CBSE 12 Chemistry Set 2 (56/3/2) 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 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 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 ligands can show linkage isomerism in a coordination compound?

(A) NH_3
(B) SO_4^{2-}
(C) NO_2^-
(D) $C_2O_4^{2-}$

Correct Answer: (C) NO_2^-

Solution: Linkage isomerism occurs when a ligand can coordinate to the central metal ion through two different atoms. In this case, NO_2^- (nitrite ion) can coordinate through the nitrogen atom (as nitro) or the oxygen atom (as nitrito), showing linkage isomerism. Other ligands like NH_3, SO_4^{2-}, and $C_2O_4^{2-}$ do not exhibit this type of isomerism.

Quick Tip

Linkage isomerism occurs in ligands that have two possible coordination sites, such as nitrite (NO_2^-) and thiocyanate (SCN^-).

---

2. On adding $AgNO_3$ solution to 1 mole of complex $NiCl_2 \cdot 4NH_3$, two moles of AgCl are formed. The secondary valency of Ni in the complex will be:

(A) 4
(B) 2
(C) 3
(D) 6

Correct Answer: (A) 4

Solution: The formation of two moles of AgCl indicates that there are two chloride ions present as ligands in the coordination sphere. Since there are 4 ammonia molecules, the complex is $[NiCl_2(NH_3)_4]$, with Ni forming 4 coordinate bonds with NH_3 and 2 coordinate bonds with chloride ions. Therefore, the secondary valency (coordination number) of Ni is 4.

Quick Tip

The secondary valency corresponds to the number of bonds a metal ion forms with its ligands in a coordination complex.

---

3. Transition elements form alloys easily because they have:

(A) same electronic configuration
(B) same enthalpies of atomisation
(C) same oxidation states
(D) nearly the same atomic size

Correct Answer: (D) nearly the same atomic size

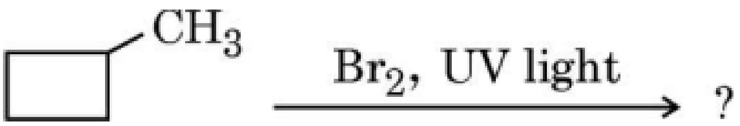
Solution: Transition elements form alloys easily because they have nearly the same atomic size, which allows them to mix in all proportions to form solid solutions. Their similar size ensures that they can fit together in a regular lattice structure without causing significant strain.

Quick Tip

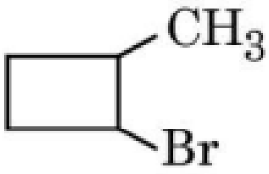
Transition metals tend to form alloys easily due to their similar atomic radii and ability to exist in various oxidation states.

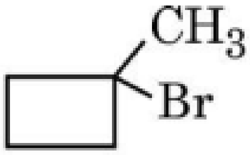
---

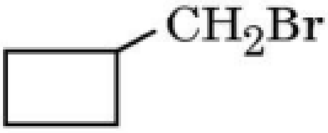
4. Consider the following reaction:

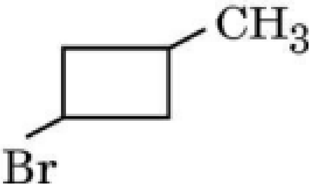


The major product obtained is :

(A) 

(B) 

(C) 

(D) 

Correct Answer: (B) CH_3CH_2Br

Solution: In the presence of bromine (Br_2) and UV light, the reaction proceeds through a free radical substitution mechanism. The hydrogen atom on the carbon next to the bromine is replaced by a bromine atom, forming 1,2-dibromoethane.

Quick Tip

Free radical halogenation reactions involve the replacement of a hydrogen atom by a halogen in the presence of UV light or heat.

---

5. Which one of the following compounds has the highest pK$_a$ value?

(A) p-Nitrophenol

(B) m-Nitrophenol

(C) p-Cresol

(D) 2,4,6-Trinitrophenol

Correct Answer: (C) p-Cresol

Solution: The pK_a value is a measure of acidity, with higher pK_a values indicating weaker acids. p-Cresol (which has a methyl group as a substituent) has the highest pK_a value because the methyl group is electron-donating, which stabilizes the phenoxide ion less than nitro groups, leading to lower acidity.

Quick Tip

Electron-donating groups (like the methyl group in p-Cresol) tend to increase the pK_a, making the compound less acidic.

---

6. $C_6H_5OCH_3$ when treated with HI gives:

(A) $C_6H_5I + CH_3OH$

(B) $C_6H_5OH + CH_3I$

(C) $C_6H_5OH + CH_3OH$

(D) $C_6H_5I + CH_3I$

Correct Answer: (B) $C_6H_5OH + CH_3I$

Solution: When phenyl methyl ether ($C_6H_5OCH_3$) is treated with HI, the ether bond undergoes nucleophilic cleavage. Iodide ion (I^-) displaces the methoxy group, resulting in the formation of phenol (C_6H_5OH) and methyl iodide (CH_3I).

Quick Tip

Iodine and acid (HI) can break ether bonds, replacing the alkoxy group with an iodine atom.

---

7. Which of the following compounds on treatment with benzene sulphonyl chloride forms product insoluble in alkali?

(A) $(CH_3)_3N$

(B) $(CH_3)_2NH$

(C) $CH_3CH_2NH_2$

(D) $C_6H_5NH_2$

Correct Answer: (B) $(CH_3)_2NH$

Solutions: The compound that forms an insoluble product when treated with benzene sulphonyl chloride is a primary amine. Among the options, $(CH_3)_2NH$ is a secondary amine that forms an insoluble sulphonamide with benzene sulphonyl chloride, which answers the question.

Quick Tip

For amines, primary and secondary amines react with benzene sulphonyl chloride to form sulphonamide products, but tertiary amines do not react due to lack of a free hydrogen.

---

8. Which of the following amines gives carbamine reaction?

(A) $C_2H_5NH_2$

(B) $(C_2H_5)_2NH$

(C) $(C_2H_5)_3N$

(D) 

Correct Answer: (A) $C_2H_5NH_2$

Solutions: The carbamine reaction involves the formation of a carbamate compound when a primary amine reacts with carbon dioxide and isocyanates. $C_2H_5NH_2$ (ethylamine) is a primary amine, and it gives a positive carbamine reaction.

Quick Tip

Only primary amines react with carbon dioxide to give a carbamate. Secondary and tertiary amines do not undergo the carbamine reaction.

---

9. ‘Night-Blindness’ is caused by the deficiency of Vitamin:

(A) B

(B) C

(C) K

(D) A

Correct Answer: (D) A

Solutions: Night-blindness is caused by the deficiency of Vitamin A. It affects vision, particularly in low-light conditions.

Quick Tip

Vitamin A is crucial for maintaining healthy vision. Its deficiency can lead to various eye-related issues, including night blindness.

---

10. 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}

Solutions: Isotonic solutions have the same osmotic pressure. Using the concept of molarity and the equation for osmotic pressure, we find that the molar mass of solute ‘X’ that makes the 1% solution isotonic with a 6% sucrose solution is 57 g mol^{-1}.

Quick Tip

For isotonic solutions, the osmotic pressure must be the same. You can use the relationship $M_1C_1 = M_2C_2$, where M is the molarity and C is the concentration, to determine the molar mass of the unknown solute.

---

11. When the initial concentration of a reactant is doubled in the reaction, the half-life period remains same. The order of reaction is:

(A) First

(B) Second

(C) Zero

(D) $\frac{1}{2}$

Correct Answer: (A) First

Solutions: For a first-order reaction, the half-life is independent of the concentration of the reactant. Therefore, if the initial concentration is doubled, the half-life remains unchanged, confirming that the reaction is of first order.

> Quick Tip
>
> In a first-order reaction, the half-life remains constant regardless of the initial concentration. For second-order reactions, the half-life depends on the concentration.

---

12. Which of the following is a secondary cell?

(A) Dry cell

(B) Lead storage cell

(C) Mercury cell

(D) Daniell cell

Correct Answer: (B) Lead storage cell

Solutions: A lead storage cell is a secondary cell because it can be recharged after discharging. The other options are primary cells that cannot be recharged.

> Quick Tip
>
> Secondary cells can be recharged and used multiple times, while primary cells are used once and then discarded.

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): $\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}V$ are zero for non-ideal solutions.

Reason (R): Solute-solvent interactions are not same as pure solute-solute and pure solvent-solvent interactions in non-ideal solutions.

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

Solutions: In non-ideal solutions, $\Delta_{\text{mix}}H$ and $\Delta_{\text{mix}}V$ are not necessarily zero. The reason provided, solute-solvent interactions being different from pure solute-solute and solvent-solvent interactions, is true but does not explain the assertion.

Quick Tip

Non-ideal solutions exhibit changes in enthalpy and volume due to different intermolecular interactions between solute and solvent.

---

14. Assertion (A): Rate of reaction increases with increase in temperature.

Reason (R): Number of effective collisions increase with increase in temperature.

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

Solutions: The rate of reaction increases with temperature as the number of effective collisions between reactants increases. This is a direct consequence of the increase in kinetic energy with temperature.

Quick Tip

The relationship between rate and temperature is described by the Arrhenius equation, which shows that an increase in temperature increases the number of collisions and, hence, the reaction rate.

---

15. Assertion (A): The boiling point of ethanol is higher than that of dimethyl ether.
Reason (R): Dimethyl ether molecules are associated through hydrogen bonding.

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

Solutions: Ethanol has a higher boiling point than dimethyl ether due to hydrogen bonding between ethanol molecules, whereas dimethyl ether does not exhibit such bonding. The reason provided (hydrogen bonding in dimethyl ether) is incorrect.

Quick Tip

Hydrogen bonding significantly increases the boiling point of compounds like ethanol compared to molecules that cannot form such bonds, like dimethyl ether.

---

16. Assertion (A): Aniline undergoes Friedel-Crafts reaction.
Reason (R): Aniline forms salt with AlCl3, the Lewis acid in Friedel-Crafts reaction.

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

Solutions: Aniline does not undergo Friedel-Crafts reactions due to the deactivating effect of the amino group. However, it can form a salt with AlCl3, a Lewis acid, which can facilitate other reactions. Therefore, the reason is true, but the assertion is false.

Quick Tip

Aniline generally does not participate in Friedel-Crafts reactions because the amino group is a deactivating group. However, it can form a complex with AlCl3, a Lewis acid, which can facilitate other reactions.

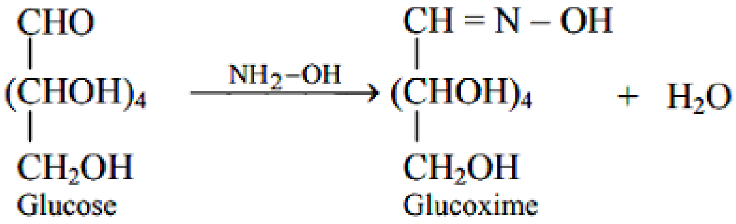
SECTION B

17. Write the reactions of glucose with:

(a) $H_2N - OH$

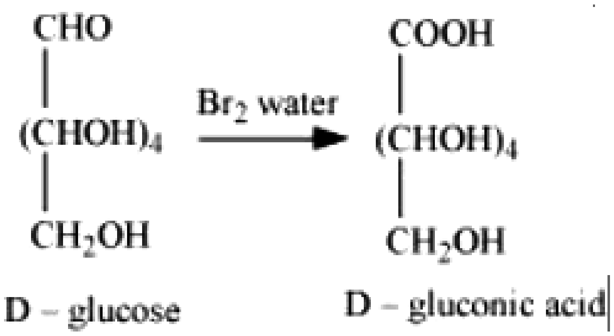
(b) Br_2 water

Solutions: (a) Reaction with hydroxylamine (NH_2OH): When glucose (an aldose) reacts with hydroxylamine, the aldehyde group ($-CHO$) reacts to form an oxime. This is a typical reaction for aldehydes where the hydroxylamine attaches to the carbonyl group, resulting in the formation of glucose oxime. The reaction is as follows:



This reaction helps in the identification of aldehydes, as the oxime formation is characteristic of aldehydes and some ketones.

(b) Reaction with bromine water: When glucose reacts with bromine water, it undergoes oxidation. The aldehyde group in glucose is oxidized to a carboxylic acid group, resulting in the formation of gluconic acid. Bromine water is a mild oxidizing agent and is commonly used to test for aldehyde groups.



This reaction shows the oxidizing nature of bromine and confirms the presence of aldehydes in glucose.

Quick Tip

Oximes are formed when aldehydes or ketones react with hydroxylamine. Bromine water oxidizes aldehydes to acids, which is a common test for aldehyde detection.

---

18. Complete and balance the following chemical equations:

(a) $KMnO_4 \xrightarrow{\text{heat}}$

(b) $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow$

Solutions: (a) Reaction of Potassium Permanganate ($KMnO_4$) with heat: When potassium permanganate is heated, it decomposes to form potassium manganate (K_2MnO_4), manganese dioxide (MnO_2), and oxygen gas (O_2). The reaction is a thermal decomposition and is as follows:

$$2KMnO_4 \xrightarrow{\text{heat}} K_2MnO_4 + MnO_2 + O_2$$

This reaction is often used in laboratory settings to produce oxygen gas and to demonstrate the reduction of manganese species.

(b) Reaction of Permanganate with Oxalate in Acidic Medium: This is a redox reaction where potassium permanganate (MnO_4^-) is reduced while oxalate ions ($C_2O_4^{2-}$) are oxidized. The manganese in MnO_4^- is reduced from +7 oxidation state to +2, and oxalate is oxidized to carbon dioxide. The balanced equation is:

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

This reaction is used in titrations and as an example of a redox reaction involving permanganate.

Quick Tip

In redox reactions, potassium permanganate often acts as an oxidizing agent, and oxalate ions are reduced. These types of reactions are useful in various analytical techniques.

---

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

OR

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

Solutions: (a) Molal Depression Constant: The molal depression constant, denoted by K_f, is defined as the decrease in the freezing point of a solvent when 1 mole of a non-volatile solute is dissolved in 1 kg of the solvent. It is an important property used to calculate colligative properties in solutions. The formula for the depression in freezing point (ΔT_f) is:

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

where m is the molality of the solution. The molal depression constant is related to the enthalpy of fusion ($\Delta_f H^0$) of the solvent. It is derived from the thermodynamic principles that govern freezing point depression and the phase transition from liquid to solid. The relationship between the molal depression constant and the enthalpy of fusion is given by:

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

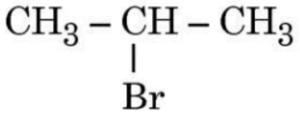
This relationship helps in understanding the energy changes during freezing and fusion processes.

(b) Deviation in Ethanol and Acetone Mixture: Ethanol and acetone exhibit positive deviation from Raoult's law. This is because the intermolecular forces between ethanol and acetone molecules are weaker than the forces between pure ethanol molecules and between pure acetone molecules. As a result, the vapor pressure of the mixture is higher than expected, which is characteristic of positive deviation. This mixture forms a minimum boiling azeotrope, meaning the mixture boils at a lower temperature than either of the pure components.

Quick Tip

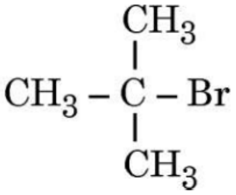
Positive deviation occurs when the interactions between the components are weaker than the pure component interactions, leading to higher vapor pressures. Azeotropes form when the vapor composition and liquid composition are identical at the boiling point.

20. (a) Which halogen compound in the following pair will react faster in SN1 reaction and why?



$CH_3-\underset{Br}{CH}-CH_3$

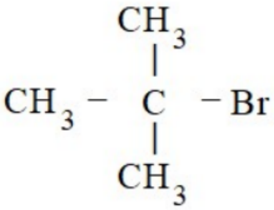
or



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

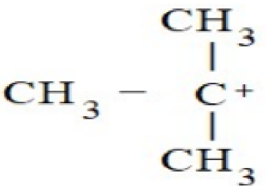
(b) Why is the dipole moment of chlorobenzene lower than that of cyclohexyl chloride?

Solutions: (a) Due to the stability of tertiary carbocation: The compound $CH_3C_3H_3Br$ (tertiary halide) will react faster in an SN1 reaction. This is because in an SN1 reaction, the rate-determining step involves the formation of a carbocation. Tertiary carbocations are more stable than primary or secondary carbocations due to the inductive and hyperconjugation effects, which stabilize the positive charge on the carbocation.
- primary halide



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br$

would form a primary carbocation, which is highly unstable and thus reacts slower.
- tertiary halide



$CH_3-\overset{CH_3}{\underset{CH_3}{C^+}}$

forms a stable tertiary carbocation, which facilitates the SN1 reaction by lowering the activation energy.
(b) Why is the dipole moment of chlorobenzene lower than that of cyclohexyl chloride?
Chlorobenzene has a C-Cl bond where the chlorine atom is attached to a benzene ring, which is sp^2 hybridized. This makes the C-Cl bond highly polarized, but the dipole moment is reduced due to the resonance effect of the benzene ring. In contrast, cyclohexyl chloride has

an sp^3 hybridized C-Cl bond, and there is no resonance effect, leading to a higher dipole moment compared to chlorobenzene.

Quick Tip

In SN1 reactions, tertiary carbocations are more stable and thus form faster, while in SN2 reactions, the rate decreases with increased steric hindrance.

---

21. (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?
(b) State a condition under which a bimolecular reaction is kinetically a first-order reaction. Give an example of such a reaction.

Solutions: (a) Determining the order of reaction The rate law for a reaction is given by:

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

Where p is the order of the reaction. According to the problem, if the concentration of reactant X is tripled, the rate increases by a factor of 23:

$$23\,\text{Rate} = k[3X]^p$$

This simplifies to:

$$23 = 3^p$$

Solving for p, we find $p = 3$. Therefore, the reaction is third-order.
(b) Condition for a bimolecular reaction to be first-order A bimolecular reaction is typically second-order, as it involves two reactants. However, under certain conditions, such as when one reactant is in excess, the reaction can effectively behave like a first-order reaction with respect to the limiting reactant. For example, the hydrolysis of an ester in the presence of excess water is a bimolecular reaction that behaves like a first-order reaction with respect to the ester concentration.

Quick Tip

When one reactant in a bimolecular reaction is present in large excess, the reaction becomes effectively first-order with respect to the limiting reactant.

SECTION C

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

(a)

$$CH_3CH_2Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2, 0°C} C$$

Solution: In this reaction, chloroethane (CH_3CH_2Cl) undergoes nucleophilic substitution with potassium cyanide (KCN) to form ethyl cyanide (CH_3CH_2CN) as compound A.

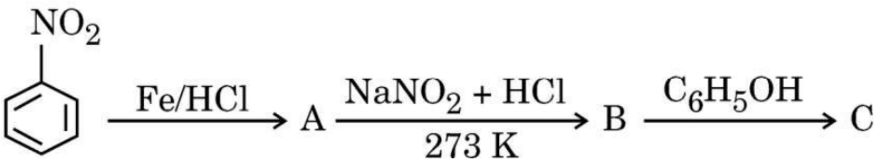
Then, using lithium aluminum hydride ($LiAlH_4$), the nitrile group is reduced to an amine, giving ethylamine ($CH_3CH_2NH_2$) as compound B.

Finally, the amine undergoes diazotization with nitrous acid (HNO_2) at 0°C to form ethanol (CH_3CH_2OH) 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.

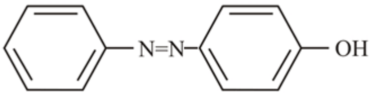
(b)



Solution: In this reaction, nitrobenzene (NO_2) is reduced using iron and hydrochloric acid to form aniline ($C_6H_5NH_2$) as compound A.

Then, aniline undergoes diazotization using sodium nitrite ($NaNO_2$) and hydrochloric acid (HCl) at 233 K to form a diazonium salt ($C_6H_5N_2Cl$) as compound B.

Finally, the diazonium salt is coupled with phenol (C_6H_5OH) to form the final product,



as compound C.

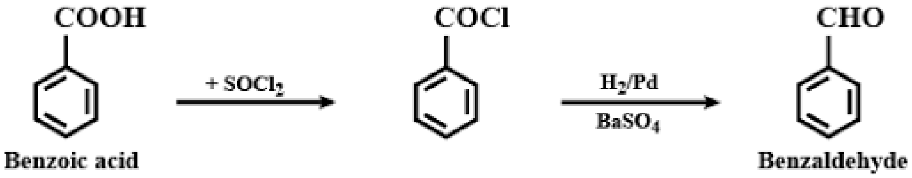
Quick Tip

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

23.How will you bring about the following conversions ? (any three)

(a). Benzoic acid to Benzaldehyde

Solution: Benzoic acid (C_6H_5COOH) is first converted into benzoyl chloride (C_6H_5COCl) using thionyl chloride ($SOCl_2$). The resulting benzoyl chloride undergoes Rosenmund reduction using hydrogen and palladium catalyst on barium sulfate ($H_2/Pd\text{-}BaSO_4$) to form benzaldehyde.

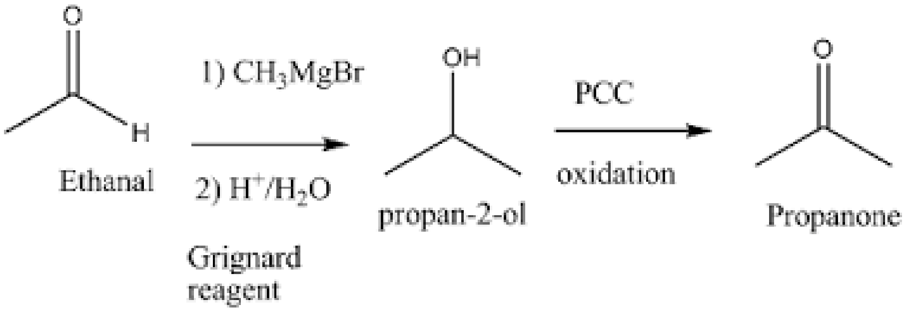


Quick Tip

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

(b). 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).

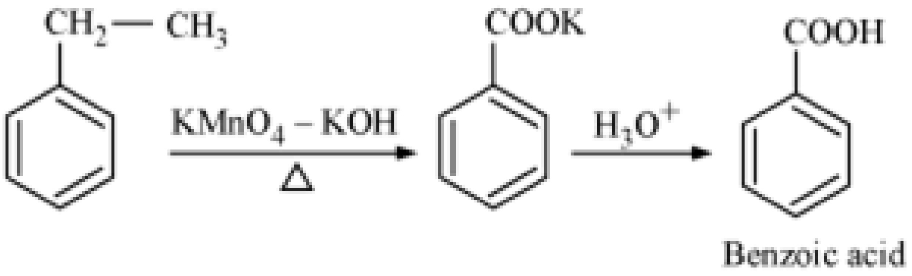


Quick Tip

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

(c). Acetophenone to Benzoic acid

Solution: Acetophenone ($C_6H_5COCH_3$) is oxidized using alkaline potassium permanganate ($KMnO_4/KOH$), which cleaves the methyl ketone group and converts it into benzoate ion ($C_6H_5COO^-$). The solution is then acidified with dilute HCl to yield benzoic acid.

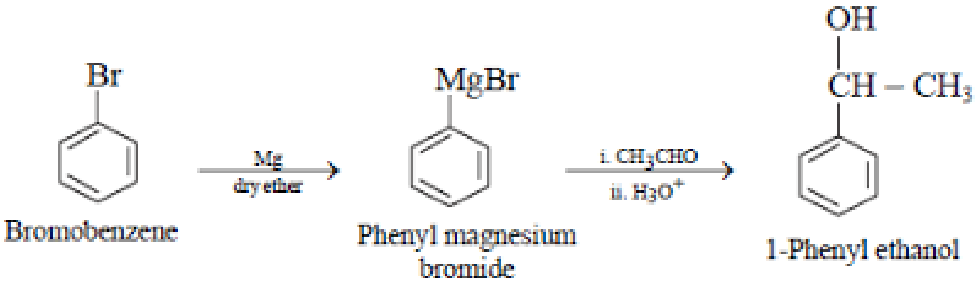


Quick Tip

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

(d). Bromobenzene to 1-Phenylethanol

Solution: Bromobenzene (C_6H_5Br) is first converted into phenylmagnesium bromide (C_6H_5MgBr) 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.

---

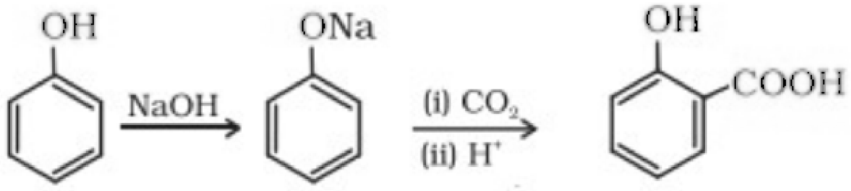
24. (a) Write the reactions involved in the following:

(i) Reimer-Tiemann reaction

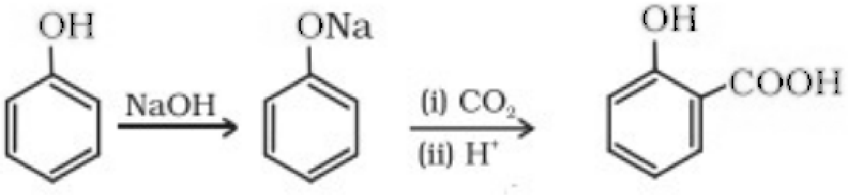
(ii) Kolbe's reaction

Solution:

(i) Reimer-Tiemann Reaction: The Reimer-Tiemann reaction involves the introduction of a formyl group (–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:



24. (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 (-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:

$$C_6H_5OH + 3Br_2 \xrightarrow{H_2O} C_6H_2(Br)_3OH$$

- 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 (–OH) increases the reactivity of phenol.

---

25. 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.

---

26. (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.

$$CH_3CH_2C(Br)H_2 \rightarrow CH_3C(+)H_2$$

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

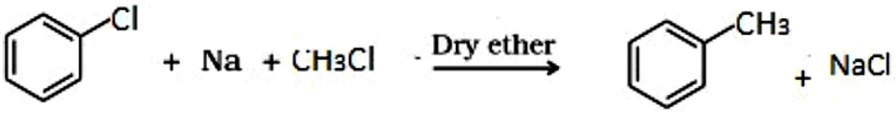
Quick Tip

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.

---

26. (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 ($C_6H_5CH_3$).



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.

---

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

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

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.

---

28. 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.

SECTION D

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

29. Proteins are the most abundant biomolecules of the living system. Proteins are the polymers of about twenty different a-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 $-\text{NH}_3^+$, 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.

---

30. 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.

SECTION E

31. Attempt any five of the following:

(a) Write the IUPAC name of the complex:

$[Co(H_2O)(CN)(en_2)^{2+}]$

Solution :

The IUPAC name of the complex

$$[Co(H_2O)(CN)(e\ n)]^{2+}$$

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

- ”aqua” represents the two water molecules (H_2O) 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):

$[Co(NH_3)_6]^{3+}$, $[CoF_6]^{3-}$, $[Co(CN)_6]^{3-}$

Solution :

The crystal field splitting energy (Δ_0) depends on the ligand field strength. The order of field strength for ligands is: $CN^- > NH_3 > F^-$. Therefore, the complexes will be arranged in the following order of increasing Δ_0:

$$[CoF_6]^{3-} < [Co(NH_3)_6]^{3+} < [Co(CN)_6]^{3-}$$

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 $[Ni(CO)_4]$ on the basis of valence bond theory.

[Atomic No. Ni = 28]

Solution:

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

- Hybridization: In $[Ni(CO)_4]$, 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 $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$, 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.

---

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

$$\text{Zn (s)}|\text{Zn}^{2+}(0.001M)||\text{Cd}^{2+}(1M)|\text{Cd (s)}$$

Given:

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

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

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

Substituting the values:

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

Then, we apply the Nernst equation:

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

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.

32(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

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

$$\text{Fe (s)} + \text{Ag}^+(aq) \rightleftharpoons \text{Fe}^{2+}(aq) + \text{Ag (s)}$$

Given:

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

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

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

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

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

Finally, calculate K_c using the equation:

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

Quick Tip

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

32(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.

32(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:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^-$$

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

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

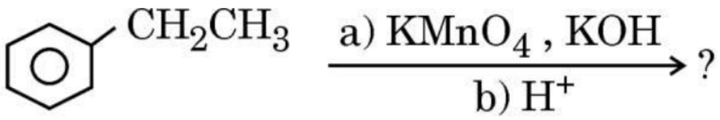
Quick Tip

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

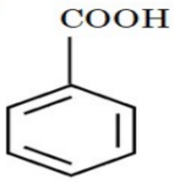
---

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

(1)



Solution: In this reaction, CH_3CH_2Cl (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 (C_6H_5COOH), as the ethyl group gets oxidized to a carboxyl group and the resulting compound is aromatic.

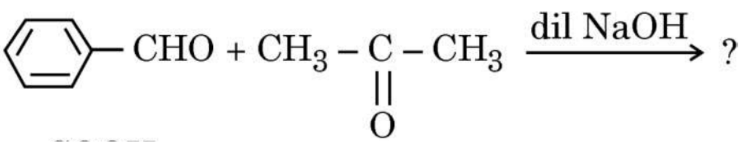


Quick Tip

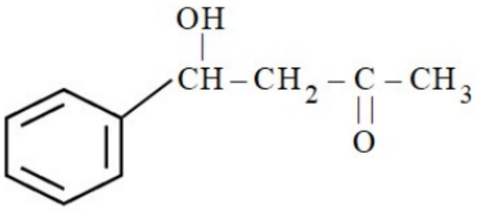
$KMnO_4$ is a very strong oxidizing agent and oxidizes alkyl groups to carboxylic acids or similar functional groups, especially in aromatic compounds.

---

(2)



Solution: In this reaction, the aldehyde group (CHO) and the ketone group ($CH_3CH_2C - CH_3$) 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.

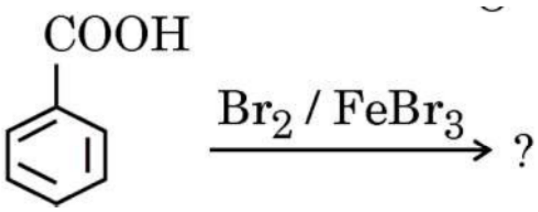


Quick Tip

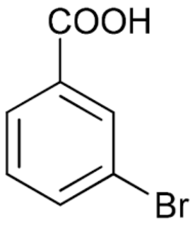
Aldol condensation is a powerful reaction to form carbon-carbon bonds in aldehydes and ketones. The product typically has a hydroxyl group attached to the β-carbon.

---

(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 $FeBr_3$.

---

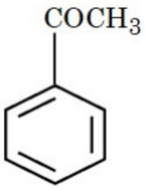
33. (ii) Give simple chemical tests to distinguish between the following pairs of compounds:

(1)

Solution:

For acetophenone ($C_6H_5COCH_3$) and ethyl phenyl ketone ($C_6H_5COCH_2CH_3$), 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.

---

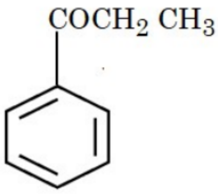
(2)

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 ($Ag(NH_3)_2^+$), 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 $-NH_2$ 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 $-NH_2$ group of semicarbazide is involved in the formation of semicarbazone is that the second $-NH_2$ 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:

$$CH_3COOH, \quad O_2N\text{-}CH_2COOH, \quad HCOOH$$

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

$$O_2N\text{-}CH_2COOH > HCOOH > CH_3COOH$$

The nitro group (NO_2) in O_2N-CH_2COOH 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:

$$CH_3 - CH = CH - CH_2 - CN \xrightarrow{?} CH_3 - CH = CH - CH_2 - CHO$$

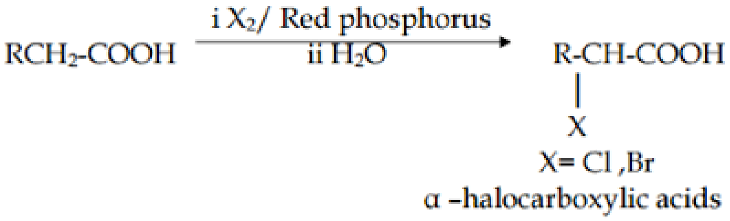
Solution: The reagent in this reaction is dilute NaOH, which facilitates the hydrolysis of the nitrile group (CN) to a carboxylic acid group (COOH).

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:



$$RCH_2\text{-}COOH \xrightarrow[\text{ii } H_2O]{\text{i } X_2/\text{ Red phosphorus}} \underset{\underset{X}{|}}{R\text{-}CH}\text{-}COOH$$

This reaction uses bromine (Br_2) 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.
