carboxylic acids by cleaving carbon-carbon bonds.

27(d). How will you bring about the conversion of Bromobenzene to 1-Phenylethanol?

Solution: Bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) is first converted into phenylmagnesium bromide ($\text{C}_6\text{H}_5\text{MgBr}$) using dry ether. This Grignard reagent then undergoes nucleophilic addition with acetaldehyde (CH_3CHO), forming an intermediate which is hydrolyzed with dilute acid to yield 1-phenylethanol.

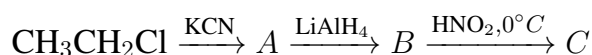


Quick Tip

Grignard reagents react with aldehydes to give secondary alcohols, while reactions with ketones yield tertiary alcohols.

28. Give the structures of A, B, and C in the following reactions:

(a)



Solution: In this reaction, chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$) undergoes nucleophilic substitution with potassium cyanide (KCN) to form ethyl cyanide ($\text{CH}_3\text{CH}_2\text{CN}$) as compound A.

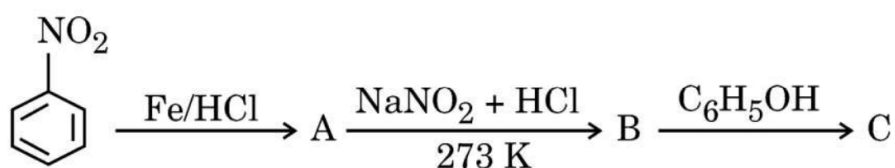
Then, using lithium aluminum hydride (LiAlH_4), the nitrile group is reduced to an amine, giving ethylamine ($\text{CH}_3\text{CH}_2\text{NH}_2$) as compound B.

Finally, the amine undergoes diazotization with nitrous acid (HNO_2) at 0°C to form ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) as compound C.

Quick Tip

Nitriles can be reduced to amines using LiAlH_4 , and amines can be diazotized to form alcohols in a two-step reaction.

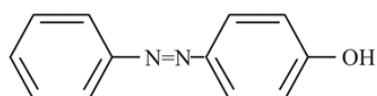
(b)



Solution: In this reaction, nitrobenzene (NO_2) is reduced using iron and hydrochloric acid to form aniline ($\text{C}_6\text{H}_5\text{NH}_2$) as compound A.

Then, aniline undergoes diazotization using sodium nitrite (NaNO_2) and hydrochloric acid (HCl) at 273 K to form a diazonium salt ($\text{C}_6\text{H}_5\text{N}_2\text{Cl}$) as compound B.

Finally, the diazonium salt is coupled with phenol ($\text{C}_6\text{H}_5\text{OH}$) to form the final product,



as compound C.

Quick Tip

Diazotization is a reaction in which an amine is treated with nitrous acid to form a diazonium salt, which can further undergo coupling reactions.

SECTION D

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

29. The involvement of $(n - 1)d$ electrons in the behaviour of transition elements impart certain distinct characteristics to these elements. Thus, in addition to variable oxidation states, they exhibit paramagnetic behaviour, catalytic properties, and a tendency for the formation of coloured ions. The transition metals react with a number of non-metals like oxygen, nitrogen, and halogens. $KMnO_4$ and $K_2Cr_2O_7$ are common examples. The two series of inner transition elements, lanthanoids and actinoids, constitute the f-block of the periodic table. In the lanthanoids, there is a regular decrease in atomic size with an increase in atomic number due to the imperfect shielding effect of 4f-orbital electrons, which causes contraction.

Answer the following questions:

(a) Why do transition metals and their compounds act as good catalysts?

Solution:

Transition metals and their compounds act as good catalysts because they have multiple oxidation states, which allows them to participate in electron transfer during reactions. Additionally, their ability to form complex intermediates and adsorb reactants on their surface reduces the activation energy, facilitating the reaction.

Quick Tip

Catalysts work by lowering the activation energy for a reaction, often by providing an alternative reaction pathway. Transition metals are especially effective because of their variable oxidation states.

(b) What is the cause of contraction in the atomic size of lanthanoids?

Solution:

The contraction in the atomic size of lanthanoids is due to the poor shielding effect of the 4f-orbitals. As we move across the lanthanoid series, the 4f-electrons are added, but they do not shield the increasing nuclear charge effectively, leading to a gradual decrease in atomic size.

Quick Tip

The poor shielding by 4f-electrons in lanthanoids causes an increase in effective nuclear charge, resulting in a contraction of atomic size as we move from left to right in the series.

(c) Define lanthanoid contraction. How does it affect the atomic radii of the third transition series and the second transition series?

Solution:

Lanthanoid Contraction refers to the gradual decrease in atomic size across the lanthanoid series, due to the ineffective shielding of the 4f-electrons. This contraction affects the atomic radii of the third transition series, which are smaller than expected compared to the second transition series. The increased nuclear charge in the lanthanoids results in a stronger pull on the electrons, reducing their size.

Quick Tip

Lanthanoid contraction is caused by the poor shielding effect of 4f-electrons, leading to a consistent decrease in atomic size as we move across the lanthanoid series.

OR

(c) In aqueous media, which is a stronger reducing agent — Cr^{2+} or Fe^{2+} and why?

Solutions: Cr^{2+} is a stronger reducing agent than Fe^{2+} . The reason lies in the electronic configuration and stability of the ions in aqueous medium: - For Cr^{2+} to Cr^{3+} , the transition is from d^4 to d^3 , which is more favorable as the d^3 configuration is relatively stable. - On the other hand, for Fe^{2+} to Fe^{3+} , the transition is from d^6 to d^5 , which is less favorable due to the

stability of the d^5 configuration. - In aqueous solutions, the d^3 configuration in Cr^{3+} is more stable compared to d^5 in Fe^{3+} , making Cr^{2+} a stronger reducing agent.

Quick Tip

In transition metals, the stability of the resulting electron configuration after oxidation plays a crucial role in determining the strength of a reducing agent. The transition from d^4 to d^3 is more favorable than from d^6 to d^5 .

30. Proteins are the most abundant biomolecules of the living system. Proteins are the polymers of about twenty different α -amino acids which are linked by peptide bonds. Ten amino acids are called essential amino acids. In zwitter ionic form, amino acids show amphoteric behaviour as they react both with acids and bases.

On the basis of their molecular shape, proteins are classified into two types: Fibrous and Globular proteins. Structure and shape of proteins can be studied at four different levels: primary, secondary, tertiary, and quaternary, each level being more complex than the previous one. The secondary or tertiary structure of proteins gets disturbed on change of pH or temperature, and they are not able to perform their functions. This is called denaturation of proteins.

Answer the following questions:

(a) What are essential amino acids?

Solution:

Essential amino acids are amino acids that the body cannot synthesize on its own and must be obtained through diet. Examples include leucine, lysine, and tryptophan.

Quick Tip

Essential amino acids are those that cannot be synthesized by the body and must be consumed through diet to maintain proper metabolic function.

(b) What is meant by zwitter ionic form of amino acids?

Solution:

In the zwitter ionic form, amino acids have both a positive and a negative charge within the same molecule. The amino group ($-NH_2$) is protonated to form $-NH_3^+$, and the carboxyl group ($-COOH$) is deprotonated to form COO^- .

Quick Tip

Amino acids exist in a zwitterionic form at physiological pH, where they have both a positive and negative charge, making them amphoteric.

(c) (i) Give one example each for Fibrous protein and Globular protein.

Solution:

- Fibrous Protein: Collagen is an example of a fibrous protein. It is elongated and provides structural support in connective tissues.
- Globular Protein: Hemoglobin is an example of a globular protein. It is compact and involved in transporting oxygen in the blood.

(ii) What type of linkages hold monomers of proteins together?

Solution

Monomers of proteins are held together by peptide bonds, which form between the carboxyl group of one amino acid and the amino group of another.

Quick Tip

Peptide bonds are covalent bonds formed between the amino group of one amino acid and the carboxyl group of another, linking amino acids in a protein chain.

OR

(c) (i) What is the structural feature that characterizes a reducing sugar?

Solution:

A reducing sugar contains a free aldehyde or ketone group, which allows it to act as a reducing agent. This group can undergo oxidation, as seen in glucose and maltose.

(ii) What is the structural difference between nucleoside and nucleotide?

Solution:

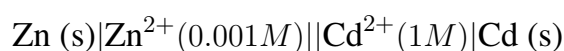
A nucleoside consists of a nitrogenous base and a sugar (ribose or deoxyribose), while a nucleotide includes a nucleoside plus a phosphate group attached to the sugar.

Quick Tip

Nucleotides are the building blocks of nucleic acids, and they consist of a nitrogenous base, a sugar, and a phosphate group. Nucleosides lack the phosphate group.

SECTION E

31. (a) (i) Calculate emf of the following cell at 25°C:



Given:

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}, \quad E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.40 \text{ V}, \quad [\log 10 = 1]$$

Solution: We use the Nernst equation to calculate the emf of the cell:

$$E_{\text{cell}} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

Substituting the values:

$$E_{\text{cell}} = -0.40 - (-0.76) = 0.36 \text{ V}$$

Then, we apply the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \left[\frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]} \right]$$

Substitute the concentrations:

$$E_{\text{cell}} = 0.36 - \frac{0.059}{2} \log \left[\frac{0.001}{1} \right] = 0.36 - \frac{0.059}{2} \log(10^{-3})$$
$$E_{\text{cell}} = 0.36 - \frac{0.059}{2} \times (-3) = 0.36 + 0.089 = 0.449 \text{ V}$$

Quick Tip

In the Nernst equation, the concentration of ions in the cell affects the emf. The greater the difference in concentration, the larger the potential difference.

31(a)(ii). State Faraday's second law of electrolysis. How will the pH of aqueous NaCl solution be affected when it is electrolyzed?

Solution: Faraday's second law of electrolysis states that when the same amount of electricity is passed through electrolytic solutions connected in series, the amount of substance deposited or liberated at each electrode is directly proportional to the chemical equivalent weights of the substances.

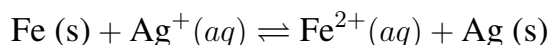
For NaCl electrolysis, at the anode, chlorine gas is liberated, and at the cathode, hydrogen gas is liberated. The liberation of hydrogen at the cathode will increase the concentration of OH^- ions, leading to an increase in pH.

Quick Tip

In electrolysis of NaCl, the anode releases chlorine gas (Cl_2) while the cathode releases hydrogen gas (H_2), making the solution more basic.

OR

31(b)(i). Calculate the $\Delta_r G^\circ$ and $\log K_c$ for the following cell reaction:



Given:

$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}, \quad E_{\text{Ag}^+/\text{Ag}}^\circ = +0.80 \text{ V}, \quad 1F = 96500 \text{ C mol}^{-1}$$

Solution: First, calculate the standard cell potential (E_{cell}°):

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 0.80 - (-0.44) = 1.24 \text{ V}$$

Next, use the relation between $\Delta_r G^\circ$ and E_{cell}° :

$$\Delta_r G^\circ = -nFE_{\text{cell}}^\circ = -2 \times 96500 \times 1.24 \text{ J mol}^{-1} = -239320 \text{ J mol}^{-1}$$

Finally, calculate K_c using the equation:

$$\log K_c = \frac{nE_{\text{cell}}^\circ}{0.059} = \frac{2 \times 1.24}{0.059} = 42.0$$

Quick Tip

The standard cell potential can be used to calculate Gibbs free energy change ($\Delta_r G^\circ$) and equilibrium constant (K_c).

31(b)(ii). Write any two advantages of the fuel cells over primary and secondary batteries.

Solution:

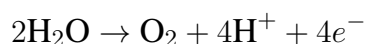
1. Fuel cells are more efficient because they convert chemical energy directly into electrical energy with minimal losses, unlike batteries that rely on stored energy.
2. Fuel cells are environmentally friendly, emitting only water and heat as byproducts, making them a cleaner energy source compared to batteries, which can release harmful chemicals.

Quick Tip

Fuel cells offer advantages of higher efficiency and lower environmental impact compared to traditional battery technologies.

31(b)(iii). How many Faradays are required for the oxidation of 1 mole of H_2O to O_2 ?

Solution: The oxidation of water to oxygen gas involves the transfer of 4 electrons per molecule of water:



Since 1 mole of H_2O requires 2 moles of electrons for oxidation, the number of Faradays required is:

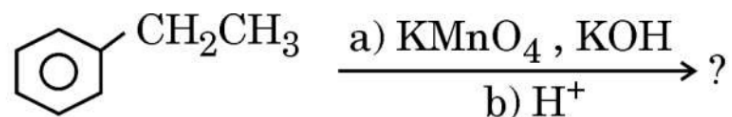
$$2 \times 1 \text{ F} = 2 \text{ Faradays}$$

Quick Tip

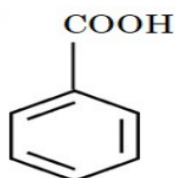
One Faraday corresponds to the charge required to oxidize or reduce 1 mole of electrons in a reaction.

32. (a)(i) Write the major product(s) in the following reactions:

(1)



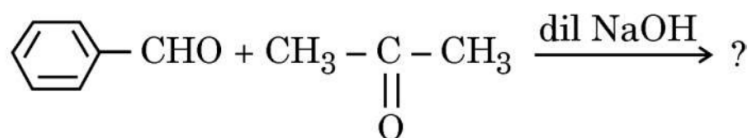
Solution: In this reaction, $\text{CH}_3\text{CH}_2\text{Cl}$ (ethyl chloride) undergoes oxidation in the presence of potassium permanganate (KMnO_4) and potassium hydroxide (KOH). The KMnO_4 oxidizes the ethyl group, converting it to a carboxyl group. Therefore, the major product is benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$), as the ethyl group gets oxidized to a carboxyl group and the resulting compound is aromatic.



Quick Tip

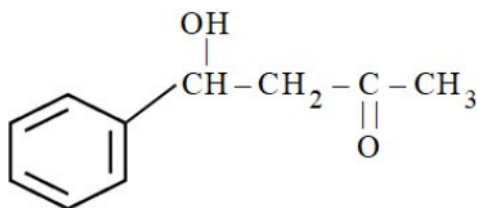
KMnO_4 is a very strong oxidizing agent and oxidizes alkyl groups to carboxylic acids or similar functional groups, especially in aromatic compounds.

(2)



Solution: In this reaction, the aldehyde group (CHO) and the ketone group ($\text{CH}_3\text{C}(=\text{O})\text{CH}_3$) undergo aldol condensation in the presence of dilute sodium hydroxide (NaOH). The reaction involves the formation of an enolate ion that attacks the carbonyl

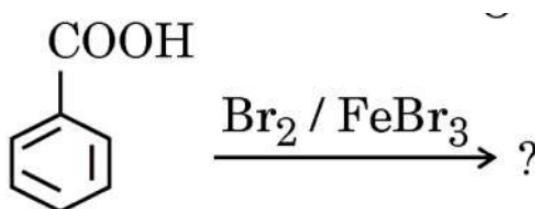
group, resulting in a β -hydroxy ketone, which is the major product. This type of condensation is typical when an aldehyde and ketone are present in the reaction mixture.



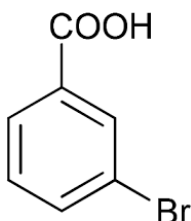
Quick Tip

Aldol condensation is a powerful reaction to form carbon-carbon bonds in aldehydes and ketones. The product typically has a hydroxyl group attached to the β -carbon.

(3)



Solution: In this reaction, the carboxylic acid (COOH) group undergoes bromination in the presence of bromine (Br_2) and iron bromide (FeBr_3), which acts as a catalyst. The bromination typically occurs at the para position on the aromatic ring (relative to the carboxyl group) because the carboxyl group is an electron-withdrawing group and deactivates the ring at the ortho positions. Therefore, the major product is 4-bromobenzoic acid.

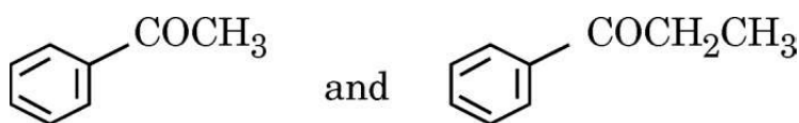


Quick Tip

In electrophilic aromatic substitution reactions, carboxylic acids direct incoming electrophiles to the meta position, but bromination tends to occur at the para position due to the effects of FeBr_3 .

32. (ii) Give simple chemical tests to distinguish between the following pairs of compounds:

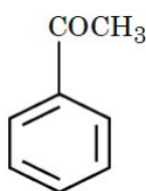
(1)



Solution:

For acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$) and ethyl phenyl ketone ($\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$), the following test can be used:

- Iodoform Test: Acetophenone gives a positive iodoform test when heated with sodium hydroxide (NaOH) and iodine (I_2), forming a yellow precipitate of CHI_3 (iodoform). Ethyl phenyl ketone, on the other hand, does not give a yellow precipitate under the same conditions.



Quick Tip

The iodoform test is useful for identifying compounds with a methyl ketone group (CH_3CO), such as acetophenone.

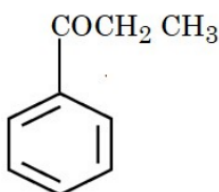
(2)

Pentanal and Pentan-3-one

Solution:

For pentanal (an aldehyde) and pentan-3-one (a ketone), the following test can be used:

- Tollen's Reagent Test: When pentanal is treated with Tollen's reagent ($\text{Ag}(\text{NH}_3)_2^+$), a silver mirror is formed, indicating the presence of an aldehyde group. However, pentan-3-one, which is a ketone, does not give a silver mirror under the same conditions.



Quick Tip

Tollen's reagent is used to distinguish aldehydes from ketones. Aldehydes reduce silver ions to metallic silver, forming a silver mirror.

OR

(b). (i) Give reasons for the following:

(1) In semicarbazide, only one $-\text{NH}_2$ group is involved in the formation of semicarbazone.

(2) Acetaldehyde is more reactive than acetone towards addition of HCN.

Solution:

(1) The reason only one $-\text{NH}_2$ group of semicarbazide is involved in the formation of semicarbazone is that the second $-\text{NH}_2$ group is sterically hindered by the carbonyl group and cannot effectively participate in the reaction.

(2) Acetaldehyde is more reactive than acetone in the addition of HCN because in acetone, the two alkyl groups (methyl groups) donate electron density to the carbonyl group, reducing

its electrophilicity and making it less reactive compared to the aldehyde group in acetaldehyde.

Quick Tip

The presence of electron-donating groups, such as alkyl groups, on a carbonyl compound can decrease its reactivity by reducing the electrophilicity of the carbonyl carbon.

(ii). (1) Arrange the following in decreasing order of their acidic strength:



Solution: The acidic strength of these compounds can be arranged as follows:

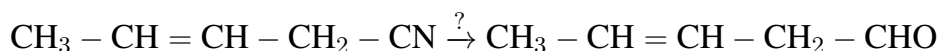


The nitro group (NO_2) in $\text{O}_2\text{N-CH}_2\text{COOH}$ is electron-withdrawing, which stabilizes the conjugate base and increases the acidity. Formic acid (HCOOH) is more acidic than acetic acid (CH_3COOH) because the additional methyl group in acetic acid has a slight electron-donating effect, making the conjugate base less stable.

Quick Tip

Electron-withdrawing groups (such as NO_2) increase the acidity of carboxylic acids by stabilizing the conjugate base.

(ii). (2) Name the reagent in the following reaction:



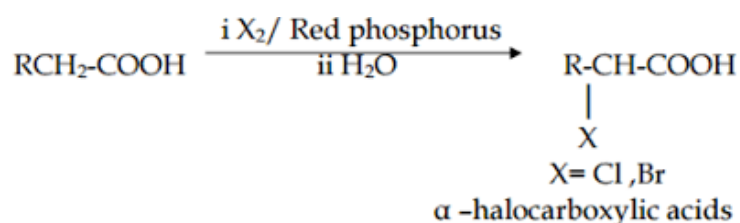
Solution: The reagent in this reaction is dilute NaOH , which facilitates the hydrolysis of the nitrile group (CN) to a carboxylic acid group (COOH).

Quick Tip

The hydrolysis of nitriles to carboxylic acids is commonly carried out using dilute NaOH or other suitable basic reagents.

(iii) Write the reaction involved in Hell-Volhard-Zelinsky reaction.

Solution: The Hell-Volhard-Zelinsky reaction involves the halogenation of a carboxylic acid at the alpha position. The general reaction is as follows:



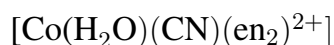
This reaction uses bromine (Br₂) and phosphorus (P) to introduce a bromine atom at the α-carbon of the carboxylic acid.

Quick Tip

The Hell-Volhard-Zelinsky reaction selectively halogenates the α-carbon of carboxylic acids using bromine and phosphorus.

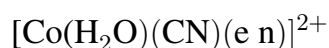
33. Attempt any five of the following:

(a) Write the IUPAC name of the complex:



Solution :

The IUPAC name of the complex



is diaquacyanido-bis(ethylenediamine)cobalt(III) ion.

- "aqua" represents the two water molecules (H₂O) ligands,

- "cyano" represents the cyanide (CN) ligand,

- "ethylenediamine" represents the bidentate ligand (en),
- Cobalt is in the +3 oxidation state.

Quick Tip

In naming coordination compounds, list the ligands alphabetically and indicate the oxidation state of the central metal ion in Roman numerals.

(b) Why is geometrical isomerism not possible in tetrahedral complexes having two different types of unidentate ligands coordinated with the central metal?

Solution :

Geometrical isomerism is not possible in tetrahedral complexes with two different unidentate ligands because of the symmetry of the tetrahedral geometry. In a tetrahedral complex, all four positions are equivalent, and swapping the two different ligands does not result in distinct spatial arrangements. Therefore, no isomers with different spatial arrangements are possible.

Quick Tip

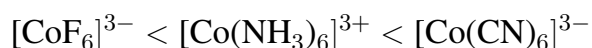
Geometrical isomerism is possible in square planar or octahedral complexes, but tetrahedral complexes generally lack enough symmetry to support distinct isomers.

(c) Arrange the following complex ions in increasing order of their crystal field splitting energy (Δ_0):



Solution :

The crystal field splitting energy (Δ_0) depends on the ligand field strength. The order of field strength for ligands is: $\text{CN}^- > \text{NH}_3 > \text{F}^-$. Therefore, the complexes will be arranged in the following order of increasing Δ_0 :



Explanation:

- Cyanide (CN^-) is a strong field ligand, causing a large splitting of the d-orbitals, leading to

a high Δ_0 .

- Ammonia (NH_3) is a moderate field ligand, causing moderate splitting.
- Fluoride (F^-) is a weak field ligand, leading to the smallest splitting of d-orbitals.

Quick Tip

Ligand field strength influences the crystal field splitting energy (Δ_0). Cyanide (CN^-) is a strong field ligand, followed by ammonia (NH_3), and fluoride (F^-) is a weak field ligand.

(d) Write the hybridization and magnetic character of the complex $[\text{Ni}(\text{CO})_4]$ on the basis of valence bond theory.

[Atomic No. Ni = 28]

Solution:

For the complex $[\text{Ni}(\text{CO})_4]$, nickel is in the +0 oxidation state. The electronic configuration of Ni is $3d^8 4s^2$.

- Hybridization: In $[\text{Ni}(\text{CO})_4]$, the CO ligands are strong field ligands that cause the pairing of the 3d electrons, resulting in the hybridization sp^3 . The geometry of the complex is tetrahedral.

- Magnetic character: Since all electrons are paired in the complex, it is diamagnetic.

Explanation:

- In the presence of CO, which is a strong field ligand, the 3d electrons are paired, leading to a tetrahedral geometry with sp^3 hybridization and no unpaired electrons, thus the complex is diamagnetic.

Quick Tip

The hybridization of a metal complex depends on the geometry and the nature of the ligands. CO is a strong field ligand that leads to electron pairing, resulting in a tetrahedral geometry.

(e) Out of $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$, which complex is:

(i) More stable?

(ii) The high-spin complex?

Solution :

- (i) More stable: The $[Co(C_2O_4)_3]^{3-}$ complex is more stable than $[CoF_6]^{3-}$ because oxalate ($C_2O_4^{2-}$) is a chelating ligand, which provides additional stability through chelation.

- (ii) High-spin complex: The $[CoF_6]^{3-}$ complex is a high-spin complex because fluoride is a weak field ligand that does not cause significant pairing of electrons.

Explanation:

- Chelating ligands such as oxalate lead to greater stability due to their ability to form multiple bonds with the central metal.
- Weak field ligands, such as fluoride, lead to high-spin complexes where electrons occupy higher-energy orbitals to minimize electron-electron repulsion.

Quick Tip

Chelating ligands like oxalate form more stable complexes due to their ability to bind to the metal at multiple points, resulting in greater stability.

(f) What is the difference between an ambidentate ligand and a bidentate ligand?

Solution:

- Ambidentate ligand: A ligand that can coordinate to the central metal through two different atoms, but not simultaneously, is called an ambidentate ligand. For example, the cyanide ion (CN^-) can bind through either the carbon or nitrogen atom.

- Bidentate ligand: A ligand that can form two bonds with the central metal ion through two different donor atoms is called a bidentate ligand. For example, ethylenediamine (en) can form two bonds with the central metal.

Explanation:

- Ambidentate ligands bind through two possible donor atoms, while bidentate ligands always bind through two atoms, resulting in a more stable complex due to chelation.

Quick Tip

Ambidentate ligands can bind through multiple donor atoms, while bidentate ligands always bind through two atoms.

(g) Write the electronic configuration of d^5 in terms of t_{2g} and e_g in an octahedral field as:

(i) $\Delta_o > P$

(ii) $\Delta_o < P$

Solution:

- (i) $\Delta_o > P$: When the crystal field splitting energy (Δ_o) is greater than the pairing energy (P), the electrons will occupy the lower-energy t_{2g} orbitals first, leading to the configuration $t_{2g}^6 e_g^0$. This corresponds to a low-spin configuration.

- (ii) $\Delta_o < P$: When Δ_o is smaller than P , the electrons will prefer to occupy the higher-energy e_g orbitals to minimize repulsion, leading to the configuration $t_{2g}^4 e_g^1$, a high-spin configuration.

Explanation:

- Crystal field splitting energy and pairing energy determine whether a complex is high-spin or low-spin. A larger Δ_o favors low-spin, while a smaller Δ_o favors high-spin.

Quick Tip

The relative strength of Δ_o and P determines whether a complex is high-spin or low-spin. A larger Δ_o favors low-spin, while a smaller Δ_o favors high-spin.