CBSE 12 Chemistry Set 1 (56/2/1) 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 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.

SECTION A

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

- 1. When MnO_2 is fused with KOH in air, it gives:
- (A) KMnO₄
- (B) K_2MnO_4
- (C) Mn_2O_7
- (D) Mn_2O_3

Correct Answer: (B) K₂MnO₄

Solution: When manganese dioxide (MnO₂) is fused with potassium hydroxide (KOH) in the presence of oxygen, it undergoes oxidation to form potassium manganate (K₂MnO₄).

$$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$$

- This reaction occurs at high temperature and is an example of oxidative fusion. - Potassium manganate (K_2MnO_4) is a green compound that can be further oxidized to purple potassium permanganate (KMnO₄) in an acidic medium.

Quick Tip

Further oxidation of K₂MnO₄ in acidic medium produces KMnO₄ (potassium permanganate), which is a strong oxidizing agent.

2. Ligand EDTA $^{4-}$ is an example of a:

- (A) Monodentate ligand
- (B) Didentate ligand
- (C) Tridentate ligand
- (D) Polydentate ligand

Correct Answer: (D) Polydentate ligand

Solution: EDTA⁴⁻ (Ethylenediaminetetraacetate) is a hexadentate ligand, meaning it can

coordinate to a metal ion through six donor atoms (four oxygen atoms from carboxyl groups and two nitrogen atoms from amine groups).

- This ability allows EDTA to form very stable chelate complexes with metal ions, making it a powerful chelating agent. - It is widely used in: - Water treatment (to remove metal impurities). - Medical applications (chelating excess metal ions from the body in cases of poisoning). - Analytical chemistry (complexometric titrations).

Quick Tip

EDTA forms octahedral complexes with many transition metals, stabilizing them against hydrolysis.

3. Which of the following ligands forms a chelate complex?

- (A) $C_2O_4^{2-}$
- (B) Cl⁻
- (C) NO_{2}^{-}
- (D) NH₃

Correct Answer: (A) C₂O₄²⁻

Solution: The oxalate ion $(C_2O_4^{2-})$ is a bidentate ligand, meaning it can coordinate to a metal ion at two different sites (via two oxygen atoms), forming a stable five-membered chelate ring.

- Chelation increases stability of the metal complex due to the chelate effect, which is an entropy-driven stabilization phenomenon. - Common metal-oxalate complexes include: - $[Fe(C_2O_4)_3]^{3-}(Ferricoxalate) - [Cr(C_2O_4)_3]^{3-}(Chromium(III)oxalate)$

Quick Tip

Chelate complexes are more stable because they form cyclic structures that resist ligand dissociation.

4. Which of the following contains sp² hybridized carbon bonded to X?

 $(A) CH_2 = CH - CH_2 - X$

$$_{(B)}$$
 \bigcirc $^{CH_2-X}$

(C)
$$CH_2 = CH - X$$

(D)
$$CH_3 - CH_2 - X$$

Correct Answer: (C) $CH_2 = CH - X$

Solution: In $CH_2 = CH - X$, the carbon atom involved in the double bond (C=C) is sp²-hybridized because:

- Each double-bonded carbon forms three sigma bonds and one pi bond. - The bond angles are approximately 120°, leading to trigonal planar geometry.

Quick Tip

sp²-hybridized carbons form planar structures, which contribute to conjugation in unsaturated systems.

4

5. Which of the following is most acidic?

$$(C)$$
 OH

Solution: p-Chlorophenol is the most acidic because:

- The Cl group is an electron-withdrawing group (-I effect), which stabilizes the conjugate base. - This increases the acidity compared to normal phenol and other alcohols.

Quick Tip

Electron-withdrawing groups increase acidity by stabilizing the conjugate base through resonance (-M effect) and inductive (-I effect).

6. Anisole reacts with HI to give:

(A)
$$CH_3 - I$$

(B) $CH_2 - OH + CH_3 - I$

(C) $CH_2 - I + CH_3 - I$

(D) $CH_2 - I + CH_3 - OH$

Solution: Anisole ($C_6H_5OCH_3$) undergoes cleavage of the C-O bond when treated with hydroiodic acid (HI).

The reaction proceeds via the SN1 or SN2 mechanism, depending on the conditions:

$$C_6H_5OCH_3 + HI \rightarrow C_6H_5OH + CH_3I$$

Mechanism: 1. The iodide ion (I^-) acts as a nucleophile and attacks the methyl group, breaking the ether bond. 2. This forms phenol (C_6H_5OH) and methyl iodide (CH_3I). 3. Since the benzene ring is electron-rich, nucleophilic substitution does not occur at the ring. Thus, the final products are phenol and methyl iodide.

Ethers react with HI to form alcohols and alkyl halides. Aryl-oxygen bonds are resistant to cleavage, so only the alkyl part gets replaced.

7. Ethanol on heating with conc. H_2SO_4 at 413 K gives:

- (A) $C_2H_5OSO_3H$
- (B) $C_2H_5 O CH_3$
- (C) $C_2H_5 O C_2H_5$
- (D) $CH_2 = CH_2$

Correct Answer: (C) $C_2H_5 - O - C_2H_5$

Solution: When ethanol is heated with conc. sulfuric acid (H_2SO_4) at 413 K, it undergoes an intermolecular dehydration reaction, leading to the formation of diethyl ether $(C_2H_5 - O - C_2H_5)$:

$$2C_2H_5OH \xrightarrow{\mathrm{H_2SO_4},413K} C_2H_5 - O - C_2H_5 + H_2O$$

- This reaction occurs at lower temperature (413 K), favoring ether formation. - At higher temperatures (443 K), ethanol undergoes elimination to form ethene ($CH_2 = CH_2$).

Quick Tip

- At 413 K, ethanol forms ether due to intermolecular dehydration. - At 443 K, ethanol forms alkene via intramolecular dehydration.

8. An azeotropic solution of two liquids has a boiling point lower than either of them when it:

- (A) is saturated
- (B) shows positive deviation from Raoult's law
- (C) shows negative deviation from Raoult's law
- (D) shows no deviation from Raoult's law

Correct Answer: (B) shows positive deviation from Raoult's law

Solution: An azeotropic mixture that has a boiling point lower than its components is called a minimum boiling azeotrope. This occurs when:

- The intermolecular forces between different components are weaker than those in the pure liquids. - This results in a higher vapor pressure and, consequently, a lower boiling point than either of the individual components. - It occurs when the mixture exhibits a positive deviation from Raoult's Law.

Example: Ethanol-Water mixture (boiling point 78.2°C) boils at a lower temperature than pure ethanol or pure water.

Quick Tip

A positive deviation from Raoult's Law means that intermolecular forces in the mixture are weaker than in the pure components.

- 9. The relative lowering of vapor pressure of an aqueous solution containing a non-volatile solute is 0.0225. The mole fraction of the non-volatile solute is:
- (A) 0.80
- (B) 0.725
- (C) 0.15
- (D) 0.0225

Correct Answer: (D) 0.0225

Solution: Relative lowering of vapor pressure is given by Raoult's Law:

$$\frac{P_0 - P}{P_0} = X_B$$

where: - P_0 is the vapor pressure of pure solvent, - P is the vapor pressure of the solution, - X_B is the mole fraction of the solute.

Since relative lowering of vapor pressure is given as 0.0225, we directly get:

$$X_B = 0.0225$$

For dilute solutions, the mole fraction of solute can be approximated as the relative lowering of vapor pressure.

10. During electrolysis of an aqueous solution of NaCl:

- (A) $H_2(g)$ is liberated at cathode
- (B) Na is formed at cathode
- (C) $O_2(g)$ is liberated at anode
- (D) $Cl_2(g)$ is liberated at cathode

Correct Answer: (A) $H_2(g)$ is liberated at cathode

Solution: During the electrolysis of aqueous NaCl, the following reactions occur:

At the Cathode (–): Reduction occurs:

$$2H_2O + 2e^- \rightarrow H_2(q) + 2OH^-$$

Since the reduction potential of H^+ (-0.83 V) is more positive than Na^+ (-2.71 V), H_2 gas is liberated instead of Na deposition.

At the Anode (+): Oxidation occurs:

$$2Cl^- \rightarrow Cl_2(q) + 2e^-$$

Since the oxidation potential of Cl⁻ is higher than that of water, Cl₂ gas is released at the anode.

Thus, H₂ gas is liberated at the cathode.

Quick Tip

In aqueous electrolysis, hydrogen is reduced at the cathode, and halide ions (Cl⁻) are oxidized at the anode instead of water.

11. The addition of a catalyst during a chemical reaction alters which of the following quantities of the reaction?

- (A) Enthalpy
- (B) Activation energy
- (C) Entropy
- (D) Internal energy

Correct Answer: (B) Activation energy

Solution: A catalyst functions by providing an alternative reaction pathway that has a lower activation energy (E_a) , thereby increasing the reaction rate.

- Catalysts do not alter: Enthalpy (ΔH): Since the reactants and products remain the same.
- Internal energy (U): The total energy of the system is unchanged. Entropy (ΔS): The disorder of the system remains unaffected.

Thus, a catalyst only lowers the activation energy, making it easier for reactants to reach the transition state.

Quick Tip

A catalyst speeds up a reaction by decreasing activation energy, but it does not affect the thermodynamic properties of the reaction.

12. For the elementary reaction $P \to Q$, the rate of disappearance of 'P' increases by a factor of 8 upon doubling the concentration of 'P'. The order of the reaction with respect to 'P' is:

- (A) 3
- (B)4
- (C) 2
- (D) 1

Correct Answer: (A) 3

Solution: The rate law for a reaction is given by:

$$\mathsf{Rate} = k[P]^n$$

where n is the order of reaction.

Given that doubling the concentration of *P* causes the rate to increase by a factor of 8, we can write:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[P]_2}{[P]_1}\right)^n$$

Substituting the values:

$$8 = \left(\frac{2[P]}{[P]}\right)^n$$

$$8 = 2^n$$

Since $2^3 = 8$, we get:

$$n = 3$$

Thus, the order of the reaction with respect to *P* is 3.

Quick Tip

The reaction order is determined by analyzing how the rate changes with concentration variation.

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): Aliphatic primary amines can be prepared by Gabriel phthalimide synthesis.

Reason (**R**): Alkyl halides undergo nucleophilic substitution with anion formed by phthalimide.

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

Solution: - Gabriel phthalimide synthesis is a method used to prepare primary aliphatic amines by reacting phthalimide with alkyl halides, forming an intermediate that hydrolyzes to yield the amine. - This occurs via nucleophilic substitution (SN2 mechanism), where the phthalimide anion attacks the alkyl halide. - Since both the assertion and reason are correct, and Reason (R) explains Assertion (A), option (A) is correct.

Quick Tip

Gabriel synthesis is not suitable for aryl amines, as aryl halides do not undergo SN2 substitution.

14. Assertion (A): Uracil base is present in DNA.

Reason (R): DNA undergoes self-replication.

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

Solution: - Uracil is not present in DNA; instead, thymine (T) is present. Uracil is found in RNA, not DNA. - However, DNA does undergo self-replication via semi-conservative replication, making the reason true. - Since Assertion (A) is false but Reason (R) is true, option (D) is correct.

Quick Tip

In DNA, thymine pairs with adenine, while in RNA, uracil replaces thymine and pairs with adenine.

15. Assertion (**A**): Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Reason (**R**): Diazonium salts of aliphatic amines show resonance.

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

Solution: - Aromatic diazonium salts are more stable than aliphatic diazonium salts due to resonance stabilization by the benzene ring. - Aliphatic diazonium salts do not show resonance and decompose readily. - Since Assertion (A) is true, but Reason (R) is false, option (C) is correct.

Quick Tip

Aromatic diazonium salts are useful in azo coupling reactions, forming azo dyes.

16. Assertion (A): p-Nitroaniline is a weaker base than p-toluidine.

Reason (R): The electron-withdrawing effect of $-NO_2$ group in p-nitroaniline makes it a weaker base.

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

Solution: - p-Nitroaniline is weaker than p-toluidine because the $-NO_2$ group is electron-withdrawing (-M and -I effect), decreasing the electron density on the nitrogen of the amine, reducing its basicity. - In contrast, the $-CH_3$ group in p-toluidine is electron-donating (+I effect), increasing electron density on nitrogen and enhancing basicity. - Since both the assertion and reason are correct, and Reason (R) explains Assertion (A), option (A) is correct.

Quick Tip

Electron-withdrawing groups decrease basicity, while electron-donating groups increase basicity in aromatic amines.

SECTION B

17. A 6% solution of glucose (molar mass = 180 g mol^{-1}) is isotonic with a 2.5% solution of an unknown organic substance. Calculate the molecular weight of the unknown organic substance.

Solution:

Since the two solutions are isotonic, their osmotic pressures are equal, meaning the concentrations in terms of molarity are the same:

$$C_G = C_U$$

where: - $C_G = \frac{6}{180}$ (Glucose solution molarity) - $C_U = \frac{2.5}{M_U}$ (Unknown substance molarity) Since,

$$\frac{6}{180} = \frac{2.5}{M_{IJ}}$$

Rearranging to solve for M_U :

$$M_U = \frac{2.5 \times 180}{6}$$

$$M_U = 75 \, g \, mol^{-1}$$

Quick Tip

If two solutions are isotonic, their osmotic pressures and molar concentrations must be equal.

18. A first-order reaction has a rate constant $1.25 \times 10^{-3} \, s^{-1}$. How long will 5 g of this reactant take to reduce to 2.5 g?

$$[log2=0301,log3=04771,log4=06021]$$

Solution: For a first-order reaction, the integrated rate law is:

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

where: - $k=1.25\times 10^{-3}\,s^{-1}$ - $[R]_0=5$ g - [R]=2.5 g

Substituting the values:

$$1.25 \times 10^{-3} = \frac{2.303}{t} \log \left(\frac{5}{2.5} \right)$$

Since $\log 2 = 0.301$, we get:

$$1.25 \times 10^{-3} = \frac{2.303}{t} \times 0.301$$

Solving for *t*:

$$t = \frac{2.303 \times 0.301}{1.25 \times 10^{-3}}$$

$$t = \frac{0.693}{1.25 \times 10^{-3}}$$

$$t = 554.5 s \text{ or } 5.54 \times 10^2 s$$

Quick Tip

For first-order reactions, the half-life formula:

$$t_{1/2} = \frac{0.693}{k}$$

can be used to estimate the reaction time.

19. (a) What is lanthanoid contraction? Actinoid contraction is greater from element to element than lanthanoid contraction. Why?

Solution:

Lanthanoid contraction refers to the gradual decrease in atomic or ionic radii across the lanthanoid series from La to Lu. This occurs due to the poor shielding effect of the 4f

subshell. As the atomic number increases, the additional electrons are added to the 4f orbitals, which do not effectively shield the nucleus from the increasing nuclear charge. This results in a stronger pull on the electrons, causing the atomic or ionic size to decrease.

Actinoid contraction is even greater than the lanthanoid contraction because the 5f subshell in actinoids is even less effective at shielding the nucleus. The 5f orbitals are more diffuse and less capable of shielding the nuclear charge, causing a stronger nuclear attraction and, therefore, a greater contraction in atomic and ionic radii.

Thus, the actinoid series shows a larger decrease in atomic size as we move across the series, compared to the lanthanoid series, due to the poorer shielding effect of the 5f electrons.

Quick Tip

In lanthanoids, the poor shielding by 4f electrons leads to a steady decrease in size. In actinoids, the 5f electrons are even less effective at shielding, leading to a greater contraction.

(b) Why do transition metals have high enthalpy of atomization? Which element of the 3d-series has the lowest enthalpy of atomization?

Solution: - Transition metals have a high enthalpy of atomization due to the large number of unpaired d-electrons in their atoms, resulting in strong metal-metal bonding and interatomic interactions. - The enthalpy of atomization increases as the metal atoms form stronger bonds due to these unpaired d-electrons. - The element Zinc (Zn) from the 3d-series has the lowest enthalpy of atomization, because it has a filled d-orbital $(3d^{10})$, resulting in weaker metal-metal bonding.

Quick Tip

Zinc (Zn) has a fully filled $3d^{10}$ configuration, so it has fewer unpaired electrons and weaker bonding, leading to the lowest enthalpy of atomization in the 3d series.

20. (a) In the following pair of compounds, which compound undergoes an $\mathbf{S}_N\mathbf{2}$ reaction faster and why?

$$\bigwedge^{\rm I}$$
 or $\bigwedge^{\rm Br}$

Solution: - The SN2 reaction rate depends on the leaving group. The better the leaving group, the faster the SN2 substitution. - Iodine (I^-) is a better leaving group than bromine (Br $^-$), due to the larger size and weaker bond of I^- with the carbon atom. - Therefore, ethyl iodide (CH₃CH₂I) will undergo the SN2 reaction faster than ethyl bromide (CH₃CH₂Br).

$$\nearrow$$
 I

Quick Tip

In SN2 reactions, a better leaving group (I⁻ ¿ Br⁻) facilitates a faster substitution reaction.

(b) Write the major product in the following reaction:

$$\begin{array}{c} & & & \\ & & \\ \hline \end{array} \begin{array}{c} \text{CH}_2\text{CH}_3 \\ & & \\ \hline \end{array} \begin{array}{c} \text{Cl}_2 \,, \,\, \text{UV light} \\ \end{array}$$

Solution: - The reaction involves ethyl chloride (CH_3CH_2Cl) in the presence of UV light, which typically promotes a free radical substitution reaction. - The major product of this reaction is ethene ($CH_2=CH_2$) due to the elimination of HCl by the free radicals formed under UV light.

UV light can break the C-Cl bond in alkyl chlorides, generating free radicals that lead to elimination reactions.

21. Define the following terms:

- (a) Denaturation of protein
- (b) Invert sugar

Solution:

- (a) Denaturation of Protein: Denaturation refers to the process in which a protein loses its native structure due to physical or chemical factors such as temperature, pH changes, or the presence of organic solvents. This results in the loss of biological activity of the protein because its secondary, tertiary, and quaternary structures are disrupted.
- (b) Invert Sugar: Invert sugar is a mixture of glucose and fructose formed by the hydrolysis of sucrose. During hydrolysis, the sucrose molecule splits into its component monosaccharides, glucose and fructose, causing a change in optical rotation (from dextrorotatory to levorotatory). This is why it is called invert sugar.

Quick Tip

Denaturation of proteins does not affect their primary structure, but disrupts their secondary, tertiary, and quaternary structures, leading to loss of function.

SECTION C

22. Write the structures of A, B, and C in the following reactions:

(a)
$$CH_3 - CH_2 - Br \xrightarrow{KCN} A \xrightarrow{OH^-} Partial hydrolysis \rightarrow B \xrightarrow{NaOH + Br_2} C$$

(b) $Fe + HCl \rightarrow A \xrightarrow{NaNO_2 + HCl} B \xrightarrow{C_2H_5OH} C$

(a)

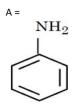
$$A = CH_3CH_2CN$$
 (Ethyl Cyanide)
 $B = CH_3CH_2CONH_2$ (Ethyl Amide)

 $C = CH_3CH_2NH_2 \quad \text{(Ethyl Amine)}$

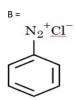
- Step 1: In this reaction, ethyl bromide (CH₃CH₂Br) reacts with KCN (potassium cyanide) in a nucleophilic substitution to form ethyl cyanide (A).
- Step 2: The ethyl cyanide (A) undergoes partial hydrolysis in the presence of OH⁻, converting the nitrile group to an amide to form ethyl amide (B).
- Step 3: Finally, the ethyl amide (B) reacts with NaOH + Br_2 to form ethyl amine (C) through halogenation and basic hydrolysis.

(b)

- Step 1: Nitrobenzene reacts with Fe + HCl (reduction reaction) to form aniline (A).



- Step 2: The aniline (A) reacts with NaNO₂ + HCl at 273-278 K to form diazonium salt (B).



- Step 3: Finally, the diazonium salt (B) undergoes coupling with phenol (C) to form phenol (C) in the presence of NaOH.



- Ethyl cyanide and ethyl amide are intermediates in this nucleophilic substitution and hydrolysis sequence. - In diazotization reactions, the diazonium ion is formed by reacting amines with nitrous acid.

23. Write the reaction involved in the following:

(a) Wolff-Kishner reduction

Solution:

In the Wolff-Kishner reduction, a carbonyl compound (C=O) is treated with hydrazine (NH_2NH_2) and water to form a hydrazone intermediate (C=NH₂). The reaction is then heated in the presence of KOH and ethylene glycol, which removes the nitrogen as N_2 , resulting in the reduction of the carbonyl group to a methylene group (CH₂).

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} C = O & \frac{NH_2NH_2}{-H_2O} \end{array} \end{array} \end{array} \begin{array}{c} \begin{array}{c} C = NNH_2 & \frac{KOH/ethylene\ glycol}{heat} \end{array} \end{array} \begin{array}{c} \begin{array}{c} CH_2 + N_2 \end{array}$$

(b) Decarboxylation reaction

Solution: In the Decarboxylation reaction, sodium salts of aromatic carboxylic acids (Ar/RCOONa) undergo decarboxylation when treated with sodium hydroxide (NaOH) and calcium oxide (CaO) at high temperature (Δ). This results in the formation of a hydrocarbon (Ar-H/R-H) and sodium carbonate (Na₂CO₃).

$$Ar/RCOONa + NaOH \xrightarrow{CaO, \Delta} Ar-H/R-H + Na_2CO_3$$

(c) Cannizzaro reaction

Solution: In the Cannizzaro reaction, formaldehyde (HCHO), in the presence of concentrated sodium hydroxide (NaOH) and heat (Δ), undergoes disproportionation. This reaction involves two molecules of formaldehyde. One molecule is reduced to methanol

(CH $_3$ OH), while the other is oxidized to formate anion (HCOO $^-$), which then combines with a sodium ion (Na $^+$).

$$2\text{HCHO} \xrightarrow{\text{Conc. NaOH, } \Delta} \text{HCOO}^-\text{Na}^+ + \text{CH}_3\text{OH}$$

Quick Tip

- Wolff-Kishner reduction is a key method for reducing carbonyl groups to methylene groups (CH₂). - The decarboxylation reaction is widely used to remove carboxyl groups from aromatic compounds. - The Cannizzaro reaction is a redox reaction that occurs in the absence of an aldehyde with no hydrogen atom attached to the carbonyl group.

24. Give the equations of reactions for the preparation of: (any three)

(a) Phenol from chlorobenzene

Solution:

The Wurtz-Fittig reaction is used here. Chlorobenzene (C_6H_5Cl) undergoes nucleophilic substitution with NaOH under high temperature and pressure (623K, 300 atm), followed by acidic hydrolysis, to form phenol.

(b) Salicyaldehyde from phenol

Solution:

Phenol (C₆H₅OH) undergoes haloform reaction with CHCl₃ and NaOH to produce salicylic acid intermediate, which then undergoes acid hydrolysis to yield salicyaldehyde.

$$\begin{array}{c}
\text{OH} \\
& \text{CHO}
\end{array}$$

(c) 2-Methoxyacetophenone from anisole

Solution:

Anisole ($C_6H_5OCH_3$) reacts with acetyl chloride (CH_3COCl) in the presence of anhydrous $AlCl_3$ to form 2-methoxyacetophenone.

(d) Picric acid from phenol

Solution:

Phenol is nitrated with concentrated nitric acid (HNO₃) to produce picric acid (2,4,6-trinitrophenol).

$$\begin{array}{c}
OH \\
Conc. HNO_3
\end{array}$$

$$\begin{array}{c}
O_2N \\
NO_2
\end{array}$$

$$\begin{array}{c}
NO_2
\end{array}$$

Quick Tip

- Phenol preparation via Wurtz-Fittig reaction involves nucleophilic substitution and hydrolysis. - Salicyaldehyde is obtained by the haloform reaction, a method of introducing an aldehyde group. - Acetylation of anisole forms 2-methoxyacetophenone through electrophilic substitution with acetyl chloride. - Nitration of phenol using conc. HNO₃ introduces nitro groups and leads to picric acid.

25. Give reasons for the following:

(a) Chlorine is ortho/para directing in electrophilic aromatic substitution reactions, though chlorine is an electron withdrawing group.

Chlorine is ortho/para directing in electrophilic aromatic substitution reactions Although chlorine is an electron-withdrawing group through its inductive effect, it acts as an electron-donating group through resonance by donating lone pairs on chlorine to stabilize the intermediate carbocation. This effect is more pronounced at the ortho and para positions relative to the chlorine atom.

(b) Racemic mixture is optically inactive.

Solution:

Racemic mixture is optically inactive A racemic mixture contains two enantiomers in equal proportions. Enantiomers are non-superimposable mirror images of each other, and in a racemic mixture, the optical activities of these enantiomers cancel each other out, leading to zero optical rotation.

(c) Allyl chloride is hydrolysed more readily than n-propyl chloride.

Solution:

Allyl chloride is hydrolysed more readily than n-propyl chloride The allyl carbocation is stabilized by resonance with the adjacent double bond, making the reaction proceed more easily. In contrast, the n-propyl carbocation does not have this resonance stabilization, making it less stable and slower to undergo hydrolysis.

Quick Tip

- Chlorine is ortho/para directing because of the stabilization of the carbocation through resonance. Racemic mixtures result in optical inactivity due to the equal amounts of enantiomers canceling each other's rotation. Allyl chloride is more readily hydrolyzed than n-propyl chloride due to the resonance stabilization of the allyl carbocation.
- 26. The vapour pressure of a solvent at 283 K is 100 mm Hg. Calculate the vapour pressure of a dilute solution containing 1 mole of a strong electrolyte AB in 50 moles of the solvent at 283 K (assuming complete dissociation of solute AB).

The formula for the relative lowering of vapour pressure is:

$$\frac{p^{\circ} - p_s}{p^{\circ}} = i \times \chi$$

Where: - p_0 is the vapour pressure of the pure solvent - p_s is the vapour pressure of the solution - i is the Van't Hoff factor (which represents the number of particles produced from dissociation; for a strong electrolyte AB, i=2) - χ is the mole fraction of the solute For a dilute solution:

$$\frac{100 - p_s}{100} = 2 \times \frac{n_{AB}}{n_{\text{solvent}}}$$

Where: - $n_{AB} = 1$ mole (the amount of solute AB) - $n_{\text{solvent}} = 50$ moles (the amount of solvent)

Substituting these values in:

$$\frac{100 - p_s}{100} = 2 \times \frac{1}{50}$$

Simplifying:

$$\frac{100 - p_s}{100} = \frac{2}{50}$$

$$100 - p_s = 4$$

$$p_s=96\,\mathrm{mm~Hg}$$

Quick Tip

- The Van't Hoff factor i is critical in determining the effect of dissociation on the vapour pressure of a solution. For strong electrolytes, i represents the number of ions produced.
- The relative lowering of vapour pressure is used to calculate the new vapour pressure of the solvent when a solute is added.

27. Calculate emf of the following cell:

$$Zn(s)|Zn^{2+}(0.1M)||Sn^{2+}(0.001M)|Sn(s)$$

Given:

$$E_{\mathrm{Zn^{2+}/Zn}}^{\circ} = -0.76\,\mathrm{V}, \quad E_{\mathrm{Sn^{2+}/Sn}}^{\circ} = -0.14\,\mathrm{V}$$

$$[\log 10 = 1]$$

The equation for the emf of the cell is:

$$E_{\text{cell}} = (E_{\text{c}}^{\circ} - E_{\text{a}}^{\circ}) - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Sn}^{2+}]}$$

Substituting the given values:

$$E_{\text{cell}} = [(-0.14) - (-0.76)] - \frac{0.059}{2} \log \frac{0.1}{0.001}$$

$$E_{\text{cell}} = +0.62 - 0.059$$

$$E_{\text{cell}} = (0.62 - 0.059) \,\mathbf{V} = 0.561 \,\mathbf{V}$$

Quick Tip

- The Nernst equation helps calculate the emf of electrochemical cells by considering the concentrations of the ions involved. - The formula involves standard reduction potentials and logarithmic terms for concentration ratios.

28. The rate of a gaseous reaction triples when temperature is increased from 17° C to 27° C. Calculate the energy of activation for this reaction.

$$[Given: 2303R = 1915JK^{-1}mol^{-1}, log3 = 048]$$

Solution:

The Arrhenius equation is:

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Substituting the known values for the rate constants and temperatures into the equation.

$$k_2/k_1 = 3$$
, $T_1 = 290 K$, and $T_2 = 300 K$:

$$\log\left(\frac{3k_1}{k_1}\right) = \frac{E_a}{19.15} \left(\frac{1}{290} - \frac{1}{300}\right)$$

we get:

$$0.48 = \frac{E_a}{19.15} \left(\frac{10}{290 \times 300} \right)$$

Activation energy, E_a , by multiplying both sides of the equation:

$$E_a = 0.48 \times 19.15 \times 290 \times 300 \quad \Rightarrow \quad E_a = \frac{0.48 \times 19.15 \times 290 \times 300}{10}$$

Finally, calculate the value of E_a . The result gives the activation energy in J/mol. After performing the calculation, we find:

$$E_a = 79970 \,\mathrm{J \, mol}^{-1} \quad \text{or} \quad E_a = 79.970 \,\mathrm{kJ \, mol}^{-1}$$

Quick Tip

- The Arrhenius equation is useful to calculate the energy of activation when the rate constant changes with temperature. - The rate of reaction is highly sensitive to temperature, and small temperature changes can significantly impact the rate.

SECTION D

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

29. Carbohydrates are essential for life in both plants and animals. Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Chemically they are polyhydroxy aldehydes or ketones. On the basis of their behaviour on hydrolysis, carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides. All monosaccharides are reducing sugars, i.e., they are oxidized by Tollens' reagent and Fehling's solution. A monosaccharide like glucose is aldose and its molecular formula was found to be $C_6H_12O_6$. After reacting with different reagents like HI, H_2N –OH,

Bromine water, $(CH_3)_2O$, etc., its structure was found to contain one aldehyde group, one primary alcoholic group, $(-CH_2OH)$ and four secondary alcoholic groups (>CHOH). Despite having the aldehyde group, glucose does not give some of the reactions of aldehyde group like Schiff's test, NaHSO₃ addition. This explains the existence of glucose in two cyclic hemiacetal forms which differ only in the configuration of the hydroxyl group at C-1.

29(a). What are reducing sugars?

Solution: Reducing sugars are sugars that can reduce Tollens' reagent or Fehling's solution due to the presence of a free aldehyde or ketone group. These groups are capable of donating electrons to reduce the reagents. Most monosaccharides like glucose, fructose, and galactose are reducing sugars. Disaccharides like lactose can also be reducing sugars if they have a free reducing end. Sucrose, however, is a non-reducing sugar since both of its anomeric carbons are involved in a glycosidic bond, preventing it from reducing reagents.

Quick Tip

- Reducing sugars are sugars that reduce chemical reagents like Tollens' or Fehling's solution. - The presence of free aldehyde or ketone groups in the sugar molecules allows them to act as reducing agents.

(b). Classify the following into monosaccharides and disaccharides: Fructose, Sucrose, Lactose, Galactose

Solution: - Monosaccharides: These are the simplest sugars and cannot be hydrolyzed into simpler sugars. Fructose and Galactose are both monosaccharides, as they consist of a single sugar unit.

- **Disaccharides:** These consist of two monosaccharides linked by a glycosidic bond. Sucrose and Lactose are disaccharides, formed by the combination of two monosaccharide units. Sucrose consists of glucose and fructose, while lactose consists of glucose and galactose.

- Monosaccharides like glucose, fructose, and galactose cannot be further hydrolyzed.
- Disaccharides like sucrose and lactose can be broken down into two monosaccharides through hydrolysis.

(c). Name the polysaccharide which is known as 'animal starch'. Why is it called 'animal starch'?

Solution: The polysaccharide known as 'animal starch' is Glycogen. Glycogen is a branched polymer of glucose molecules, and it is the primary storage form of glucose in animals, particularly in the liver and muscles. It is similar to amylopectin, which is found in plants, but glycogen has more frequent branching. The name 'animal starch' reflects its role as the animal equivalent of plant starch, storing energy for later use.

Quick Tip

- Glycogen is more highly branched than amylopectin, making it more readily accessible for quick energy release. - The structure of glycogen enables rapid mobilization of glucose when required by the body.

OR ((c)) (i) Name the isomers of glucose which in the cyclic form differ only in the configuration of the –OH group at C – 1.

Solution: The isomers of glucose that differ only in the configuration of the –OH group at C-1 in the cyclic form are α -D-Glucose and β -D-Glucose. These are anomers, which are a type of stereoisomer that differ in the orientation of the substituent group (in this case, the –OH group) at the anomeric carbon (C-1). In α -D-glucose, the –OH group at C-1 is on the opposite side of the ring relative to the CH2OH group, whereas in β -D-glucose, the –OH group at C-1 is on the same side as the CH2OH group.

- Anomers are cyclic sugars that differ in the configuration of the –OH group at the anomeric carbon. - α -D-Glucose and β -D-Glucose are examples of anomers formed by glucose in its cyclic form.

(c)(ii). Presence of which functional group was detected when glucose reacted with ${\bf Br}_2$ water?

Solution: When glucose reacts with Br_2 water, the presence of the aldehyde group (CHO) is detected. This is because the aldehyde group in glucose is capable of reducing bromine water, which leads to the oxidation of the aldehyde group. The reaction with Br_2 water helps identify the presence of the aldehyde functional group in reducing sugars like glucose.

Quick Tip

- The aldehyde group in glucose reacts with bromine water, indicating its reducing nature. This reaction is a common test for the presence of aldehydes, which undergo oxidation to carboxylic acids.
- 30. Transition metals have incomplete d-subshell either in neutral atom or in their ions. The presence of partly filled d-orbitals in their atoms makes transition elements different from that of the non-transition elements. With partly filled d-orbitals, these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a variety of ligands. The transition metals and their compounds also exhibit catalytic properties and paramagnetic behaviour. The transition metals are very hard and have low volatility. An examination of the $\mathbf{E}^0_{M^{2+}/M}$ values shows the varying trends:

$\mathrm{E}_{\mathrm{M}^{2+}/\mathrm{M}}^{\mathrm{o}}$		
V	- 1 ⋅18	
Cr	- 0.91	
Mn	- 1.18	
Fe	- 0.44	
Co	- 0.28	
Ni	- 0.25	
Cu	+ 0.34	
Zn	- 0.76	

30(a). On what basis can we say that Cu is a transition element but Zn is not? (Atomic number: Cu = 29, Zn = 30)

Solution: Cu is a transition element because it has an incomplete d-orbital in its +2 oxidation state, whereas Zn has a fully filled d-orbital in its ground state as well as in +2 oxidation state, making it a non-transition element. Transition elements must have at least one oxidation state with an incomplete d-orbital.

Quick Tip

- Transition elements typically have an incomplete d-orbital in one or more oxidation states. - Non-transition elements like Zn have a full d-orbital in all of their oxidation states.

(b). Why do transition elements show a variety of oxidation states?

Solution: Transition elements show a variety of oxidation states because both (n-1)d and ns subshell electrons take part in bond formation due to their comparable energies. This allows for the formation of multiple oxidation states. The presence of unpaired electrons in d-orbitals also contributes to this variability.

- Transition metals can exhibit multiple oxidation states due to the participation of both d and s electrons in bonding. - The presence of unpaired electrons in the d-orbitals allows for flexibility in oxidation states.

(c)(i). Why do ${\bf E}^0_{M^{2+}/M}$ values show irregular trends from Vanadium to Zinc?

Solution: The irregular trends in $E^0_{M^{2+}/M}$ values from Vanadium to Zinc are due to irregular values of $(\Delta H_1 + \Delta H_2)$ and sublimation enthalpies. These values are influenced by factors like the ionization energies and the differences in the stability of the ions formed.

Quick Tip

- Irregular trends in E^0 values are often due to ionization energies, sublimation enthalpies, and other thermodynamic factors. - The transition elements show varying trends due to these complex thermodynamic effects.

(c)(ii). How is the variability in oxidation states of transition metals different from that of non-transition elements?

Solution: In transition metals, oxidation states vary by +1, whereas in non-transition metals, oxidation states differ by +2. This is due to the involvement of d-orbitals in transition metals, which allows for a greater variety of oxidation states.

Quick Tip

- Transition metals have more flexibility in oxidation states because of the availability of d-orbitals. - Non-transition elements tend to show fewer oxidation states, typically differing by 2.

OR (c) (i) Of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing. Why? (Atomic number: Cr = 24, Mn = 25)

Solution: Cr^{2+} is strongly reducing because it will be converted to Cr^{3+} , which has a more stable half-filled t_2g configuration. On the other hand, Mn^{3+} is strongly oxidizing because it changes to Mn^{2+} , which has a more stable half-filled d^5 configuration. The stability of these configurations makes Cr^{2+} more likely to donate electrons, and Mn^{3+} more likely to accept electrons.

Quick Tip

- Chromium in the +2 oxidation state is reducing, while Mn in the +3 oxidation state is oxidizing due to their electronic configurations. - The stability of half-filled d-orbitals drives these oxidation and reduction tendencies.

(c)(ii). Complete the following ionic equation:

$$2MnO_4^- + H_2O + I^- \longrightarrow$$

Solution: The ionic equation is:

$$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$$

Quick Tip

- The reaction shows the reduction of MnO_4^- and the oxidation of I^- . - The balance of charges and atoms is important when completing ionic equations.

SECTION E

31. Answer any five of the following: 31(a). How is the crystal field splitting energy for octahedral complex (Δ_o) related to that of tetrahedral complex (Δ_t) ?

Solution: The crystal field splitting energy for octahedral complex (Δ_o) is related to that of the tetrahedral complex (Δ_t) by the following equation:

$$\Delta_t = \left(\frac{4}{9}\right) \Delta_o$$

This relation arises due to the difference in the ligand field splitting between the two geometries.

Quick Tip

- Octahedral complexes experience a larger splitting of d-orbitals compared to tetrahedral complexes. - The ratio of Δ_t to Δ_o is derived based on their geometry and ligand interactions.

31(b). Write the IUPAC name of the following complex: $[PtCl_2(en)_2](NO_3)_2$

Solution: The IUPAC name of the complex is Dichloridobis(ethane-1,

2-diamine)platinum(IV) nitrate. Here, "en" stands for ethane-1,2-diamine, and platinum is in the +4 oxidation state.

Quick Tip

- The IUPAC name involves naming ligands in alphabetical order before the metal, followed by its oxidation state. - "en" is the abbreviation for ethane-1,2-diamine, a bidentate ligand.

31(c). Write the geometry and magnetic behaviour of the complex $[Ni(CO)_4]$ on the basis of Valency Bond Theory (VBT).

Solution: The geometry of $[Ni(CO)_4]$ is tetrahedral. According to Valency Bond Theory (VBT), the metal ion (Ni) undergoes sp^3 hybridization to form four bonds with the CO ligands. The complex is diamagnetic as all the electrons in CO ligands are paired.

- In tetrahedral complexes, the central metal atom undergoes sp³ hybridization. - Diamagnetic behavior is observed when all electrons are paired, and there are no unpaired electrons in the system.

31(d). What type of isomerism is shown by the complex $[Co(NH_3)_6][Cr(CN)_6]$?

Solution: The complex $[Co(NH_3)_6][Cr(CN)_6]$ shows coordination isomerism. In this case, the ligands are interchangeable between the metal ions, leading to the possibility of different coordination compounds.

Quick Tip

- Coordination isomerism occurs when ligands can be exchanged between the metal ions in a complex. - This type of isomerism is possible in complexes where there are two different metal ions with different ligands.

31(e). For the coordination compound on the basis of crystal field theory, write the electronic configuration for d^4 ion if $\Delta_o < P$. Is the coordination compound a high spin or low spin complex?

Solution: For a d^4 ion with $\Delta_o < P$, the electronic configuration is $t_{2g}^3 e_g^1$, which corresponds to a high spin complex. This is because the pairing energy is higher than the crystal field splitting energy, causing electrons to occupy higher energy orbitals rather than pair up.

Quick Tip

- In high spin complexes, the electrons prefer to occupy higher energy orbitals to minimize pairing. - Low spin complexes occur when Δ_o $\dot{\xi}$ P, leading to pairing of electrons.

31(f). Out of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$, which complex is heteroleptic and why?

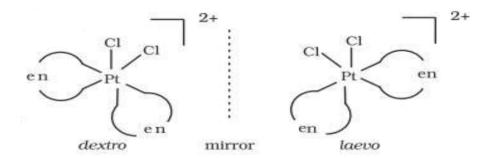
Solution: The complex $[Co(NH_3)_4Cl_2]^+$ is heteroleptic because it contains two different types of ligands $(NH_3 \text{ and } Cl^-)$. In contrast, $[Co(NH_3)_6]^{3+}$ is homoleptic as it contains only one type of ligand (NH_3) .

Quick Tip

- Heteroleptic complexes contain more than one type of ligand. - Homoleptic complexes contain only one type of ligand.

31(g). Draw the structures of optical isomers of $[PtCl_2(en)_2]^{2+}$.

Solution: The optical isomers of $[PtCl_2(en)_2]^{2+}$ are dextrorotatory (d) and levorotatory (l) isomers. These isomers are mirror images of each other and cannot be superimposed. They are non-superimposable, making them optical isomers.



- Optical isomers are non-superimposable mirror images. - They rotate plane-polarized light in opposite directions.

32(a)(i). Account for the following:

- 1. Oxidation of aldehydes is easier as compared to ketones.
- 2. The alpha (α) hydrogen atoms of aldehydes are acidic in nature.

Solution:

- 1. Oxidation of aldehydes is easier because it involves the cleavage of the C-H bond, which is weaker than the C-C bond found in ketones. This makes aldehydes more susceptible to oxidation.
- 2. The alpha (α) hydrogen atoms of aldehydes are acidic due to the electron-withdrawing nature of the carbonyl group. This effect stabilizes the conjugate base through resonance, making the alpha hydrogens more acidic.

Quick Tip

- The C-H bond in aldehydes is weaker than the C-C bond in ketones, making aldehydes easier to oxidize. - The electron-withdrawing carbonyl group in aldehydes enhances the acidity of the alpha hydrogens.

(ii). Write the products in the following reactions:

$$(1) \qquad \stackrel{\text{COCH}_3}{\longrightarrow} ? + ?$$

$$(2) \qquad \stackrel{\text{COCl}}{\longleftarrow} + (\text{CH}_3)_2\text{Cd} \longrightarrow ? + \text{CdCl}_2$$

Solution:

1. The reaction of acetophenone (C₆H₅COCH₃) with NaOH and I₂ forms a yellow precipitate of iodoform (CHI₃) as follows:

$$C_6H_5COCH_3 + NaOH/I_2 \rightarrow C_6H_5COONa + CHI_3$$

$$COONa + CHI_3$$

$$+ CHI_3$$

2. The reaction of benzoyl chloride (C_6H_5COCl) with dimethylcadmium ((CH_3) $_2Cd$) results in the formation of a ketone ($C_6H_5COCH_3$) and cadmium chloride ($CdCl_2$) as follows:

$$C_6H_5COCl + (CH_3)_2Cd \rightarrow C_6H_5COCH_3 + CdCl_2$$



- The reaction of aldehydes and methyl ketones with NaOH and I_2 leads to the formation of iodoform (CHI₃). - The reaction with dimethylcadmium results in the formation of a ketone and the release of CdCl₂.

(iii). Give a simple chemical test to distinguish between ethanoic acid and ethanal.

Solution: A simple test to distinguish between ethanoic acid and ethanal is the iodoform test. When ethanal (acetaldehyde) is heated with NaOH and iodine (I₂), it forms a yellow precipitate of iodoform (CHI₃). This occurs because ethanal contains the structure –CHO (an aldehyde group) that can undergo oxidation and give a yellow iodoform precipitate. However, ethanoic acid (acetic acid), which contains a carboxyl group (–COOH), does not react in the same way. Therefore, ethanoic acid will not produce a yellow precipitate with NaOH and iodine, making this test a reliable way to differentiate the two.

Quick Tip

- The iodoform test specifically identifies compounds with a methyl group directly attached to a carbonyl group, like ethanal or methyl ketones. - Ethanoic acid does not have a methyl group on its carbonyl group, so it does not give a yellow precipitate in the test.

OR

32(b)(i). Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

Solution: The structure of the 2,4-dinitrophenylhydrazone of benzaldehyde is shown below:

$$CH = NNH$$

$$NO_2$$

$$NO_2$$

This compound is formed by the reaction of 2,4-dinitrophenylhydrazine with benzaldehyde.

Quick Tip

- The formation of hydrazones is a common test for aldehydes and ketones. - The presence of nitro groups in the phenyl ring enhances the reactivity of the hydrazone derivative.

(ii). Arrange the following in increasing order of their reactivity towards HCN:

$$CH_3COCH_3$$
, $(CH_3)_3C - COCH_3$, CH_3CHO

Solution: The reactivity of these compounds towards HCN can be arranged in the following order:

$$(CH_3)_3C - COCH_3 < CH_3COCH_3 < CH_3CHO$$

Aldehydes are more reactive towards HCN than ketones due to the ease with which the carbonyl carbon in aldehydes is attacked.

Quick Tip

- Aldehydes are generally more reactive than ketones because they have a less sterically hindered carbonyl group. - The presence of bulky groups in ketones like in tert-butyl ketone reduces the reactivity towards nucleophiles.

(iii). How can you convert phenyl magnesium bromide to benzoic acid?

Solution: Phenyl magnesium bromide (C_6H_5MgBr) can be converted to benzoic acid by reacting it with carbon dioxide (CO_2) followed by hydrolysis. The reaction steps are:

$$C_6H_5MgBr+CO_2\left(dry\;ether\right)\to C_6H_5COOMgBr$$

Then, hydrolyze the intermediate with water and acid:

$$C_6H_5COOMgBr + H_2O/H^+ \rightarrow C_6H_5COOH$$

This converts the Grignard reagent into benzoic acid.

Quick Tip

- The reaction of a Grignard reagent with carbon dioxide and subsequent acid hydrolysis forms a carboxylic acid. - This reaction is known as the Grignard reaction for carboxylation.

(iv). Give a simple chemical test to distinguish between benzaldehyde and ethanal.

Solution: On heating with NaOH and I_2 , ethanal gives a yellow precipitate of iodoform (CHI₃), whereas benzaldehyde does not react. This reaction is known as the iodoform test, which is specific for aldehydes with a methyl group on the carbonyl carbon.

Quick Tip

- The iodoform test distinguishes aldehydes with a methyl group next to the carbonyl group, like ethanal. - Benzaldehyde does not react with NaOH and I₂, making it a useful distinguishing feature.

(v). Write the main product in the following reaction:

$$\begin{array}{ccc} \mathrm{CH_3} - \mathrm{C} - \mathrm{CH_2} - \mathrm{COOC_2H_5} & \xrightarrow{(\mathrm{i)} \ \mathrm{NaBH_4}} & ? \\ \mathrm{O} & & \end{array}$$

Solution: The main product of the reaction is the reduction of the ester to a primary alcohol. Sodium borohydride (NaBH₄) reduces the ester group to an alcohol. The product after hydrolysis is 3-phenylpropanol.

The ester is reduced to the corresponding alcohol (3-phenylpropanol), and the acetic acid is formed as a by-product after hydrolysis.

Quick Tip

- Sodium borohydride (NaBH₄) is a selective reducing agent that reduces esters to alcohols. - Hydrolysis of the intermediate gives the final alcohol and carboxylic acid.

33(a)(i). The resistance of 0.05 M CH $_3$ COOH solution is found to be 100 ohm. If the cell constant is 0.0354 cm $^{-1}$, calculate the molar conductivity of the acetic acid solution.

Solution: The molar conductivity (Λ_m) can be calculated using the formula:

$$\Lambda_m = \frac{k}{M} \times 1000$$

Where: - k is the conductivity, - M is the molarity of the solution.

First, calculate the conductivity (k) using the given values:

$$k = \frac{1}{R} \times L/A = \frac{G}{R}$$

Where: $-R = 100 \Omega$, $-G = 0.0354 \text{ cm}^{-1}$.

Thus:

$$k = \frac{1}{100} \times 0.0354 = 3.54 \times 10^{-4} \,\Omega^{-1} \,\mathrm{cm}^{-1}.$$

Now, calculate Λ_m using the formula:

$$\Lambda_m = \frac{3.54 \times 10^{-4}}{0.05} \times 1000 = 7.08 \,\mathrm{S \, cm^2 \, mol^{-1}}.$$

The molar conductivity of the acetic acid solution is $7.08\,\mathrm{S}\;\mathrm{cm}^2\,\mathrm{mol}^{-1}$.

Quick Tip

- The molar conductivity is calculated by dividing the conductivity by the molarity and multiplying by 1000. - The cell constant G is used to calculate the conductivity of the solution from the resistance.

(ii). State Faraday's first law of electrolysis. How much charge in Faraday is required for the reduction of 1 mol of MnO_4^- to Mn^{2+} ?

Solution: Faraday's first law of electrolysis states that:

The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte. The equation is:

$$m = ZIt$$

Where: - m is the mass of the substance deposited, - Z is the electrochemical equivalent, - I is the current, - t is the time.

For the reduction of 1 mole of MnO_4^- to Mn^{2+} , the number of electrons required is 5 (because MnO_4^- is reduced to Mn^{2+} by gaining 5 electrons). Thus, the charge required to reduce 1 mole of MnO_4^- to Mn^{2+} is given by:

$$Q = n \times F = 5 \times 96500 = 482500$$
 Coulombs.

Therefore, the charge required for the reduction of 1 mole of MnO_4^- to Mn^{2+} is 482500 Coulombs.

Quick Tip

- Faraday's law helps determine the amount of substance deposited during electrolysis based on the charge passed through the electrolyte. - The number of electrons involved in the reduction or oxidation process is key to calculating the total charge.

OR

33(b)(i). The conductivity of 0.0025 mol L⁻¹ acetic acid is 5.25×10^{-5} S cm⁻¹. Calculate its degree of dissociation if Λ_m° for acetic acid is 390 S cm² mol⁻¹.

Solution: The molar conductivity (Λ_m) is calculated as follows:

$$\Lambda_m = \frac{k}{M} \times 1000$$

Where: - $k = 5.25 \times 10^{-5} \,\mathrm{S \ cm}^{-1}$ (given conductivity), - $M = 0.0025 \,\mathrm{mol} \,\mathrm{L}^{-1}$ (molarity).

Thus, the molar conductivity is:

$$\Lambda_m = \frac{5.25 \times 10^{-5}}{0.0025} \times 1000 = 21 \,\mathrm{S \, cm}^2 \,\mathrm{mol}^{-1}.$$

The degree of dissociation (α) is calculated by the formula:

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{21}{390} = 0.053.$$

Thus, the degree of dissociation is 0.053.

Quick Tip

- The degree of dissociation is the ratio of the observed molar conductivity to the theoretical molar conductivity at complete dissociation. - Molar conductivity depends on both concentration and the dissociation degree of the compound.

33(b)(ii). Write the anode, cathode, and overall reaction of lead storage battery.

Solution: In a lead storage battery, the reactions at the anode, cathode, and overall reaction are as follows:

- Anode (oxidation):

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$$

- Cathode (reduction):

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$$

- Overall reaction:

$$Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$$

This is the reaction that takes place during the discharge of a lead storage battery.

Quick Tip

- In a lead storage battery, lead and lead dioxide act as the electrodes, with sulfuric acid serving as the electrolyte. - The overall reaction involves the conversion of lead and lead dioxide into lead sulfate.