CBSE 12 Chemistry (56/5/3) Question Paper with Solutions

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

General Instructions

Read the following instructions very carefully and strictly follow them :

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

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

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

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

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

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

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

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

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

(x) Use of calculators is not allowed.

1. Van't Hoff factor for K_2SO_4 solution, assuming complete ionization is:

(A) 1

(B) 3

(C) 13

(D) 2

Correct Answer: (B) 3

Solution: When K_2SO_4 dissociates completely in water, it dissociates as follows:

$$K_2SO_4 \to 2K^+ + SO_4^{2-}.$$

Since it dissociates into 3 ions (2 potassium ions and 1 sulfate ion), the Van't Hoff factor (i) is 3. Hence, the correct answer is (B) 3.

Quick Tip

The Van't Hoff factor (i) represents the number of particles into which a solute dissociates. For ionic compounds like K_2SO_4, i equals the number of ions produced upon complete dissociation.

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2. Dilution affects both conductivity as well as molar conductivity. Effect of dilution on both is as follows:

(A) both increase with dilution.

(B) both decrease with dilution.

(C) conductivity increases whereas molar conductivity decreases on dilution.

(D) conductivity decreases whereas molar conductivity increases on dilution.

Correct Answer: (D) conductivity decreases whereas molar conductivity increases on dilution.

Solution: When a solution is diluted, the conductivity (which is the ability of the solution to conduct electricity) typically decreases because the ions are spread out in a larger volume, leading to fewer collisions between the ions and less efficient movement of charge.

However, molar conductivity (which is the conductivity per mole of ions) increases with dilution because as the ions are spread out, they experience less ion pairing, allowing for greater mobility and, therefore, a higher molar conductivity.

This behavior is described by the relation:

$$\Lambda_m = \frac{\kappa}{c}$$

where Λ_m is the molar conductivity, κ is the conductivity, and c is the concentration of the solution.

Thus, conductivity decreases, while molar conductivity increases as the solution is diluted.

Quick Tip

Dilution results in the decrease of conductivity due to fewer ions per unit volume. However, molar conductivity increases because ions move more freely when diluted.

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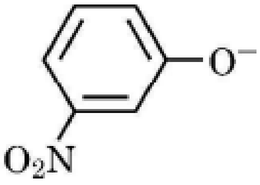
3. Which of the following species can act as the strongest base?

(A) OH^-

(B) $C_6H_5O^-$

(C) $RO-$

(D) 

Correct Answer: (C) $RO-$

Solution: The basicity of a species is determined by its ability to donate electrons (i.e., its nucleophilicity and its tendency to accept a proton). The stronger the conjugate base, the stronger the base. Here's the analysis of the species:

1. $OH-$: Hydroxide is a strong base, but it is less basic than alkoxides because it is the conjugate base of water, which is a relatively weak acid.

2. $C_6H_5O^-$: Phenoxide ion is a weaker base compared to alkoxides because the negative charge on the oxygen is delocalized into the aromatic ring, stabilizing the anion but

decreasing the availability of the electron pair for protonation.

3. $RO-$: Alkoxide ions (such as methoxide, CH_3O^-) are stronger bases than hydroxide ions because the negative charge is localized on oxygen, and alkyl groups are electron-donating, increasing the basicity.

4. O_2N^-: Nitro group has a strong electron-withdrawing effect, making this species a very weak base.

Thus, $RO-$ (alkoxide) is the strongest base among these species.

Quick Tip

Alkoxide ions are stronger bases than hydroxide and phenoxide due to the electron-donating effect of alkyl groups, which increases the negative charge on oxygen, making it more likely to accept a proton.

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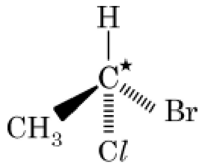
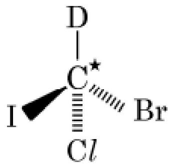
4. In which of the following molecules, the C atom marked with asterisk is chiral?

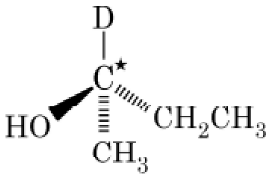
(I)



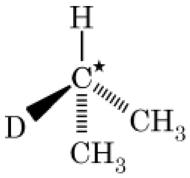
(II)



(III)



(IV)



(A) I, II, III

(B) I, II, III, IV

(C) II, III, IV

(D) I, III, IV

Correct Answer: (A) I, II, III

Solution: A chiral center is a carbon atom that is attached to four different substituents. Let's analyze the molecules:

1. Molecule I: The carbon marked with an asterisk is attached to H, CH_3, Br, and Cl, all of which are different. Thus, it is chiral.

2. Molecule II: The carbon marked with an asterisk is attached to Cl, Br, and two Cl groups. Since two substituents are not identical (Cl), this carbon is chiral.

3. Molecule III: The carbon marked with an asterisk is attached to HO, CH_3, and CH_2CH_3, all of which are different. Thus, it is chiral.

4. Molecule IV: The carbon marked with an asterisk is attached to D, CH_3, and two CH_3 groups. Since two substituents are identical (CH_3), this carbon is not chiral.

Hence, the chiral molecules are I, II and III.

Quick Tip

A chiral carbon must be attached to four different groups. If two or more groups are identical, the carbon is not chiral.

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5. The rate of a reaction increases sixteen times when the concentration of the reactant increases four times. The order of the reaction is:

(A) 2.5

(B) 2.0

(C) 1.5

(D) 0.5

Correct Answer: (B) 2.0

Solution: The rate law equation is given by:

$$\text{Rate} = k[\text{A}]^n.$$

When the concentration of the reactant increases 4 times, the rate increases 16 times. Using the relation:

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

we substitute the known values:

$$16 = 4^n.$$

Taking the logarithm of both sides:

$$\log 16 = n \log 4.$$

Since $\log 16 = 1.2041$ and $\log 4 = 0.6021$, solving for n:

$$n = \frac{1.2041}{0.6021} = 2.0.$$

Therefore, the order of the reaction is 2.0.

Quick Tip

The order of a reaction can be determined experimentally by measuring how the rate of reaction changes with the concentration of reactants.

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6. Which of the following cell is used in hearing aids ?

(A) Mercury cell

(B) H_2-O_2 fuel cell

(C) Dry cell

(D) Ni-Cd cell

Correct Answer: (A) Mercury cell

Solution: The correct answer is Mercury cell. Mercury cells are used in hearing aids because they are compact and provide a steady and reliable voltage output for long periods of time. These cells are small, which makes them ideal for use in hearing aids.

Quick Tip

Mercury cells are often used in small electronic devices, such as hearing aids, due to their high energy density and stable voltage output.

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7. Isotonic solutions have the same:

(A) density

(B) refractive index

(C) osmotic pressure

(D) volume

Correct Answer: (C) osmotic pressure

Solution: Isotonic solutions are solutions that have the same osmotic pressure. Osmotic pressure is the pressure exerted by a solvent when it moves through a semipermeable membrane to balance the concentrations of solute on both sides of the membrane. Isotonic solutions are crucial for maintaining the equilibrium in biological systems, especially for red blood cells.

For two solutions to be isotonic, the concentration of solute particles (ions, molecules) in the two solutions must be the same. This ensures that there is no net movement of water across the membrane, preventing cell shrinkage (crenation) or bursting (lysis).

For example, an isotonic saline solution used in medical treatments has the same osmotic pressure as the human blood plasma, ensuring that the cells do not undergo osmotic stress.

Quick Tip

Osmotic pressure is the key property that defines isotonic solutions. This ensures that cells retain their shape by maintaining equal concentrations of solutes inside and outside the cell.

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8. Transition metals are known to make interstitial compounds. Formation of interstitial compounds makes the transition metal:

(A) more hard

(B) more soft

(C) more ductile

(D) more metallic

Correct Answer: (A) more hard

Solution: Interstitial compounds are formed when small atoms, such as carbon, hydrogen, or nitrogen, occupy the interstitial spaces between the larger metal atoms in the crystal lattice. This creates a more rigid structure as the smaller atoms obstruct the movement of the metal atoms.

For transition metals, which have relatively large atomic radii, the presence of smaller atoms in the interstitial sites restricts the mobility of the metal atoms, thus increasing the hardness of the metal. For example, the formation of steel (iron-carbon alloy) results in a much harder material than pure iron due to the carbon atoms occupying the interstitial spaces in the iron lattice.

The formation of interstitial compounds typically leads to increased hardness, but the material may become less ductile and more brittle, which makes it harder, not softer.

Quick Tip

Interstitial compounds restrict the movement of metal atoms, increasing hardness but often decreasing ductility. This is why steel is harder than pure iron due to the carbon atoms filling interstitial spaces.

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9. Auto-oxidation of chloroform in air and light produces a poisonous gas known as:

(A) Phosphine

(B) Mustard gas

(C) Phosgene

(D) Tear gas

Correct Answer: (C) Phosgene

Solution: The auto-oxidation of chloroform $(CHCl_3)$ in the presence of air and light leads to the formation of phosgene $(COCl_2)$, a highly toxic gas. Phosgene is produced when chloroform is exposed to oxygen and ultraviolet light, which breaks down the chloroform and produces phosgene along with other by-products such as hydrogen chloride (HCl).

- Phosgene is used as a chemical warfare agent due to its toxicity, and it can cause severe damage to the lungs when inhaled.

Quick Tip

Phosgene is a toxic gas and must be handled carefully, especially in the presence of chloroform and light. The reaction is a classic example of the dangers of auto-oxidation.

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10. Out of the following alkenes, the one which will produce tertiary butyl alcohol on acid catalysed hydration is:

(A) $CH_3CH_2CH = CH_2$

(B) $CH_3CH = CH_2$

(C) $CH_3 - CH = CH - CH_3$

(D) $(CH_3)_3C = CH_2$

Correct Answer: (D) $(CH_3)_2C = CH_2$

Solution: In acid-catalyzed hydration of alkenes, the reaction follows Markovnikov's rule, which states that the proton (H^+) adds to the carbon atom of the double bond that has the greater number of hydrogen atoms, while the hydroxyl group (OH) adds to the carbon with fewer hydrogen atoms.

For the given options:

- (D) $(CH_3)_2C = CH_2$ is tert-butene, and when it undergoes acid-catalyzed hydration, the addition of the proton to the carbon in the double bond produces a tertiary carbocation ($(CH_3)_3C^+$), which is stable. The hydroxyl group then adds to this carbon, forming tertiary butyl alcohol.
- The other alkenes (A, B, C) will not form a tertiary carbocation, leading to a different set of products.

Quick Tip

In acid-catalyzed hydration, Markovnikov's rule governs the addition of H^+ and OH^-. Tertiary carbocations are the most stable and thus favored during the reaction.

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11. The correct name of the given reaction is:

$$\text{Ar-N}_2^+\text{X}^- \xrightarrow{\text{Cu CN, KCN}} \text{Ar-CN} + N_2$$

(A) Sandmeyer's reaction

(B) Gabriel Phthalimide synthesis

(C) Carbyl amine reaction

(D) Hoffmann bromamide degradation reaction

Correct Answer: (A) Sandmeyer's reaction

Solution: The given reaction is a Sandmeyer's reaction, which is used to prepare aryl halides and other aryl derivatives from diazonium salts. In this specific case, the aryl diazonium salt (Ar-N_2^+) reacts with copper (Cu) in the presence of potassium cyanide (KCN) to form an aryl cyanide (Ar-CN) along with the evolution of nitrogen gas (N_2). This reaction is widely used to introduce various substituents onto aromatic rings, such as halides, cyanides, and hydroxyl groups.

- Reaction Mechanism: In this reaction, the diazonium group is first formed by the reaction of an arylamine with nitrous acid. The copper(I) chloride or copper(I) cyanide facilitates the substitution of the diazonium group by the cyanide ion (CN^-) to form the aryl cyanide.

Quick Tip

Sandmeyer's reaction is an important method in synthetic organic chemistry for replacing the diazonium group with various substituents, such as Cl, CN, and OH, using different reagents like CuCl, CuCN, etc.

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12. The specific sequence in which amino acids are arranged in a protein is called its:

(A) Primary structure

(B) Secondary structure

(C) Tertiary structure

(D) Quaternary structure

Correct Answer: (A) Primary structure

Solution: The primary structure of a protein refers to the linear sequence of amino acids in the polypeptide chain. This sequence is encoded by the genetic material (DNA) and is unique for each protein. The amino acids are connected by peptide bonds, which are covalent bonds formed through dehydration reactions between the amino group of one amino acid and the carboxyl group of another.

The sequence of amino acids in the primary structure determines the overall shape of the protein and, consequently, its function. Even a small change (mutation) in the amino acid sequence can drastically alter the function of a protein, leading to diseases such as sickle-cell anemia.

Quick Tip

The primary structure is the foundation for all higher-level protein structures (secondary, tertiary, and quaternary). Any change in the amino acid sequence can potentially change the protein's function.

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13. Assertion (A): The units of rate constant of a zero order reaction and rate of reaction are the same. Reason (R): In zero order reaction, the rate of reaction is independent of concentration of reactants.

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

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

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

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

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

Solution: - Assertion (A) is true: In a zero-order reaction, the rate of reaction is independent of the concentration of reactants. The rate constant and rate of the reaction share the same unit of mol $\text{L}^{-1}\text{s}^{-1}$.

- Reason (R) is true: In a zero-order reaction, the rate does not depend on the concentration of the reactant, meaning the rate is constant, and the rate law is written as:

$$\text{Rate} = k[\text{A}]^0 = k$$

Thus, the rate of reaction is independent of the concentration, confirming the reason.

Quick Tip

In a zero-order reaction, the rate remains constant regardless of the concentration of reactants, and the units of the rate constant and the rate of reaction are the same.

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14. Assertion (A): Zr and Hf are of almost similar atomic radii. Reason (R): This is due to Lanthanoid contraction.

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

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

Solution: - Assertion (A) is true: Zirconium (Zr) and Hafnium (Hf) are in the same group of the periodic table, and their atomic radii are almost the same.
- Reason (R) is also true: The reason for this similarity is the Lanthanoid contraction, a phenomenon where the atomic radii of the lanthanoids decrease due to poor shielding of the nuclear charge by the f-electrons. As a result, elements following the lanthanoids (like Zr and Hf) experience a similar effective nuclear charge, leading to nearly the same atomic radii.

Quick Tip

Lanthanoid contraction refers to the gradual decrease in size of the elements in the lanthanide series, affecting the elements in the same period after them, such as Zr and Hf.

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15. Assertion (A): p-methoxyphenol is a stronger acid than p-nitrophenol. Reason (R): Methoxy group shows +I effect whereas nitro group shows -I effect.

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

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

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

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

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

Solution: - Assertion (A) is false: p-Nitrophenol is actually a stronger acid than p-methoxyphenol. The nitro group is an electron-withdrawing group, which stabilizes the negative charge on the conjugate base (phenoxide ion) more effectively, making it a stronger acid.

- Reason (R) is true: The methoxy group exhibits a +I effect (electron-donating), which increases the electron density on the aromatic ring and makes the phenol less acidic, whereas the nitro group exhibits a -I effect (electron-withdrawing), which makes the phenol more acidic.

Quick Tip

Electron-withdrawing groups like the nitro group stabilize the conjugate base, making the compound more acidic, whereas electron-donating groups like methoxy make the compound less acidic.

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16. Assertion (A): Inversion of configuration is observed when 1-Bromobutane is hydrolysed.

Reason (R): The reaction is S_N2 and proceeds with the formation of transition state.

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

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

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

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

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

Solution: Inversion of configuration occurs during an S_N2 reaction due to the backside attack of the nucleophile, which leads to the inversion of the leaving group. This is true for 1-bromobutane when it undergoes hydrolysis.
However, the reason given in the statement (R) is incorrect. The S_N2 mechanism involves a backside attack and results in the inversion of configuration. While a transition state is indeed formed, this alone doesn't explain the inversion of configuration; rather, it's the specific nature of the S_N2 mechanism (backside attack) that causes the inversion.
Therefore, Assertion (A) is true, but Reason (R) is false.

Quick Tip

In an S_N2 reaction, the nucleophile attacks from the opposite side of the leaving group, leading to the inversion of configuration. A transition state is formed, but this doesn't directly explain the inversion.

17(a). Carry out the following conversions: (i) Nitrobenzene to Aniline. (ii) Aniline to Phenol.

Solution: (i) Nitrobenzene to Aniline: To convert nitrobenzene to aniline, a reduction reaction is required. This can be achieved by reducing the nitro group (-NO_2) using reducing agents such as iron (Fe) and hydrochloric acid (HCl) or catalytic hydrogenation:

$$C_6H_5NO_2 + 3H_2 \xrightarrow{\text{Fe/HCl}} C_6H_5NH_2$$

This process reduces the nitro group $(-NO_2)$ to an amino group $(-NH_2)$, resulting in the formation of aniline.

(ii) Aniline to Phenol: To convert aniline $(C_6H_5NH_2)$ to phenol (C_6H_5OH), the amino group must be oxidized to a hydroxyl group. This can be done using an oxidizing agent such as bromine in the presence of water:

$$C_6H_5NH_2 + Br_2 \xrightarrow{H_2O} C_6H_5OH + 2HBr$$

The reaction replaces the amino group $(-NH_2)$ with a hydroxyl group (-OH), forming phenol.

Quick Tip

Reduction of nitrobenzene to aniline requires an electron-donating reduction, while the conversion of aniline to phenol involves oxidation using bromine in water.

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17. (b) (i) Write a chemical test to distinguish between Dimethyl amine and Ethanamine.

Solution: To distinguish Dimethylamine (CH_3NH_2) from Ethanamine $(C_2H_5NH_2)$, we can use the Nitrous acid test.

- Test for Dimethylamine: When Dimethylamine is treated with nitrous acid (HNO_2), it forms a blue solution due to the formation of a methyl diazonium salt. The reaction is as follows:

$$\mathrm{CH_3NH_2 + HNO_2 \rightarrow CH_3N_2^+ + H_2O}$$

The blue color indicates the presence of Dimethylamine.

- Test for Ethanamine: When Ethanamine is treated with nitrous acid, it forms ethanol and nitrogen gas, and there is no color formation:

$$\mathrm{C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O}$$

Hence, Ethanamine does not produce a color change.

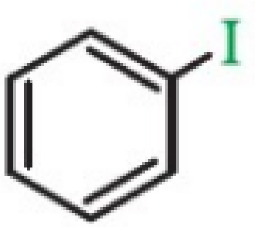
Thus, Dimethylamine gives a blue color with nitrous acid, while Ethanamine does not.

Quick Tip

Dimethylamine forms a blue-colored solution with nitrous acid, distinguishing it from Ethanamine, which produces no such color.

(ii) Write the product formed when benzene diazonium chloride is treated with KI.

Solution:



When benzene diazonium chloride $(C_6H_5N_2^+Cl^-)$ is treated with potassium iodide (KI), the diazonium group undergoes a nucleophilic substitution reaction with the iodide ion (I^-). The product formed is iodobenzene (C_6H_5I). The reaction is as follows:

$$\mathrm{C_6H_5N_2^+Cl^- + KI \rightarrow C_6H_5I + N_2 + KCl}$$

This reaction is an example of a diazonium substitution reaction, where the diazonium ion is replaced by an iodine atom, forming iodobenzene.

Quick Tip

Benzene diazonium chloride reacts with potassium iodide to form iodobenzene, which is a useful halogenation reaction in organic synthesis.

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18. Define the following terms:

(a) Limiting molar conductivity (Λ°) It is defined as the conductivity of a solution containing one mole of electrolyte dissolved in a large volume of solvent. It is represented by the symbol Λ° and can be determined experimentally by measuring the conductivity of the solution at infinite dilution. It is calculated using the formula:

$$\Lambda^\circ = \frac{\kappa}{c}$$

where κ is the conductivity of the solution and c is the concentration of the solution.

(b) Fuel cell A fuel cell is an electrochemical cell that generates electrical energy by using a fuel (such as hydrogen) and an oxidant (such as oxygen) through a redox reaction. The most common type of fuel cell is the hydrogen fuel cell, where hydrogen gas reacts with oxygen to form water and produce electricity. The general reaction is:

$$2H_2 + O_2 \to 2H_2O + \text{electricity}$$

Fuel cells are used in a variety of applications, including portable power supplies and electric vehicles.

Quick Tip

Limiting molar conductivity refers to the maximum conductivity of an electrolyte at infinite dilution, whereas a fuel cell is a clean energy source that converts chemical energy directly into electrical energy.

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19. Classify the following sugars into monosaccharides and disaccharides: Surcose , Lactose Glucose, and Fructose.

Solution: - Monosaccharides:

- Fructose and Glucose are monosaccharides, meaning they consist of a single sugar unit and cannot be hydrolyzed into simpler sugars. Both are important sources of energy in the body and are involved in the synthesis of larger carbohydrates.
- Disaccharides:
- Lactose and Surcose are disaccharides, consisting of two monosaccharide units linked by a glycosidic bond. Lactose is composed of one molecule of glucose and one of galactose, while maltose is made up of two glucose molecules.

Quick Tip

Monosaccharides are simple sugars like glucose and fructose, while disaccharides are made of two monosaccharide units, such as surcose (glucose-glucose) and lactose (glucose-fructose).

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20. Resistance of a conductivity cell filled with 0.2 mol L^{-1} KCl solution is 200 ohm. If the resistance of the same cell when filled with 0.05 mol L^{-1} KCl solution is 620 ohm,

calculate the conductivity and molar conductivity of 0.05 mol L^{-1} KCl solution. The conductivity of 0.2 mol L^{-1} KCl solution is 0.0248 S cm^{-1}.

Solution: Step 1: Calculate the Cell Constant The cell constant (G*) is given by:

$$\text{Cell constant} = \text{Conductivity} \times \text{Resistance}$$

Substituting values for 0.2 mol L^{-1} KCl solution:

$$G^* = 0.0248 \times 200 = 4.96\,\text{cm}^{-1}$$

Step 2: Calculate Conductivity of 0.05 mol L^{-1} KCl Solution Using the relation:

$$\text{Conductivity}(\kappa) = \frac{\text{Cell Constant (G*)}}{\text{Resistance (R)}}$$

$$\kappa = \frac{4.96}{620} = 0.008\,\text{S cm}^{-1}$$

Step 3: Calculate Molar Conductivity Molar conductivity Λ_m is given by:

$$\Lambda_m = \kappa \times \frac{1000}{C}$$

where $C = 0.05$ mol L^{-1}:

$$\Lambda_m = 0.008 \times \frac{1000}{0.05} = 160\,\text{S cm}^2\text{mol}^{-1}$$

Quick Tip

The cell constant remains the same for different solutions in the same conductivity cell. Conductivity decreases with dilution, but molar conductivity increases as the ions move more freely.

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21. A first order reaction takes 40 min for 75% decomposition. Calculate rate constant.

[Given: log 2 = 0.30, log 4 = 0.60]

Solution:

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

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

Where:

- t = time taken for the reaction (in this case, 40 min)
- $[A]_0$ = initial concentration
- $[A]$ = concentration after time t
- k = rate constant

Since 75% decomposition occurs, 25% of the reactant remains, i.e., $[A] = 25\%$ and $[A]_0 = 100\%$.

Substituting the values:

$$40\,\text{min} = \frac{2.303}{k} \log \left(\frac{100}{25} \right)$$

Now calculate $\log(100/25)$:

$$\log \left(\frac{100}{25} \right) = \log(4) = 0.60$$

Now substitute into the equation:

$$40\,\text{min} = \frac{2.303}{k} \times 0.60$$

Solve for k:

$$k = \frac{2.303 \times 0.60}{40} = 0.0345\,\text{min}^{-1}$$

Quick Tip

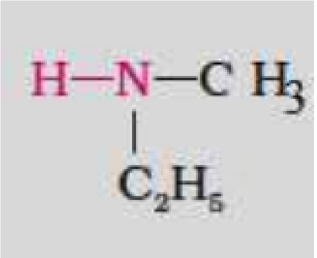
For first order reactions, the rate constant can be calculated using the integrated rate law. Always use the correct logarithmic values and units for accurate calculations.

22. A compound 'X' with molecular formula C_3H_9N reacts with $C_6H_5SO_2Cl$ to give a solid, insoluble in alkali. Identify 'X' and give the IUPAC name of the product. Write the reaction involved.

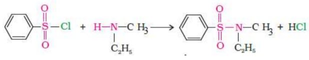
Solution: The given molecular formula C_3H_9N corresponds to an amine. The reaction with benzene sulfonyl chloride ($C_6H_5SO_2Cl$) leads to the formation of a sulfonamide derivative, which is insoluble in alkali. The reaction follows:

$$C_2H_5 - NH - CH_3 + C_6H_5SO_2Cl \rightarrow C_6H_5SO_2N(C_2H_5)(CH_3) + HCl$$

- Here, X is identified as **N-Ethylmethylamine**.



- The IUPAC name of the product is **N-Ethyl-N-methylbenzenesulfonamide**.



- The sulfonamide formed is **insoluble in alkali** due to the absence of an acidic hydrogen.

Quick Tip

Sulfonamides are generally **insoluble in alkali** due to the strong electron-withdrawing nature of the sulfonyl group, making the nitrogen non-basic.

---

23. Account for the following:

(a) Haloalkanes react with AgCN to form isocyanide as the main product.

Solution: Haloalkanes undergo a nucleophilic substitution reaction with silver cyanide (AgCN) to form isocyanides (also known as isonitriles). The cyanide ion (CN^-) acts as a nucleophile and attacks the carbon atom of the halide, displacing the halide ion. This reaction follows the S_N2 mechanism, where the nucleophile directly attacks the electrophilic carbon from the opposite side of the leaving group.

$$\text{R-X} + \text{AgCN} \rightarrow \text{R-NC} + \text{AgX}$$

Here, X is a halide ion such as Cl^-, Br^-, or I^-, and the product formed is an isocyanide.

Quick Tip

In nucleophilic substitution reactions, the cyanide ion (CN^-) can act as a strong nucleophile and react with alkyl halides to form isocyanides. The S_N2 mechanism involves a backside attack by the nucleophile, displacing the leaving group.

(b) Allyl chloride shows high reactivity towards S_N1 reaction.

Solution: Allyl chloride undergoes S_N1 reactions readily because the resulting allyl carbocation is highly stabilized by resonance. When the chloride ion leaves, the positive charge formed on the carbon is delocalized onto the adjacent carbon atoms, stabilizing the carbocation intermediate. This resonance stabilization makes the formation of the carbocation energetically favorable, thus promoting the S_N1 reaction mechanism.

Quick Tip

In S_N1 reactions, the formation of a stable carbocation intermediate is essential. Allyl chloride is highly reactive in S_N1 reactions due to the resonance stabilization of the allyl carbocation formed after the chloride ion leaves.

(c) Haloarenes are extremely less reactive towards nucleophilic substitution reactions.

Solution: Haloarenes, where a halogen (e.g., chlorine, bromine, or iodine) is bonded to a carbon atom of an aromatic ring, show very low reactivity in nucleophilic substitution reactions. This is because the halogen's lone pair of electrons participates in resonance with the aromatic ring, delocalizing the electron density and making the carbon-halo bond more stable. This resonance effect makes the carbon-halogen bond less susceptible to nucleophilic attack, thus hindering the substitution reaction. The halogen is less likely to leave due to the strong resonance stabilization of the ring.

Quick Tip

In haloarenes, the lone pair on the halogen participates in resonance with the aromatic ring, stabilizing the bond and making the carbon-halo bond less reactive toward nucleophilic substitution. This resonance effect lowers the reactivity of haloarenes in nucleophilic substitution reactions.

---

24. Write the IUPAC names of the following coordination compounds (any three):

(A) $[Co(NH_3)_4Cl(NO_2)]Cl$

(B) $[Ni(NH_3)_6]Cl_2$

(C) $K_3[Cr(C_2O_4)_3]$

(D) $[Co(en)_2Br_2]^+$

Solution:

(a) The compound $[Co(NH_3)_4Cl(NO_2)]Cl$ is named as *Tetraamminchloridonitrito-N-cobalt (III) chloride*. In this compound, the central metal ion is cobalt (III), which is coordinated with four ammonia (NH_3) molecules, one chloride ion (Cl^-), and one nitrito (NO_2) ligand. The complex is balanced with the chloride ion as the counter ion. The ligand names are written with their respective prefixes (tetra- for four and chloro- for chloride). The nitrito ligand is described as nitrito-N because it is bound through the nitrogen atom.

(b) The compound $[Ni(NH_3)_6]Cl_2$ is named as *Hexaamminenickel(II) chloride*. In this case, nickel is in the +2 oxidation state, and it is coordinated with six ammonia molecules. The ligand ammonia is denoted as ”ammine” (not ammonium), and the coordination number of nickel is six. Two chloride ions act as counterions to balance the charge of the complex cation.

(c) The compound $K_3[Cr(C_2O_4)_3]$ is named as *Potassium trioxalatochromate (III)*. The chromium in this complex is in the +3 oxidation state and is coordinated with three oxalate ions (C_2O_4) as ligands. The oxalate ligand is a bidentate ligand, meaning it binds through both oxygen atoms. Potassium ions are present to balance the negative charge of the complex anion.

(d) The compound $[Co(en)_2Br_2]^+$ is named as *Dibromidobis(ethane-1,2-diamine)cobalt (III) ion*. The central metal ion is cobalt in the +3 oxidation state, and it is coordinated with two ethylenediamine (en) ligands, each of which is a bidentate ligand. Two bromide ions are also coordinated to cobalt. The name follows IUPAC conventions for bidentate ligands and uses the appropriate prefixes to denote the number of each type of ligand.

Quick Tip

- When naming coordination compounds, remember to list the ligands in alphabetical order.
- Use the appropriate prefixes for the number of each type of ligand (e.g., di-, tri-, tetra-, etc.).
- Always specify the oxidation state of the metal in Roman numerals inside parentheses.
- For bidentate ligands (such as ethylenediamine), use the correct nomenclature (e.g., ”ethane-1,2-diamine”).

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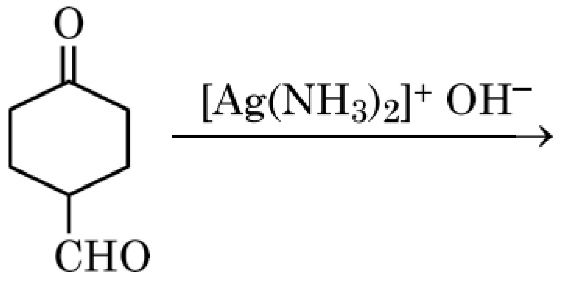
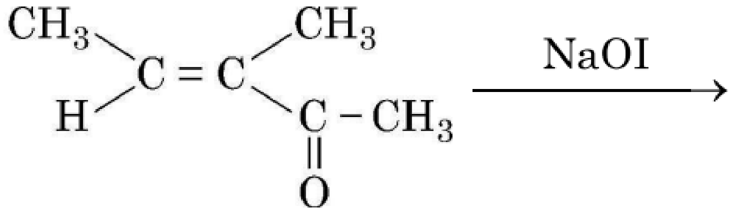
25. Draw the structures of major product(s) in each of the following reactions:

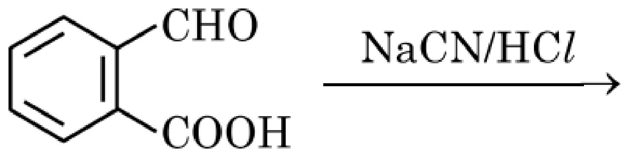
(a)



(b)



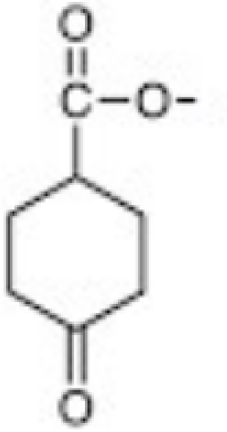
(c)



Solution: (a) Reaction with $[Ag(NH_3)_2]^+OH^-$ (Tollens’ Test)

- The given compound Cyclohexanone undergoes oxidation by Tollens’ reagent.

- The aldehyde group in Cyclohexanone is oxidized to form a carboxylate anion.



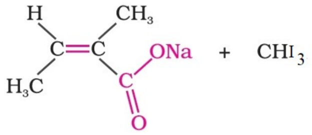
- The reaction mechanism follows:

$$\text{Cyclohexanone} + [Ag(NH_3)_2]^+ + OH^- \rightarrow \text{Cyclohexanone carboxylate} + Ag + NH_3 + H_2O$$

Major Product: Cyclohexanone carboxylate ion.

(b) Iodoform Reaction with NaOI

- The given compound 4-Methylpent-3-en-2-one contains a methyl ketone $(-COCH_3)$ group.
- In the presence of NaOI, the iodoform test occurs, where the methyl ketone group is cleaved.
- This leads to the formation of Sodium propionate $(CH_3CH = CHCOONa)$ and Iodoform (CHI_3).

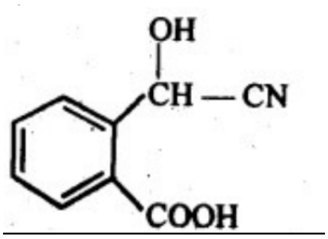


Major Products:

$$\text{Sodium propionate } (\text{CH}_3\text{CH=CHCOONa}) + \text{Iodoform } (\text{CHI}_3)$$

(c) Cyanohydrin Formation with NaCN/HCl

- The given compound p-Carboxybenzaldehyde reacts with NaCN/HCl.
- The cyanohydrin reaction occurs, where the cyanide ion $(CN^{)}$ attacks the carbonyl group.
- The aldehyde (-CHO) is converted into a cyanohydrin (-CH(OH)CN).



Major Product:

4-Carboxybenzaldehyde cyanohydrin (p-Carboxybenzylcyanohydrin)

Quick Tip

1. Tollens' test oxidizes aldehydes to carboxylate ions.
2. Iodoform test cleaves methyl ketones, forming carboxylates and iodoform (CHI_3).
3. Cyanohydrin formation adds a cyanide (-CN) to an aldehyde, producing a cyanohydrin (-CH(OH)CN).

---

26. Calculate the emf of the following cell:

$$\text{Ni(s)} + 2\text{Ag}^{+}(0.01M) \rightarrow \text{Ni}^{2+}(0.1M) + 2Ag(s)$$

Given that $E^\circ_{\text{cell}} = 1.05$ V, log 10 = 1.

Solution: Using the Nernst equation:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^{+}]^2}$$

Substituting the given values:

$$E_{\text{cell}} = 1.05 - \frac{0.059}{2} \log \frac{(0.1)}{(0.01)^2}$$

$$E_{\text{cell}} = 1.05 - \frac{0.059}{2} \times \log(0.1/0.0001)$$

$$E_{\text{cell}} = 1.05 - \frac{0.059}{2} \times \log(1000)$$

$$E_{\text{cell}} = 1.05 - \frac{0.059}{2} \times 3$$

$$E_{\text{cell}} = 1.05 - (0.059 \times 1.5)$$

$$E_{\text{cell}} = 1.05 - 0.0885$$

$$E_{\text{cell}} = 0.9615 \text{ V}$$

Quick Tip

1. The Nernst equation relates cell potential to ion concentration.
2. The logarithmic term uses log base 10, which simplifies calculations.
3. For correct units, express the final answer in volts (V).

---

27. Give the structure of the major product expected from the following reactions:

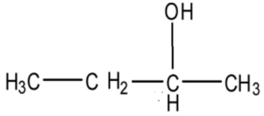
(a) Reaction of propanal with methyl magnesium bromide followed by hydrolysis.

(b) Reaction of phenol with Br_2 in CS_2.

(c) Reaction of propene with diborane followed by oxidation.

Correct Answer:

Solution: (a) Reaction of propanal with methyl magnesium bromide followed by hydrolysis: The reaction of propanal (C_3H_6O) with methyl magnesium bromide (CH_3MgBr) is a Grignard reaction. The Grignard reagent acts as a nucleophile and attacks the carbonyl carbon in the propanal molecule, leading to the formation of an intermediate alkoxide. Upon hydrolysis, the alkoxide is converted into a secondary alcohol, specifically 2-butanol ($CH_3CH(OH)CH_2CH_3$).



$$H_3C-CH_2-\overset{OH}{\underset{H}{C}}-CH_3$$

(b) Reaction of phenol with Br_2 in CS_2: The reaction of phenol (C_6H_5OH) with bromine (Br_2) in carbon disulfide (CS_2) results in a halogenation reaction. The bromine reacts with the hydroxyl group of phenol, leading to the substitution of a hydrogen atom on the benzene ring by a bromine atom. The major product is 2-bromophenol (C_6H_4BrOH), as bromination typically occurs at the ortho or para position relative to the hydroxyl group.

(c) Reaction of propene with diborane followed by oxidation: The reaction of propene (C_3H_6) with diborane (B_2H_6) results in the formation of an organoborane intermediate. Upon oxidation, the organoborane undergoes hydrolysis to produce propan-2-ol ($CH_3CH(OH)CH_3$) as the major product. This is a typical hydroboration-oxidation reaction.

Quick Tip

In Grignard reactions, a carbonyl compound reacts with a Grignard reagent to form an alcohol upon hydrolysis. In the case of phenol, bromine substitution occurs predominantly at the ortho and para positions due to the activating nature of the hydroxyl group.

---

28. The rate constant of a reaction quadruples when the temperature changes from 300 K to 320 K. Calculate the activation energy for this reaction.

[log 2 = 0.30, log 4 = 0.60, 2.303 R = 19.15 J $K^{-1}mol^{-1}$]

Solution:

Using the Arrhenius equation:

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

Given:

$$\frac{k_2}{k_1} = 4, \quad T_1 = 300\,K, \quad T_2 = 320\,K, \quad \log 4 = 0.60$$

Substituting the given values into the equation:

$$\log 4 = \frac{E_a}{2.303 \times 19.15}\left(\frac{1}{300} - \frac{1}{320}\right)$$

$$0.60 = \frac{E_a}{2.303 \times 19.15} \times \left(\frac{320 - 300}{300 \times 320}\right)$$
$$0.60 = \frac{E_a}{19.15 \times 2.303} \times \frac{20}{96000}$$
$$E_a = \frac{0.60 \times 19.15 \times 2.303 \times 96000}{20}$$
$$E_a = 55.152\,\text{kJ mol}^{-1}$$

Quick Tip

The Arrhenius equation relates rate constant (k) to activation energy (E_a).

For reactions where k quadruples, use log 4 = 0.60 to simplify calculations.

---

29. The oxidation number of the central atom in a complex is defined as the charge it would carry if all the ligands are removed along with the electron pairs that are shared with the central atom. Similarly, the charge on the complex is the sum of the charges of the constituent parts i.e. the sum of the charges on the central metal ion and its surrounding ligands.

Based on this, the complex is called neutral if the sum of the charges of the constituents is equal to zero. However, for an anion or cationic complex, the sum of the charges of the constituents is equal to the charge on the coordination sphere.

Based on the above information, answer the following questions:

(a). What is the secondary valence of Co in $[Co(NH_3)_4Cl_2]^+$?

Solution:

In coordination chemistry, the secondary valence (also known as coordination number) refers to the number of ligands attached to a central metal ion. In the complex $[Co(NH_3)_4Cl_2]^+$, cobalt is surrounded by four NH_3 molecules and two chloride ions, making the total number of ligands equal to 6. Therefore, the secondary valence (coordination number) of Co is 6.

Quick Tip

The secondary valence of a metal ion in a coordination complex is defined by the number of ligands directly bonded to it.

(b). What type of isomerism is shown by the complex $[Cr(H_2O)_6Cl_3]$ and $[Cr(H_2O)_5Cl]Cl_2.H_2O$?

Solution:

Solvate or hydrate isomerism occurs when there is a difference in the number of solvent molecules coordinated to the metal ion. In $[Cr(H_2O)_5Cl]Cl_2.H_2O$ one water molecule is coordinated to chromium along with one chloride ion, while in $[([Cr(H_2O)_6Cl_3]$,, six water molecules are coordinated to the chromium ion. The difference in the number of water molecules coordinated to the central metal ion results in solvate isomerism.

Quick Tip

In solvate or hydrate isomerism, the difference arises from the number of solvent molecules like water coordinated to the metal center.

(c). Write the electronic configuration of a d^4 ion on the basis of crystal field theory when

(i) $\Delta_0 < P$ (ii) $\Delta_0 > P$

Solution:

For a d^4 ion:

- (i) When the ligand field splitting energy Δ_0 is smaller than the pairing energy P, the electrons will occupy the higher energy e_g orbitals. Hence, the electron configuration will be $t_{2g}^3 e_g^1$.
- (ii) When Δ_0 is larger than P, the electrons will prefer to occupy the lower energy t_{2g} orbitals, leading to the electron configuration $t_{2g}^4 e_g^0$, with all four electrons in the t_{2g} orbitals.

Quick Tip

The electron configuration of a d^4 ion depends on the relative strength of the ligand field splitting energy Δ_0 and the pairing energy P.

OR

(c). Find the oxidation state and coordination number of the central metal ion in $[Co(H_2O)(CN)(en)_2]^{2+}$.

Solution:

In the given complex $[Co(H_2O)(CN)(en)_2]^{2+}$, the water (H_2O) and cyanide (CN) are neutral ligands, while ethylenediamine (en) is a bidentate ligand. The coordination number refers to the total number of bonds formed between the central metal ion and the ligands. Here, cobalt is coordinated with one water molecule, one cyanide ion, and two ethylenediamine molecules, each forming two bonds, which gives a total coordination number of 6.

For the oxidation state, considering the charge of the complex (+2) and the neutral nature of the ligands (H_2O, CN, and en), the oxidation state of cobalt can be calculated as +3.

Quick Tip

To determine the oxidation state, subtract the total charge of the ligands from the charge of the complex ion.

---

30. Certain organic compounds are required in small amounts in our diet, but their deficiency causes specific diseases. These compounds are called vitamins. Most vitamins cannot be synthesized in our body, but plants can synthesize almost all of them. So they are considered essential food factors. However, the bacteria of the gut can produce some of the vitamins required by us. All the vitamins are generally available in our diet. The term 'vitamin' was coined from the words vital + amine, since the earlier identified compounds had amino groups. Vitamins are classified into two groups depending on their solubility in water or fat, namely, fat-soluble vitamins and water-soluble vitamins.

30(a). What is the other name of vitamin B_6?

Correct Answer: Pyridoxine

Solution:

Understanding Vitamin B_6:

Vitamin B_6, also known as **Pyridoxine**, is a water-soluble vitamin that plays a crucial role in protein metabolism, neurotransmitter synthesis, and hemoglobin production. It is essential for brain development and function, as well as for the immune system.

Quick Tip

Vitamin B_6 is found in foods such as bananas, poultry, fish, and fortified cereals. It helps prevent anemia and supports neurological function.

30(b). Name the vitamin whose deficiency causes increased blood clotting time.

Correct Answer: Vitamin K

Solution:

Role of Vitamin K in Blood Clotting:

Vitamin K is a fat-soluble vitamin essential for the synthesis of clotting factors in the liver. It plays a vital role in blood coagulation by activating proteins that help in clot formation.

Deficiency and Its Effect:

A deficiency in Vitamin K leads to prolonged blood clotting time, which can cause excessive bleeding (hemorrhaging). This condition is particularly dangerous for newborns, as they have low vitamin K stores at birth.

Quick Tip

Vitamin K is found in green leafy vegetables such as spinach and kale. It is also synthesized by gut bacteria.

30(c). Xerophthalmia is caused by the deficiency of which vitamin? Give two sources of this vitamin.

Solution:

Understanding Vitamin A and Its Role:

Vitamin A is a fat-soluble vitamin that plays a key role in maintaining vision, immune function, and cell growth. It is present in two forms:

- **Retinol (animal-based)**: Found in liver, fish oils, and dairy products.
- **Beta-carotene (plant-based)**: Found in carrots, sweet potatoes, and spinach.

Vitamin A Deficiency and Xerophthalmia:

Xerophthalmia is a severe eye disorder caused by Vitamin A deficiency. It leads to:

- Night blindness (difficulty seeing in low light).
- Dryness of the conjunctiva and cornea, which can lead to irreversible blindness if untreated.

Food Sources of Vitamin A:

- **Animal sources:** Fish liver oil, egg yolk, dairy products.
- **Plant sources:** Carrots, sweet potatoes, spinach.

Quick Tip

Vitamin A is crucial for eye health and immune function. A diet rich in carrots, spinach, and dairy products can help prevent deficiencies.

OR

30(c) Why can't vitamin C be stored in our body? Name the disease caused by the deficiency of this vitamin.

Solution:

Water-Solubility of Vitamin C:

Vitamin C (Ascorbic Acid) is a water-soluble vitamin, meaning it dissolves in water and is not stored in the body. Since it is not retained for long, it must be regularly consumed through diet.

Deficiency and Scurvy:

Scurvy is caused by a deficiency of Vitamin C and is characterized by:

- Bleeding gums and loose teeth.
- Joint pain and muscle weakness.
- Delayed wound healing and anemia.

Why Vitamin C is Not Stored:

Being water-soluble, excess Vitamin C is excreted through urine. This prevents toxicity but also means that regular dietary intake is essential.

Quick Tip

Vitamin C is an antioxidant that supports the immune system and collagen formation. Citrus fruits, strawberries, and bell peppers are rich sources.

---

31. (a) (i) Ishan's automobile radiator is filled with 1.0 kg of water. How many grams of ethylene glycol (Molar mass = 62 g mol^{-1}) must Ishan add to get the freezing point of the solution lowered to $-2.8°C$. K_f for water is 1.86 K kg $\cdot$ mol^{-1}.

Solution: The depression in freezing point is given by the formula:

$$\Delta T_f = K_f \times \frac{w_B}{M_B \times w_A}$$

Substituting the given values:

$$2.8 = 1.86 \times \frac{w_B}{62 \times 1}$$

Solving for w_B:

$$w_B = \frac{2.8 \times 62}{1.86} = 93.33 \text{ g}$$

Thus, the required amount of ethylene glycol is 93.33 g.

Quick Tip

For colligative properties, use the formula $\Delta T_f = K_f \times \frac{w_B}{M_B \times w_A}$ to determine the mass of solute required to achieve a desired freezing point depression.

(a) (ii) What type of deviation from Raoult's law is shown by ethanol and acetone mixture? Give reason.

Solution: The ethanol-acetone mixture exhibits positive deviation from Raoult's law. This occurs because the intermolecular forces in pure ethanol (hydrogen bonding) are stronger than those in the ethanol-acetone mixture. When acetone is added, it disrupts ethanol's hydrogen bonding, leading to an increase in vapor pressure.

Quick Tip

A positive deviation from Raoult's law occurs when the intermolecular forces in the mixture are weaker than in the pure components, leading to higher vapor pressure than expected.

(b) (i) Boiling point of water at 750 mm Hg pressure is 99.68$^\circ C$. How much sucrose (Molar mass = 342 g mol^{-1}) is to be added to 500 g of water such that it boils at 100$^\circ C$? (K_b for water = 0.52 K kg mol^{-1}).

Solution: The change in boiling point (ΔT_b) is given by the formula:

$$\Delta T_b = K_b \times m$$

where K_b is the ebullioscopic constant of water and m is the molality of the solution.
We are given that the boiling point increases from 99.68$^\circ C$ to 100$^\circ C$, so:

$$\Delta T_b = 100^\circ C - 99.68^\circ C = 0.32^\circ C$$

Now, we can calculate the molality of the solution using the equation:

$$m = \frac{\Delta T_b}{K_b} = \frac{0.32}{0.52} = 0.615 \, \text{mol/kg}$$

Molality (m) is defined as the number of moles of solute per kilogram of solvent. We are adding sucrose to 500 g (or 0.5 kg) of water. Therefore, the number of moles of sucrose required is:

$$\text{moles of sucrose} = m \times \text{mass of solvent in kg} = 0.615 \times 0.5 = 0.3075 \, \text{mol}$$

Finally, we calculate the mass of sucrose required using the molar mass of sucrose (342 g/mol):

$$\text{mass of sucrose} = \text{moles of sucrose} \times \text{molar mass} = 0.3075 \times 342 = 105.23 \, \text{g}$$

Quick Tip

For boiling point elevation, use the formula $\Delta T_b = K_b \times \frac{w_B}{M_B \times w_A}$ to calculate the required mass of solute.

(b) (ii) State Henry's law and write its any one application.

Solution: Henry's law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution. Mathematically, it is expressed as:

$$C = k_H \cdot P$$

where C is the concentration of the gas in the liquid, P is the partial pressure of the gas, and k_H is Henry's constant.

Application: To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

Quick Tip

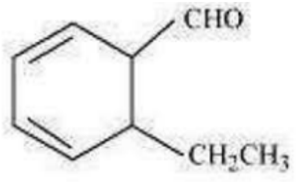
Henry's law explains the solubility of gases in liquids and is widely used in industries like carbonated beverage production and scuba diving safety.

32(a). An organic compound (A) with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Fehling solution and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid.

(i) Identify the compound (A) and write its IUPAC name.

Solution:

(i) The compound (A) has the molecular formula $C_9H_{10}O$ and shows characteristics of an aromatic aldehyde. Since it undergoes Cannizzaro reaction (which occurs in non-enolizable aldehydes), it must be an aldehyde without α-hydrogen atoms. The structure that fits these properties is **2-ethylbenzaldehyde**.



2 – Ethylbenzaldehyde

(ii) Write the reaction of compound (A) with

(1) 2, 4-Dinitrophenyl hydrazine and

(2) Fehling solution.

Solution: (ii) (1) Reaction with 2,4-Dinitrophenylhydrazine:

$$C_9H_{10}O + H_2N - NH(NO_2)_2 \rightarrow C_9H_{10}\text{=N-N}(NO_2)_2 + H_2O$$

2-Ethylbenzaldehyde reacts with 2,4-DNP reagent to form a yellow-orange precipitate of 2,4-DNP derivative.

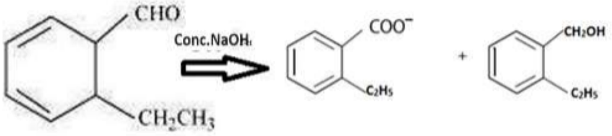
(2) Fehling's Solution Test:

Aromatic aldehydes generally do not give Fehling's test, but if attempted, some aliphatic aldehyde impurities may react. Fehling's solution is reduced by aliphatic aldehydes, forming a brick-red precipitate of Cu_2O.

(iii) Write the equation of compound (A) when it undergoes Cannizzaro reaction.

Solution:

(iii) Cannizzaro Reaction:



Since 2-ethylbenzaldehyde lacks an α-hydrogen, it undergoes disproportionation in a strong base via the Cannizzaro reaction, forming 2-ethylbenzoic acid and 2-ethylbenzyl alcohol.

Quick Tip

Aldehydes with no α-hydrogen undergo Cannizzaro reaction in the presence of a strong base. Aromatic aldehydes generally do not give Fehling's test, but aliphatic aldehydes do.

---

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

(1) The alpha (α)-hydrogens of aldehydes and ketones are acidic in nature.

Solution: (1) The acidity of α-hydrogens in aldehydes and ketones is due to the electron-withdrawing nature of the carbonyl group, which stabilizes the enolate ion formed after deprotonation. Additionally, resonance stabilization of the conjugate base further enhances the acidity.

(2) Oxidation of aldehydes is easier than ketones.

(2) Aldehydes undergo oxidation more readily than ketones because they have a hydrogen atom attached to the carbonyl carbon, making the cleavage of the C-H bond easier. In contrast, ketones require the breaking of a C-C bond, which is more difficult.

Quick Tip

The presence of an α-hydrogen in aldehydes and ketones allows for tautomerization to the enol form, which plays a crucial role in their reactivity.

(b) (ii) Arrange the following in:

(1) Decreasing reactivity towards nucleophilic addition reaction: Propanal, Acetone, Benzaldehyde.

(2) Increasing order of boiling point: Propane, Ethanol, Dimethylether, Propanal.

Solution: (1) The correct order of decreasing reactivity towards nucleophilic addition reaction is:

$$\text{Propanal} > \text{Benzaldehyde} > \text{Acetone}$$

Aldehydes are more reactive than ketones due to less steric hindrance and higher electrophilicity. Benzaldehyde is less reactive than aliphatic aldehydes due to the resonance stabilization of the carbonyl carbon.

(2) The increasing order of boiling point is:

$$\text{Propane} < \text{Dimethyl ether} < \text{Propanal} < \text{Ethanol}$$

Ethanol has the highest boiling point due to extensive hydrogen bonding, while propane has the lowest due to weak van der Waals forces.

Quick Tip

For nucleophilic addition reactions, aldehydes are more reactive than ketones because of the absence of electron-donating alkyl groups that reduce the electrophilicity of the carbonyl carbon.

(b) (iii) Give a simple chemical test to distinguish between Benzoic acid and Benzaldehyde.

Solution: Benzoic acid and benzaldehyde can be distinguished using sodium bicarbonate ($NaHCO_3$) test.

- Benzoic acid reacts with sodium bicarbonate to produce carbon dioxide gas with effervescence:

$$\mathrm{C_6H_5COOH} + NaHCO_3 \rightarrow \mathrm{C_6H_5COONa} + CO_2 + H_2O$$

- Benzaldehyde does not react with sodium bicarbonate, so no effervescence is observed.

Quick Tip

Benzoic acid can also be distinguished from benzaldehyde using Fehling's test. Benzaldehyde does not reduce Fehling's solution, whereas carboxylic acids do not react.

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33. Attempt any five of the following:

(a) Ce(III) is easily oxidised to Ce(IV). Comment.

Solution: Cerium (Ce) is a lanthanide element with the electronic configuration $[Xe]4f^15d^16s^2$. The presence of a single electron in the 4f orbital makes Ce(IV) stable. However, the stability of Ce(IV) arises due to the completely empty 4f orbital, which leads to a noble gas-like configuration ($[Xe]$). This stability provides a strong driving force for the oxidation of Ce(III) to Ce(IV). Furthermore, Ce(IV) forms stable compounds, especially with oxygen, such as CeO_2, making its oxidation favorable in aqueous solutions.

Quick Tip

Cerium is one of the few lanthanides that exists in a stable $+4$ oxidation state due to the stability of its empty 4f orbital.

(b) $E^0(Mn^{2+}/Mn)$ is -1.18 V. Why is this value highly negative in comparison to neighbouring d-block elements?

Solution: The standard reduction potential of Mn^{2+}/Mn is highly negative due to the extra stability of the Mn^{2+} ion, which has a half-filled $3d^5$ configuration. This half-filled d-orbital provides additional exchange energy, which stabilizes Mn^{2+} and makes its reduction to metallic manganese thermodynamically less favorable. In contrast, neighboring elements like Fe and Cr have more favorable reduction potentials because they do not possess the same level of half-filled stability in their $+2$ oxidation states.

Quick Tip

The extra stability of the $3d^5$ half-filled configuration in Mn^{2+} makes its reduction less favorable, resulting in a highly negative standard reduction potential.

(c) Which element of the 3d series has the lowest enthalpy of atomisation and why?

Solution: Zinc (Zn) has the lowest enthalpy of atomisation among the 3d series elements. This is due to its completely filled $3d^{10}$ electronic configuration, which results in weak metallic bonding. Metallic bonding strength is primarily influenced by the number of unpaired electrons available for delocalization, and since zinc lacks unpaired d-electrons, the metallic bonding is weaker. This weak bonding reduces the energy required to separate Zn atoms in the metallic lattice, leading to a lower enthalpy of atomisation.

Quick Tip

Zinc has a completely filled $3d^{10}$ configuration, leading to weak metallic bonding and low enthalpy of atomisation.

(d) What happens when sodium chromate is acidified?

Solution: Sodium chromate (Na_2CrO_4) is yellow in color and exists in basic medium. When acidified, chromate ions (CrO_4^{2-}) undergo a chemical equilibrium shift towards dichromate formation:

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Dichromate ions ($Cr_2O_7^{2-}$) are orange in color. This color change from yellow to orange is a characteristic reaction used in analytical chemistry to distinguish between basic and acidic environments.

Quick Tip

Chromate ions (CrO_4^{2-}) convert to dichromate ($Cr_2O_7^{2-}$) in acidic medium, changing color from yellow to orange.

(e) Zn, Cd, and Hg are soft metals. Why?

Solution: Zinc, cadmium, and mercury belong to group 12 of the periodic table and have completely filled d^{10} electronic configurations. Due to the lack of unpaired d-electrons, the metallic bonding in these elements is weak, leading to their characteristic softness. Additionally, mercury is liquid at room temperature due to the very weak interatomic forces in its metallic lattice.

Quick Tip

Zinc, cadmium, and mercury have completely filled d^{10} configurations, leading to weak metallic bonds and making them soft metals.

(f) Why is permanganate titration not carried out in the presence of HCl?

Solution: Permanganate (MnO_4^-) is a strong oxidizing agent in acidic medium. If HCl is used instead of H_2SO_4, the chloride ions (Cl^-) present in HCl get oxidized to chlorine gas

(Cl_2), leading to side reactions. This interference makes the titration inaccurate. Instead, sulfuric acid (H_2SO_4) is preferred as it does not undergo oxidation under these conditions.

Quick Tip

HCl cannot be used in permanganate titrations because Cl^- gets oxidized to Cl_2, affecting the accuracy of the titration.

(g) The lower oxides of transition metals are basic whereas the highest are amphoteric/acidic. Give reason.

Solution: The oxidation state of a transition metal determines the nature of its oxide. In lower oxidation states, transition metal oxides exhibit more ionic character, making them basic. In contrast, higher oxidation state oxides show increased covalent character, making them acidic or amphoteric. For example, MnO (manganese(II) oxide) is basic, while Mn_2O_7 (manganese(VII) oxide) is acidic. This behavior is due to the increasing oxidation state causing a greater degree of covalent bonding and polarization.

Quick Tip

Oxides in lower oxidation states are basic due to their ionic character, while those in higher oxidation states are acidic due to increased covalent character.